ECASIA'17

24-29
SEPT. 2017

MONTPELLIER,
FRANCE

EUROPEAN CONFERENCE ON APPLICATIONS OF SURFACE AND INTERFACE ANALYSIS

ABSTRACT BOOK

SFV Société Française du Vide
Montpellier Méditerranée Métropole
Chimie Paris ParisTech
cnrs
SPECS
PHYSICAL ELECTRONICS A DIVISION OF ULVAC-PHI
JEOL Solutions for Innovation
iontof
KRATOS ANALYTICAL A SHIMADZU GROUP COMPANY
Thermo Fisher SCIENTIFIC
La Région Occitanie Pyrénées - Méditerranée

TABLE OF CONTENT

Plenary lectures

PL3-433

TOWARDS SUPER-RESOLUTION METABOLIC IMAGING OF CELLS USING THE 3D ORBISIMS

I. Gilmore
National Centre of Excellence in Mass Spectrometry Imaging, NPL - Teddington (United kingdom)

Super-resolution optical microscopy using fluorescent labels has been transformational in allowing the machinery of life, e.g. proteins, to be seen at the nanoscale. There is a great desire in the life-sciences to achieve this level of insight for metabolites, the molecular products and messengers involved in metabolism. This will allow unprecedented ability to understand rewiring of metabolic networks involved in disease, understanding of the uptake of drugs in cells and construct mechanistic understanding in fundamental biology. However, this is a monumental challenge since fluorescent labelling strategies cannot be used because of the dynamic processes in the creation of metabolites and because the fluorescent labels themselves radically alter the chemistry of the metabolite.

Mass spectrometry allows label-free (or with stable isotope labelling) identification of endogenous and exogenous (e.g drugs) metabolites and when combined with high-resolution ion beams in secondary ion mass spectrometry (SIMS) allows sub-cellular resolution imaging. Substantial barriers need to be overcome to achieve a super-resolution goal (< 250 nm) including increasing sensitivity, increasing specificity (accurate identification of molecules), sample preparation methodologies (e.g. cryo-SIMS) and improvements in ion beam resolution. This lecture will review our research at NiCE-MSI using three SIMS instrument types; ToF-SIMS, 3D OrbiSIMS and a CAMECA NanoSIMS 50L.

A significant focus of our research is to image the uptake of drugs with sub-cellular resolution. We have discovered that in ToF-SIMS, the logarithm of sensitivity is directly proportional to the Log P value for many different drugs and that some drug molecules exhibit severe matrix effect resulting in no detection. Since the pharmaceutical industry is focused on making low Log P drugs ≤ 3 (Lipinski rule of five) this limits the current applicability. We have recently developed a new method for in situ matrix deposition that significantly increases sensitivity to help overcome this. Furthermore, initial experiments using laser post-ionisation show encouraging results to potentially circumvent some of these issues.

Many metabolites are of low mass (e.g. dopamine) and are in a highly congested region of the mass spectrum. Here, ToF-SIMS is inadequate to resolve the peaks especially at high-spatial resolution. We have led the development of a powerful new hybrid instrument, the 3D OrbiSIMS, combining an Orbitrap^{TM}-based Thermo Scientific^{TM} Q Exactive^{TM} HF instrument and a dedicated ToF-SIMS 5. The instrument is equipped with high-resolution ion beams including a new micron resolution argon cluster ion beam for biomolecular imaging and 3D analysis of organics and an ultra-high resolution Bi cluster focussed ion beam with < 100 nm resolution. We demonstrate the unparalleled ability for 2D and 3D metabolite imaging with sub-cellular resolution.

For imaging at the organelle scale, e.g. mitochondria and lysosomes, then a resolution of 50 nm or better is needed. This is achieved with the CAMECA NanoSIMS 50L. Normally, the solvent based sample preparation procedures used wash out drug molecules. We have developed a method that traps molecules within the organelles and use this to demonstrate the first direct evidence of drug induced phospholipidosis caused by amiodarone uptake in rat alveolar macrophages.

Significant progress has been made towards the goal of super-resolution metabolic imaging but there are many challenges ahead. A technology roadmap will be presented.

PL1-435

HETEROGENEOUS INTERFACES INVESTIGATED BY AMBIENT PRESSURE X-RAY PHOTOELECTRON SPECTROSCOPY

H. Bluhm
Lawrence Berkeley National Laboratory - Berkeley (United States of America)

Solid/liquid interfaces are ubiquitous in technological applications and govern numerous important phenomena, including corrosion, photo-electrochemical splitting of water, and electroplating. A detailed understanding of these processes requires the investigation of solid/liquid interfaces with chemical sensitivity and interface specificity under operating conditions. Ambient pressure X-ray photoelectron spectroscopy is an excellent method to probe the heterogeneous chemistry of these interfaces, and provides in addition the opportunity to measure the local potentials simultaneously with the chemical composition through the observation of shifts in the kinetic energy of the photoelectrons, which serve as a non-contact probe. The challenge for photoelectron experiments on solid/liquid interfaces under ambient conditions is not only the elevated pressure at which these experiments have to be carried out, but equally so the preparation of clean, well controlled samples with high cleanliness and reproducibility. This talk reviews the progress that has been made in the area of ambient pressure X-ray photoelectron spectroscopy experiments on liquid/solid interfaces, in particular electrochemical systems. The talk will also discuss different strategies for the preparation of liquid/solid interfaces suitable for photoelectron spectroscopy experiments, and provide an outlook on opportunities for future research in this field.

PL2-437

PREDICTING THE REACTIVITY OF TRANSITION METAL SURFACES SIMPLY BY COUNTING ATOM NEIGHBORS

P. Sautet
Dep. of Chemical and Biomolecular engineering, Dep. of Chemistry and Biochemistry
University of California, Los Angeles (United States)

Heterogeneous catalysis is at the core of sustainable chemistry, since it allows a fine control of chemical bond forming and breaking processes. For the optimal design of catalysts, a fundamental atomic scale understanding of the structure and electronic structure of the catalytic particle, in interaction with the reactant is of utmost importance. Computational chemistry today is a key method, to reach such an understanding at the molecular level of the structure of the active site and of the elementary processes occurring during the catalytic act.

The understanding of the catalytic properties of nanoparticle catalysts and the design of optimal composition and structures demands fast methods for the calculation of adsorption energies. By exploring the adsorption of O and OR (R=OH, OOH, OCH_3) adsorbates on a large range of surface sites with 9 transition metals, we propose new structure sensitive scaling relations between the adsorption energy of two adsorbates that are valid for all metals and for all surface sites.[1] This opens the way for a new class of activity volcano plots where the descriptor is not an energy but a structure-related descriptor. In addition, to better grasp finite size effects in the nanoparticles, a generalized coordination number is proposed as a leading descriptor for the adsorption strength. [2,3] In the case of oxygen reduction reaction, we show that only surfaces and nanostructures with generalized coordination larger than that of the Pt(111) surface, and hence concave defects, can surpass the activity of Pt(111), whereas convex defects are inactive.[3,4]

Simple structural descriptors as generalized coordination show hence a strong predictive potential for the in-silico design of optimal catalysts.

References

1. F. Calle-Vallejo, D. Loffreda, M. T. M. Koper and P. Sautet, Nature Chemistry, 2015, **7**, 403-410
2. F. Calle-Vallejo, J. I. Martínez, J. M. García-Lastra, P. Sautet and D. Loffreda, Angewandte Chemie International Edition 2014, **53**, 8316-8319
3. F. Calle-Vallejo, J. Tymoczko, V. Colic, Q. H. Vu, M. D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A. S. Bandarenka, Science, 2015, **350**, 185-189
4. F. Calle-Vallejo, M. D. Pohl, D. Reinisch, D. Loffreda, P. Sautet, A. S. Bandarenka, Chem. Sci., 2017, **8**, 2283-2289

PL4-438

ATOM PROBE TOMOGRAPHY: ANALYSIS OF SURFACES AND INTERFACES AT THE TOP OF THE TIP

G. Schmitz
IMW, Univ. Stuttgart - Stuttgart (Germany)

Atom probe tomography is an exciting tool in the analysis of interfaces and surface coatings. The method stands out by combining single-atom sensitivity with a direct volume reconstruction, which delivers three-dimensional maps of the atomic arrangement. Due to its direct 3D information, the method is especially suitable for the investigation of complex microstructures that comprise curved or rough interfaces. By extension with laser-assisted evaporation modes, the analysis of semiconductors and ceramics has recently become possible. Nowadays, the method is close to breaking the materials barrier towards soft matter and even liquids.

The talk will first provide an overview of the experimental technique, its physical principles and the extension with laser-assisted evaporation modes. Modern concepts for improving the data processing and the tomographic volume reconstruction are described. Atom probe tomography is well established in the analysis of solid-state materials. So, the analysis of metal/metal and metal/semiconductor interfaces, including the obtained physical insight in interfacial reactions and transport, are demonstrated with examples of nano-crystalline thin films and silicide formation.

In contrast to this, atom probe analysis of soft matter is still a widely unexplored landscape. Proper field-desorption of macromolecular materials, in the form of single atoms or at least small molecular fractions has already been confirmed by experimental studies of selfassembling monolayers and polyelectrolyte coatings. Indeed, the impact of different layer deposition conditions is well reflected in the measured mass spectra, and a basic volume representation has been obtained. An accurate volume reconstruction, however, would become possible only after having derived a detailed understanding of the complex evaporation sequences.

Finally, the possibility of combining atom probe tomography with methods of cryo-preparation is addressed. For this purpose, at the University of Stuttgart, a dedicated atom probe has been directly attached to a dual beam scanning microscope, the latter equipped with a cryostage to make the transfer of cryogenic samples as direct as possible. Furthermore, a new preparation technique is enabled through a more flexible atom probe geometry. The unique direct combination of techniques has the potential of analysing liquid/liquid and solid/liquid interfaces. Exemplary successful analyses that demonstrate the cutting-edge possibilities of the innovative instrument are presented.

PL-475
SURFACE ANALYSIS: FROM SINGLE CRYSTALS TO BIOMATERIALS

D. Castner
National ESCA and Surface Analysis Center for Biomedical Problems - Seattle (United States of America)

Surface analysis plays an important role in a wide range of research and development areas such catalysis, biomaterials, microelectronics, clean energy and corrosion. The toolbox of surface analysts allows us to easily move across research topics and make significant impacts in both industrial and academic settings. The typical surface analyst is an expert in multiple techniques, surface modification, sample preparation/handling and instrumentation. However, we have all benefited from the significant and numerous advances that have occurred in the past 40 years in terms of improved instrumentation, introduction of new techniques and development of sophisticated data analysis methods, which has allowed us to perform detailed analysis of increasing complex samples. For example, comprehensive analysis of surfaces and surface immobilized molecules with modern surface analysis instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized molecules. Results from x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) and quartz-crystal microbalance with dissipation (QCM-D) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy combined with computation methods such as molecular dynamic (MD) and Monte Carlo (MC) simulations provide important information about surface chemistry and structure. However, even with the advances that have been achieved with these powerful surface analysis techniques, there still remain many significant challenges for surface analysis. These include characterizing the surface chemistry and structure of nanoparticles, determining the atomic level structure of complex molecules bound to surfaces, 3D imaging of samples, and improved sample preparation methods that maintain materials in a relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss my adventures as a surface scientist/analyst starting from chemisorption and reactivity studies of small molecules on single crystal surfaces followed by industrial catalysis research and eventually moving to biomedical surface analysis with side ventures into areas such as clean energy. It has been an exciting journey and I will use it to provide some examples of multidisciplinary role of surface analysis as the field has advanced.

Keynote lectures

ADH - Adhesion

KN6-428

INTERFACE, SURFACE AND SINGLE ATOMS STUDIES BY ABERRATION-CORRECTED ELECTRON MICROSCOPY

O. Krivanek
Nion Co., Kirkland & Arizona State University - Tempe (United States of America)

Monochromated, aberration-corrected scanning transmission electron microscopes (MAC-STEMs) are able to form intense electron probes as small as 0.5-1 Å in diameter, to analyze single atoms spectroscopically in situ (by electron energy loss spectroscopy (EELS) or energy-dispersive X-ray spectroscopy (EDXS)), to map the elemental composition and even the local chemistry of materials in 2D and 3D at atomic resolution, and to probe the chemical composition of organic materials by vibrational spectroscopy, while avoiding radiation damage.

Nion has pioneered many of these advances, by developing STEM aberration correction technology (in the 1990s and 2000s), and then a new electron microscope that is able to map the chemical composition of inorganic materials at atomic resolution, and to acquire images and spectra from single atoms (in 2008, with continuing developments since). We have also introduced a new type of a monochromator, which allows materials to be probed by vibrational EELS carried out with better than 10 meV energy resolution and a few nm spatial resolution, as well as damage-free vibrational analysis in “aloof” and “leapfrog scanning” modes. Much of this work has been one in close collaboration with leading laboratories that use Nion microscopes.

CAT - Catalytic materials

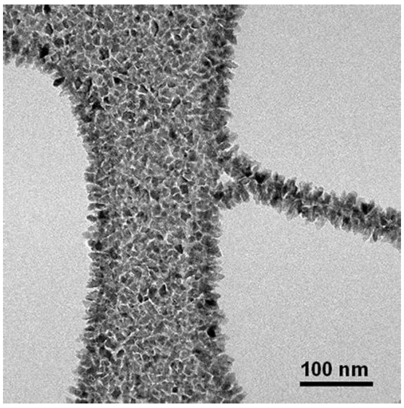
KN1-436

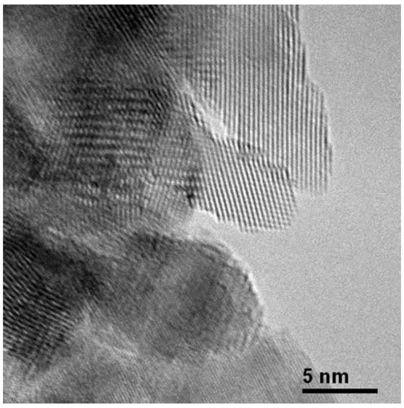
PT-DOPED CEO2 ULTRA THIN FILM CATALYSTS PREPARED BY DIRECT LIQUID INJECTION-CVD

B. Domenichini, N. Zanfoni, V. Potin, L. Imhoff, S. Bourgeois
ICB, Univ. Bourgogne - Dijon (France)

Chemical vapor deposition by direct liquid injection (DLI-CVD) is a film synthesis technique which has the advantage of being able to regulate extremely low molecule flow rates while using a very wide variety of cheap precursors. Indeed, a simple injector system can be used to introduce even solid precursors into the reaction chamber as they have been initially dissolved in a non-reactive liquid. The flow rate of each of the precursors, the reactor temperature, additional gas flow rates and the pressure in the reaction chamber are then many parameters which influence the nature and properties of the films. In particular, the oxidation state of the metallic elements, the film porosity, possible heterogeneities, the crystallinity, ... can be controlled.

In recent years, DLI-CVD was developed to synthesize complex solids such as catalysts or electrolyte materials involved in fuel cell technology. For instance, ceria was widely studied as well as ceria doped with noble metal like Pt which enhances the catalytic activity by improving the reducibility of the surface [1]. In this context, the talk will emphasize about the following points:





-> (i) how DLI-CVD is a good solution to control the morphology of films, especially by allowing the increasing of the porosity,

-> (ii) how processes involved at the substrate/film interface can be followed,

-> (iii) how multi-step DLI-CVD protocols allow to localize specific species in the particle top most layers only [2],

(iv) how depositions carried out directly on transmission electron microscopy carbon grids allow to have a direct observation at the atomic scale of the film growth in the three space directions (see pictures below in the case of ceria).

References

[1] A. Bruix & al., Angew. Chemie - Int. Ed. **201** (2014) 1.
[2] P. Simon & al., Adv. Mater. Interfaces **4** (2017) 1600821.

COR - Corrosion

KN2-362

A NOVEL POTENTIOMETRIC APPROACH TO A QUANTITATIVE CHARACTERIZATION OF OXYGEN REDUCTION KINETICS AT BURIED INTERFACES AND UNDER ULTRATHIN ELECTROLYTE LAYERS

M. Rohwerder, D. Vijayshankar, C.H.W. Wu, X. Zhong
Max-Planck-Institut für Eisenforschung GmbH - Düsseldorf (Germany)

An important step towards unravelling the underlying mechanisms of corrosion driven paint delamination was the application of the Kelvin Probe technique, established by Stratmann et al. to corrosion research (see [1]-[3]). It was found that the electrochemical stability of the buried metal-organic coating interface of painted metal is crucially governed by how effectively the oxygen reduction reaction at the interface is inhibited. As this interface is not directly accessible for study by conventional electrochemical techniques, no detailed knowledge of the kinetics of oxygen reduction at the interface and how it is governed by structural parameters is available. Even the Kelvin Probe technique per se does not provide this information, as it in principle only allows studying the progress of an advancing delamination, but not the involved interfacial reaction kinetics.

To overcome this problem, a new non-destructive method has been developed wherein hydrogen permeation, defining the reaction current density I, is used to quantitatively measure the oxygen reduction kinetics underneath coatings at the resulting equilibrium potential $U(I)$ [4]. By changing the permeation current density of hydrogen a full $U(I)$ curve can be constructed. Furthermore, also the resulting degradation process at the interface can be studied in situ [5]. While the first works have been carried out with model samples based on Pd membranes as substrates, this approach has now also been applied for studies of technically more relevant cases and also for investigating corrosion under ultra-thin electrolyte layers well below 1 micron in thickness. The general applicability of this novel technique will be discussed for a number of different examples and an outlook for future developments will be provided.

References

[1] A. Leng, H. Streckel, M. Stratmann, Corros. Sci. 41 (1998) 547.

[2] A. Leng, H. Streckel, M. Stratmann, Corros. Sci. 41 (1998) 579.

[3] A. Leng, H. Streckel, K. Hofmann, M. Stratmann, Corros. Sci. 41 (1998) 599.

[4] D. Vijayshankar, T.H. Tran, A. Bashir, S. Evers, M. Rohwerder, Electrochim. Acta 189 (2016) 111.

[5] D.Vijayshankar, A. Altin, C. Merola, A. Bashir, E. Heinen, M. Rohwerder, J. Electrochem. Soc. 163 (2016) C778.

KN5-439

DIRECT 3D ATOMIC ARRANGEMENT ANALYSIS BY ATOMIC RESOLUTION HOLOGRAPHY AND STEREOGRAPHY

H. Daimon

Nara Institute of Science and Technology (NAIST) - Nara (Japan)

3D local atomic structure around specific active-site atom, such as a dopant in Si crystal, plays cruicial role in a functional materials. The 3D atomic structure analysis around this kind of local specific atom, however, has not been possible by a standard structure analysis method because this kind of active site has no translational symmetry.

The angular distribution of core-level photoelectrons from the atom in x-ray photoelectron spectroscopy (XPS) can reveal 3D atomic structure around specific atoms, and is called photoelectron holography. Recently its accuracy improved dramatically by the development of new analysis code [1]. A new technique of direct 3D atomic structure analysis method “stereography of atomic arrangement” has also been developed [2]. Because the acuracy of the atomic structure analysis has become high enough for practical applications, we started a project of “3D active-site science” [3]. The target materials in this project ranges from inorganic to bio-materials.

Figure 1 shows an example of photoelectron holography from superconductor graphite intercalation compound $Ca_{0.11}K_{0.89}C_{7.1}$ [4]. We can see clear carbon honeycomb structure and K atoms arranging 2×2 structure. An example of stereography [5] is shown in Fig. 2, which is a direct 3D image of atomic arrangement viewed from an In atom in InP crystal toword [111] direction. The atom A looks closest to you if you see the left and right pictures by your left and right eyes, respectively. These techniques realized an emergence of a new local structure science.

References

[1] T. Matsushita *et al*.: Europhys. Lett. 71, 597 (2005).

[2] H. Daimon: Phys. Rev. Lett. 86, 2034 (2001).

[3] URL: http://www.en.3d-activesite.jp/

[4] F. Matsui *et al*.: Scientific Reports 36258 (2016).

[5] T. Matsumoto, *et al*.: e-J. Surf.Sci. Nanotech. 7, 181 (2009).

KN4-449

NON-INVASIVE CHEMICAL IMAGING OF THE PAINTING SURFACES: AN OPPORTUNITY FOR NEW INTERDISCIPLINARY RESEARCHES IN ART HISTORY

P. Walter

Sorbonne Universités, Université Pierre et Marie Curie ; Laboratoire d'archéologie moléculaire et structurale, LAMS - Paris (France)

The precious character of the Cultural Heritage artifacts and their uniqueness imply particular cautions and require instruments, which may give the maximum of information directly on the objects, in-situ in the museums or in the archaeological sites. The implementation of new analytical tools, including mobile instruments, allows a deep insight on the archaeological and artistic materials. We will show applications of different mobile instruments we built recently in the laboratory to be used in challenging work environments like Egyptian tombs and to allow in situ characterization of artistic materials:

- In the Egyptian, Greek and Roman Antiquity, buildings, tombs and statues were often painted in brightest colors. Only few traces of this splendor remain today on marbles, but their study allows gaining insight in this world of Antique polychromy. XRF and Visible-NIR hyperspectral imaging techniques allow to clearly visualizing traces of pigments different in elemental composition from the marble support or surface contaminations.

- The Impressionists are renowned for their painting technique and their approach to capture the effects of light in nature through a new use of color. We will show on a Gustave Caillebotte painting that high spatial resolution chemical data measured with a new full field X-ray fluorescence imaging instrument reveal a complex use of pigments and the formation of alteration products, and help to understand the artist's choice of materials and their manipulation with small and thin brushstrokes.

NAMA - Nanomaterials

KN3-429

IN-SITU OXIDATION STUDIES OF ALLOY SURFACES AND NANOPARTICLES FROM UHV TO ATMOSPHERIC PRESSURES

A. Stierle
DESY Nanolaboratory, Deutsches Elektronen-Synchrotron DESY and Fachbereich Physik, Research Group X-ray Physics and Nanoscience, Universität Hamburg - Hamburg (Germany)

The oxidation of metal and binary alloy surfaces attracted a lot of interest in the past because of its relevance for corrosion protection and formation of ultrathin planar oxide films with applications as model catalyst support or tunneling barriers. For alloys often selective oxidation of the less noble component takes place, leaving behind a near surface region enriched in the more noble component. The kinetics of planar oxide film growth is governed by different processes, which I will highlight in my talk for the case of NiAl, Fe_3Al and CoGa surfaces, which we investigated by surface sensitive x-ray diffraction methods [1,2]. I will especially address the role of the oxygen pressure in overcoming kinetic barriers during the formation of thicker oxide films [3,4]. In the second part of my talk I will discuss the oxidation behavior of metal and alloy nanoparticles, which is relevant for heterogeneous catalytic reactions involving 4D transition metal nanoparticles. Only recently approaches for modeling the oxidation kinetics of nanoparticles were presented, which lack thorough experimental verification. I will demonstrate how the novel technique of high energy grazing incidence x-ray diffraction allows in a unique way to address the oxidation kinetics of nanoparticles in the sub 10 nm regime [5,6]

References

[1] A. Stierle, F. Renner, R. Streitel, H. Dosch, W. Drube, and B. C. Cowie, Science 303, 1652 (2004)

[2] A. Stierle, R. Streitel, P. G. Nolte, A. Vlad, I. Costina, M. Marsman, G. Kresse, E. Lundgren, J.N. Andersen, R. Franchy, H. Dosch, New Journal of Physics 9, 331 (2007)

[3] A. Vlad, A. Stierle, N. Kasper, H. Dosch, M. Rühle, J. of Mat. Res. 21, 3047 (2006).

[4] A. Vlad, A. Stierle, M. Marsman, G. Kresse, I. Costina, H. Dosch, M. Schmid, and P. Varga, Phys. Rev. B 81, 115402 (2010)

[5] P. Nolte, A. Stierle, N. Kasper, N. Y. Jin-Phillipp, H. Reichert, A. Rühm, J. Okasinski, and H. Dosch, S. Schöder, Phys. Rev. B 77, 115444 (2008).

[6] P. Müller, U. Hejral, U. Rütt and A. Stierle, Phys. Chem. Chem. Phys. 16, 13866 (2014)

Orals conferences

ADH - Adhesion

ADH1-3O012

NEW DEVELOPMENTS ABOUT THE INTEGRATION OF PHOTOVOLTAIC FUNCTION TO CONCRETE-BASED SURFACES

M. Horgnies [1], F. Legrand [1], I. Dubois-Brugger [1], J.J. Pireaux [2]
[1] *LafargeHolcim R&D - Saint Quentin-Fallavier (France)*, [2] *University of Namur - Namur (Belgium)*

The integration of photovoltaic panels into the building envelope is a key-issue to produce more renewable electricity in sustainable “smart” cities. The recent developments in the field of Building-Integrated Photovoltaic (BIPV) [1,2] require the installation of photovoltaic panels on the vertical façades of residential and office buildings. The integration of a PV function on west and east façades would also be a solution to reduce (partially) the seasonal mismatch between production and consumption of electricity.

Based-on previous results [3] showing that the surface of ultra-high performance concrete can be well-designed in terms of smoothness and flatness (by choosing the right formworks and casting conditions), we performed experiments to establish if this type of concrete could be a good candidate to manufacture aesthetical façade panels functionalized by flexible solar cells or photovoltaic thin films.

The different processes of integration tested (by using a lamination process, deposition under vacuum of thin films by PVD/PECVD, or a direct casting process using specific adhesives) led to writing several patents and manufacturing several prototypes from a few cm² area (Figure 1) up to 3m-length panel (Figure 2). This work will detail some of the key-results obtained after characterizing the interface and studying the adhesion between photovoltaic compounds and concrete.

Thanks/Acknowledgement

The authors would like to thank Gérard Molinès (LafargeHolcim), Vivien Sébire and Laurent Houssiau (University of Namur) for their help during this study.

References

[1] Ceron I., Caamaño-Martin E., Neila F.J., « State of art » of building integrated photovoltaic products, Renewable Energy, 58 (2013) 127-133.

[2] Cronemberger J., Almagro Corpas M., Ceron I., Caamaño-Martin E., Vega Sanchez S., BIPV technology application: highlighting advances, tendencies and solutions through solar Decathlon Europe houses, Energy and Buildings, 83 (2014) 44-56.

[3] Horgnies M., Chen J.J., Superhydrophobic concrete surfaces with integrated microtexture, Cement and Concrete Composites, 52 (2014) 81-90.

ADH2-1O058

SURFACE PROPERTIES AND INTERFACIAL BONDING OF ANODIC ALUMINIUM OXIDES AND ORGANIC RESINS

S. Abrahami [1], T. Hauffman [1], J. De Kok [2], V.C. Gudla [3], R. Ambat [3], J.M.C. Mol [4], H. Terryn [1]

[1]Vrije Universiteit Brussel (VUB), Department of Materials and Chemistry, Research Group Electrochemical and Surface Engineering (SURF) - Brussels (Belgium), [2]Fokker Aerostructures BV - Papendrecht (Netherlands), [3]Technical University of Denmark (DTU), Section of Materials and Surface Engineering, Department of Mechanical Engineering - Kongens Lyngby (Denmark), [4]Delft University of Technology, Department of Materials Science and Engineering, Corrosion Technology and Electrochemistry - Delft (Netherlands)

Aluminium pretreatment for bonding purposes needs to produce a stable oxide with optimal chemical and structural characteristics for adhesion with the organic resin. Contributions at the interface region can be related to adsorptive interactions as well as mechanical interlocking between the two phases. To separate between these two effects, we applied either barrier-type or porous-type oxides on two sets of specimens. This paper presents an overview of a study on the relation between oxide properties and interfacial bonding, as affected by the nature of electrolyte and the anodizing conditions, as well as changes in the chemistry of the organic resin (epoxy, phenol, silanes). A detailed characterization of different anodic oxides and its effect on the adsorption of resin-derived functional molecules was performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Results indicate significant changes in the chemical composition of the oxides as a function of the electrolyte 1. Mechanical peel test performance indicate that the initial bond strength is independent of the oxide surface chemistry, while the stability under the ingress of water is correlated to the amount of surface hydroxyls 2. The presence of phosphates and sulphates did not alter bonding mechanisms, only the availability of hydroxyls. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the geometrical modifications to the pore- and oxide structure in porous-type oxides. In addition, energy-dispersive X-ray spectroscopy (EDS) profiles were acquired on TEM cross-sections to assess the oxide structure and concentration of resin inside the pores. Linking these morphological features to peel results show that two types of modifications are crucial for the formation of a strong and durable bonding 3. A minimum pore size is needed for the resin to fill the oxide pores for good initial adhesion. Surface roughness, on the other hand, was found beneficial for the durability of the bond upon the ingress of water. Overall, the results demonstrate that both surface chemistry and oxide morphology contribute to the strength and durability of an adhesive bond.

References

1. Abrahami, S. T., et al., J. Phys. Chem. C 2015, 119, 19967-19975.
2. Abrahami, S. T., et al., J. Phys. Chem. C 2016, 120, 19670-19677.
3. Abrahami, S. T., et al., npj Materials Degradation 2017, in press.

ADH1-1O100

CHEMICAL ANALYSIS OF BURIED INTERFACES AND INTERLAYERS

R. Hauert [1], E. Ilic [1], A. Pardo [1], P. Schmutz [1], T. Suter [1], S. Mischler [2]
[1]Empa - Dübendorf (Switzerland), [2]EPFL - Lausanne (Switzerland)

When coating a substrate material via PACVD, good adhesion is achieved when the coating atoms form a strong chemical bond with the substrate material at the interface. Depending on cross contamination during sputter cleaning and also the oxygen partial pressure during deposition, additional elements will be incorporated into the few atomic rows of the reactively formed interface material. Chemical analysis of an interlayer or an interface is demanding since a depth resolution in the nanometer range is required at the interfaces which are buried under several micrometers of coating.

We will demonstrate through adequate extremely low angle cross-section polishing with an argon beam, it is possible to polish the interfaces at an angle of less than 0.06 degrees with respect to the interface plane (less than 1/1000 steepness). This preparation expands a few nm thick interface to several micrometer laterally, allowing us to quantitatively measure the chemical composition, including the amount of contamination at an interface, by scanning Auger microscopy analysis. Figure 1 displays a SEM picture of the low angle polished interfaces and Si interlayer of a failed 4 µm DLC coated hip joint explant [1]. The Auger analysis shows the 60 nm Si interlayer and a contamination at the TIAlV/Si interface. C1 and C2 indicate two different chemical states of C. It will be shown that small amounts of contaminants at an interface correlate with an increased sensitivity toward delamination when dynamical load is applied on the interface in a corrosive media. Furthermore, the lateral expansion of the interface or interlayer by more than a factor of 1000 open the possibility of determining the corrosion and crevice corrosion sensitivity of these particular areas by electrochemical microcapillary technique.

References

[1] R. Hauert, C.V. Falub, G. Thorwarth, K. Thorwarth, C. Affolter, M. Stiefel, L.E. Podleska, G. Taeger, Acta Biomater. 8 (2012) 3170.

ADH1-2O363

XPS AND TOF-SIMS ANALYSIS OF STAINLESS STEEL TREATED USING PLASMA DOPED WITH H2O AND D2O.

D. Williams [1], E. Kellar [2], D. Jesson [1], J. Watts [1]
[1]*University of Surrey - Guildford (United kingdom),* [2]*TWI Ltd - Cambridge (United kingdom)*

Many industrial applications rely on multi material joining. This can be done by processes such as mechanical joining or adhesive bonding. Adhesive bonding is the least implemented for structural applications but has the most to offer in terms of redicing weight and joining different materials.

For this reason there is pressure to increase the uptake of adhesives in the industrial world and to develop new processes that can make it easier to apply adhesive and increase the bond strength. Currently this is done using chemical processes which require large energy inputs, have complex manufacture and waste disposal requirements and have to be closely controlled. An alternative to these processes which has been investigated is cold atmospheric plasma (CAP).

This paper focusses on the surface modification of material exposed to CAP under different conditions and using different inlet gases to generate the plasma. The aim being to find an optimal plasma for different materials. For this XPS, iXPS and ToF-SIMS have been employed to probe the surface pre and post treatment.

Generally the surface was found to have a significant reduction in carbon post treatment, this can be attributed to carbon chain scission driven by the energetic species in the plasma plume, which has been reported at ECASIA previously. This is accompanied by an increase in the oxygen intensity, as seen using SIMS in figure 1. This may be the oygenation of the remaining carbon or an exposing of the oxide layer.

It was found that there is an increase in nitrogen in the treated area, it is viable that this is from atmospheric mixing in the plasma plume. To further investigate this the plasma was doped with H2O or D2O and then the areas analysed using TOF-SIMS to probe the extent of the atmospheric mixing based on the increase of deuterated species compared to hydrogen and oxygen.

Thanks/Acknowledgement

This work was carried out as part of an Engineering Doctorate in Micro and NanoMaterials and Technologies. DFW gratefully acknowledges support from the ESPRC in providing funding for the Centre for doctoral Training (EP/L016788/1) at the University of Surrey.

BIO - Bio-interfaces & biomaterials

BIO1.1-5O009

HIGHLY SENSITIVE MERCURY (HG) DETECTION BASED ON MODIFIED POROUS SILICON NANOWIRES (PSINWR)

C. Yaddaden [1], N. Gabouze [1], M.A. Benamar [1], R. Boukherroub [2]
[1]CRTSE - Algiers (Algeria), [2]IRI - Lile (France)

In The last years, nanostructures of materials, as the porous silicon nanowires (PSiNWs), have been used extensively studied for the development of several chemical, electro-chemical and biologic sensors, because of their physical and chemical characteristics. The PSiNWs present a unique property, like the biocompatibility and the multifunctional. The PSiNWs can be elaborated from lightly n-type (100) silicon substrate by Ag assisted chemical etching method. The obtained surfaces were grafted with organic functional groups; first, we proceed by the grafting of acid monolayer on hydrogenated PSiNWs surface by hydrosylilation reaction to form Si-C covalent bond. Then, a reactive ester is generated from the terminal acid groups and subsequently this activated surface is coupled with peptide containing amines by the formation of amide bond. Another method has been used to functionalise the porous silicon nanowire consisted in silanisation procedure, consists to: First, porous silicon nanowires PSiNWr surface was hydroxylated with piranha solution (1/3 (v/v) H2O2/H2SO4), followed by silanization with 3-aminopropyltriethoxysilane (APTES). Finaly, the Glycyl-Glycyl-Glycine peptide formed a stable complex with APTES by an aminolysis reaction between the surface NH2 groups and the carboxylic acid groups of the lysine residues on Glycyl-Glycyl-Glycine in presence of mixture solution NHS, EDC. This strategy is based on that used for the immobilization of biomolecules (DNA, proteins, antibodies ...) to elaborate biosensors [1-3].

At each step of the modification, the resulting surfaces were characterized by X-ray photoelectron spectroscopy (XPS). Different characterization techniques were used to investigate the resulting nanostructures, such as SEM, XPS, and electrochemical measurements. Finally, the obtained results can find application in low-cost and high efficiency porous silicon nanowires based applications were envisaged in environmental area. The obtained hybrid structure was tested as probe electrode to the electrochemical detection of mercury (Hg II) in solution. An electrochemical study of the Gly-Gly-Glycine-modified PSiNWr electrode is achieved in the presence of mercury ions.

Thanks/Acknowledgement

porous silicon nanowires; XPS; biosensor; mercury detection

References

[1] N. Patel, M.C. Davies, M. Hartshorne, R.J. Heaton, C.J. Roberts, S.J.B. Tendler, P.M. Williams: Langmuir Vol. 13 (1997), p. 6485.

[2] F. Caruso, E. Rodda, D.N. Furlong, K. Niikura, Y. Okahata: Anal. Chem. Vol. 69 (1997), p. 2043.

[3] A. Tlili, A. Abdelghani, S. Hleli, M.A. Maaref: Sensors. Vol. 4 (2004), p. 105.

BIO1.2-1O018

CHARACTERISATION OF BIOFILMS WITH NEAR-AMBIENT PRESSURE XPS

M. Kjærvik [1], P. Dietrich [2], A. Thissen [2], K. Schwibbert [3], W. Unger [3]
[1]Technische Universität Berlin - Berlin (Germany), [2]SPECS Surface Nano Analysis GmbH - Berlin (Germany), [3]Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany)

A drawback for X-ray photoelectron spectroscopy is that the measurements must be performed under ultra-high vacuum, which limits the type of samples which can be studied. However, by applying a differentially pumped aperture positioned close to the surface, even wet samples can be measured at near ambient pressure while the energy analyser is still under ultra-high vacuum, as illustrated below. Successful XPS-measurements with pressure up to 30 mbar have been reported using this approach [1], which opens up a new world of possibilities for ambient pressure measurements with XPS.

While there are examples where NAP-XPS has been used to study electrochemical processes and heterogeneous catalysis [2], little attention has been paid to its potential use in biological materials. Until now, bacteria have only been characterised with conventional XPS, which requires tedious sample preparation usually involving freeze drying, a treatment that may degrade biological sample constituents [3]. By studying biological samples in their native wet states, new insight about composition, absorption and transport of drugs through cell membranes and extracellular polymeric substance (EPS) layers can be obtained.

Both artificial model-films of exopolysaccharides and biofilms of *Escherichia Coli* have been characterised at pressures ranging from ultra-high vacuum to 15 mbar by using SPECS' EnviroESCA NAP-XPS instrument and conventional XPS. By applying antimicrobials to model biofilms, some of which are known to be resistant towards the antimicrobial in question, the distribution of antimicrobials in biofilms has been studied. Measurement capabilities and limitations of the approach will be discussed.

Thanks/Acknowledgement

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

References

[1] S. Eriksson et al. *Rev., Sci. Instrum.* **2014**, *85*, 075119

[2] D. Starr et al. *Chem., Soc. Rev.* **2013**, *42*, 5833

[3] H. van der Mei et al., *Surf. Sci. Rep.* **2000**, *39*, 1

BIO1.1-1O147

DETECTION OF NANOPARTICLES IN LUNG TISSUE BY TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY

L. Veith, D. Breitenstein, B. Hagenhoff, M. Fartmann, R. Kersting, R. Ter Veen
Tascon GmbH - Münster (Germany)

The localized detection of nanoparticles in biological tissues is an essential part of nanotoxicological research and therefore an important necessity for nano safety. In general, the detection is carried out using techniques such as fluorescence microscopy, scanning electron microscopy-/ EDX or laser ablation ICP-MS. However, these techniques have limitations in lateral resolution, or need markers for unambiguous detection of particles. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) allows detection of the chemical composition without the use of markers at lateral resolutions below 100 nm. For most users with biological background ToF-SIMS is still a new method and not all analytical options and limitations are known. The aim of this study was therefore to demonstrate the equivalence of ToF-SIMS data with data of fluorescence microscopy and highlight its suitability for nanotoxicological analyses. For this purpose, a tissue section of a rat lung was treated with fluorescent nanoparticles. The distribution of the fluorescent particles was analyzed with the help of the established method of fluorescence microscopy. (Fig.1 Overlay of Bright field microscopic image with Fluorescence microscopy showing the distribution of fluorescent nanoparticles (green) in lung tissue (red)). ToF-SIMS Images were recorded at the identical positions and the fluorescent particles were detected by means of their masses.

A correlation analysis of data from fluorescence and SIMS results shows the suitability of the ToF-SIMS for the detection of nanoparticles in tissues. Furthermore, valuable additional information on the biological environment of nanomaterials can be obtained from the mass spectra and images.

Thanks/Acknowledgement

This work is part of the project NanoBioDetect [grant no. 03X0146A] and is supported by the German Federal Ministry of Education and Research (BMBF).

References

L. Veith, A. Vennemann, D. Breitenstein, M. Wiemann, C. Engelhard, B. Hagenhoff, 2016, submitted.

BIO2.1-1O176

SURFACE-IMMOBILIZED ANTIMICROBIAL UREA-BASED FOLDAMERS ON GOLD SURFACES: SYNTHESIS, MODIFICATION, GRAFTING AND ANTIMICROBIAL ACTIVITY

V. Humblot [1], S. Antunes [2], C. Douat [2], G. Guichard [2]
[1]LRS - Sorbonnes Universités, UPMC, UMR CNRS 7197 - Paris (France), [2]IECB - Université de Bordeaux – CNRS UMR 5248, CBMM - Pessac (France)

Biofilms, complex multicellular communities formed by microorganisms represent today a major public health problem in hospitals (nosocomial infections, antibiotic resistance, contamination of catheters and prostheses). Even though different surface treatments are available to prevent the formation of biofilms (biocidal and antiadhesive), they still do not provide an effective protection against resistant microorganisms, especially in the case of biomedical implanted equipment colonization. The development of innovative antimicrobial molecules acting according to a new mode of action is then necessary to eliminate these bacteria but also to define the emergence of new microorganisms resistant to conventional antibiotics.

Due to their high-resistance to proteolytic degradation, the design of synthetic oligomers capable of adopting well-defined structures (i.e. foldamers) has attracted considerable attention over the last twenty years. We studied urea-based foldamers ((NH-CH(R)-CH2-NH-CO)n) whose 2.5 helix structure mimics the natural antimicrobial peptides. In solution, these oligourea (OLs) showed significant antimicrobial activity on different Gram-positive and Gram-negative bacteria. The addition of a terminal cysteamine (cys) groups allows the one-pot grafting on gold surface and the formation of new antimicrobial surfaces from these foldamers. Two other types of attachment were also considered: 1) the insertion of a longer spacer between the OL and the gold surface, and 2) a lateral functionalization in the center of the OL. An exhaustive physicochemical characterization and several microbiological tests made the determination of the parameter(s) influencing the antimicrobial efficiency of these surfaces possible.

BIO1.2-2O179

LOCAL PLASMA ACTIVATION OF PS FILMS WITH A DEFINED DESIGN FOR BIOMEDICAL USE

R. Bitar [1], M. Asadian [1], S. Van Vrekhem [1], P. Cools [1], H. Declercq [2], N. De Geyter [1], R. Morent [1]

[1]*Research Unit Plasma Technology, Department of Applied Physics, Ghent University - Ghent (Belgium),* [2]*Tissue Engineering and Biomaterials Group, Department of Basic Medical Sciences, Ghent University - Ghent (Belgium)*

Air plasma treatment of polystyrene (PS) films was locally carried out by using a micro-plasma needle set-up. Patterns consisting of three vertical lines with different spacing were selected during the plasma modification process to perform chemical and physical changes at these pre-selected locations of a PS surface in an efficient one-step process. The number of treatment repeats was modified and its influence on the surface characteristics was investigated. X-ray photoelectron spectroscopy mapping was performed to show the distribution of oxygen functional groups across horizontal sections of the plasma treated line patterns. These results were compared with water contact angle measurements and showed that increasing the number of treatment repeats led to an improvement of the wettability and an increase of the percentage of oxygen incorporated in a homogeneous way over the modified regions. Atomic force microscopy analysis of the straight treated lines showed that plasma treatment led to a higher surface roughness. However, no significant change in PS topography was observed after different number of treatment repeats. Next, cell tests using human foreskin fibroblasts were carried out in order to reveal how cell attachment and proliferation were enhanced on the plasma activated lines compared to the untreated regions after 1 and 3 days of culturing (Figure 1). Cellular attachment was significantly improved on the treated lines probably due to the increased wettability and roughness [1]. Elongated cell morphology was shown by performing scanning electron microscope measurements. Therefore, the plasma exposure using this needle set-up noticeably improved the PS biocompatibility on a pre-determined area which can further have promising uses in different biomedical applications such as biosensors.

Figure 1. The fluorescence micrograph of the cell adhesion on plasma modified lines after 3 days of culturing.

Thanks/Acknowledgement

This research was supported by two research grants (G.0895.14N and 1513613N) from the Research Foundation Flanders (FWO) and has also received funding from the European Research Council (ERC) under the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. 279022 (PLASMAPOR) and ERC Grant Agreement n. 335929 (PLASMATS).

References

[1] E. Biazar et al., Int. J. Nanomedicine, 6 (2011) 631-639.

BIO1.2-3O182

A THIOLATED POLYSACCHARIDE-BASED SWITCHABLE AND RESPONSIVE BIOINTERFACE

P. Esmaeilzadeh [1], A. Liedmann [2], A. Köwitsch [1], M. Menzel [3], B. Fuhrmann [4], G. Schmidt [4], T. Groth [1]

[1]*Biomedical Materials Group, Institute of Pharmacy, Martin Luther University Halle Wittenberg, Interdisciplinary Center for Material Research Martin Luther University - Halle (saale)* (Germany), [2]*Biomedical Materials Group, Institute of Pharmacy, Martin Luther University Halle Wittenberg - Halle (saale)* (Germany), [3]*Fraunhofer Institute for Mechanics of Materials - Halle (saale)* (Germany), [4]*Interdisciplinary Center for Material Research Martin Luther University, Institute of Physics, Martin Luther University Halle Wittenberg - Halle (saale)* (Germany)

Many efforts have been made on the investigation of solid surfaces, designed as biologically active interface. Stimuli-responsive surfaces made as multilayer nano-coatings attracted wide attention due to the fact that they combine similar adaptive properties like the living biological systems. Hence, a novel cell carrier nano-coating system was developed here from two types of semisynthetic biopolymers, such as thiolated chitosan (t-Chi) and thiolated chondroitin sulfate (t-CS) to acquire redox-dependent reversibility. This system is a 10-layered polymeric assembly with an intrinsic potential for inter- and intramolecular thiol/disulfide interactions. With applying a well-suited oxidant intermediate, the obtained system renewed the molecular assembly, showing markedly enhanced cellular adhesion. While this cell attraction was significantly attenuated under a further decent reductive environment. This prompted us to exploit the system's cyclical conversion ability from an inactive to an active form and also in vice versa. The combined chemical and mechanical outputs like surface charge, wettability, thickness, elastic modulus, topography, and protein affinity were then used to read the state of the switching. In fact we realized synergistic effects of above factors as essential mediators of a dynamic control manner. This study wants to highlight the reversibility of the switching behavior of this novel nano-coating for harnessing protein adsorption/desorption and cell adhesion/repulsion [Fig 1], which can be highly important considerations for the advanced design of manufactured materials coming in contact with biological fluids.

References

1. Esmaeilzadeh P, Köwitsch A, Heyroth F, Schmidt G, Fischer S, Richter K, Groth T (2017) Synthesis of thiolated polysaccharides for formation of polyelectrolyte multilayers with improved cellular adhesion. Carbohydrate Polymers 157:1205–1214.

2. Köwitsch A, Niepel MS, Michanetzis GPA, Missirlis, YF, Groth T (2016) Effect of Immobilized Thiolated Glycosaminoglycans on Fibronectin Adsorption and Behavior of Fibroblasts. Macromol. Biosci. 16: 381–394.

BIO2.1-3O183

THE STUDY OF THIN BIOCOMPATIBLE FILM MICROSTRUCTURE GROWN ON DIFFERENT SUBSTRATES

J. Malek, V. Starý, L. Cvrcek, P. Sachr, Z. Tolde
CTU in Prague (Czech republic)

Materials for bioapplications are nowadays intensively studied as the demand for new implants increased during last years. The biocompatibility is essential for all bioapplications. It can be increased via thin biocompatible film formation on the surface while keeping the overall mechanical properties of the subsrtrate. Ti-39Nb alloy (Ti-25Nb in at.%) is known to be biocompatible beta-titanium alloy as both of the Ti and Nb elements are considered to be fully biocompatible [1]. Thin film of the biocompatible Ti-39Nb alloy has been sputtered on four different substrates in this paper. The substrates of stainless steel, pure titanium (grade 2), Ti-6Al-4V alloy and Ti-39Nb alloy were used as substrates. Those substrates were different in grain size from ~5 µm (Ti-6Al4V) to ~600 µm (Ti-39Nb). Thin film was sputtered on substrates and subsequently studied by using scanning electron microscopy, transmission electron microscopy and light microscopy. Transmission electron microscopy reveled the thin film microstructure consisting of β-Ti (bcc) and α”-Ti (bct) columns. Those columns are typical for sputtered thin films [2]. Those columns are dominant for all studied substrates. Significant differences emerged during etching especially in Ti-39Nb and Ti-grade 2 substrates where some grains are strongly etched and some remained unetched. More detailed study carried out on SEM revealed that the etched grains have rough surface consisting of etched columns and other grains exhibit more flat and quite smooth surface. This is probably connected with the microstructure where fine columns of both α”-Ti and β-Ti phases can be easily etched whereas one phase (or coarser columns) are more resistant to etching. However this has to be proved by further TEM study.

Thanks/Acknowledgement

This study was supported by the Grant Agency of the Czech Republic (grant no. 15-01558S) and by the Ministry of Education, Youth and Sport of the Czech Republic, Program NPU1, project No. LO1207.

References

[1] A. Biesiekierski, J. Wang, M. Abdel-Hady Gepreel, C. Wen: A new look at biomedical Ti-based shape memory alloys. Acta Biomaterialia 8 (2012) 1661-1669.

[2] I Petrov, P.B. Barna, L. Hultman, J.E. Greene: Microstructural evolution during film growth. Journal of Vacuum Science & Technology A21 (5) 117-128.

BIO1.2-4O200

SURFACE FUNCTIONALIZATION OF ZINC SELENIDE FOR CONTROL AND MONITORING OF BIOFILM GROWTH

E. Yunda [1], G. Francius [2], H. Alem [3], F. Quilès [2]

[1]Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), UMR 7564; Institut Jean Lamour (IJL), Parc de Saurupt CS 50840, 54011 - Nancy (France), [2]Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME), UMR 7564, F-54600 - Villers-Lès-Nancy (France), [3]Institut Jean Lamour (IJL), Parc de Saurupt CS 50840, 54011 - Nancy (France)

Bacterial adhesion to surfaces with subsequent development into closely linked populations – biofilms – is a great cause for concern, particularly, in food industries and medicine fields. The control of the formation of biofilms requires the understanding of the initial step of the bacterial adhesion that is influenced, among other things, by the surface properties of the support material. Therefore, depending on these surface properties the biofilm growth can be enhanced or prevented. Surface properties can be controlled using functionalization with self-assembled monolayers (SAM). SAM on zinc selenide (ZnSe) possesses particular interest for studying biofilms due to transparency of ZnSe in the infrared region [1]. However, only few attempts of its functionalization have been reported [2-3]. In the present work self-assembly of alkanethiols $HS(CH_2)_nX$ ($X=CH_3$, OH, NH_2, and COOH with $n = 11$ or 10) on nude ZnSe and on gold coated ZnSe were studied. Functionalized surfaces were characterized using a combination of X-ray photoelectron spectroscopy, IR spectroscopy, AFM, and contact angle measurements. The adhesion of Lactobacillus rhamnosus GG (LGG) was tested onto the nude ZnSe and the functionalized surfaces. The interactions forces between LGG and the functional groups were addressed by AFM force spectroscopy. The biofilm growth was monitored using infrared spectroscopy in attenuated total reflexion mode on the different surfaces. We showed that the biofilm growth was surface properties-dependent. This was related to the difference of interactions between bacteria and various functional groups (Figure 1). Our results provide support for the better understanding of LGG adhesion and biofilm formation onto abiotic surfaces and they can be further used to extend the area of ZnSe applications.

References

1. Quilès, F., Saadi, S., Francius, G., Bacharouche, J. & Humbert, F. Biochimica and Biophysica Acta - Biomembranes 1858, 75–84 (2016).
2. Noble-Luginbuhl, A. R. & Nuzzo, R. G. Langmuir 17, 3937–3944 (2001).
3. Riccardi, C. S., Hess, D. W. & Mizaikoff, B. Analyst 136, 4906–4911 (2011).

BIO2.2-1O213

INITIAL STAGES OF CARBONIZATION OF OXIDIZED LIGNIN STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY

A. Hinterreiter [1], J. Duchoslav [2], M. Kehrer [1], C. Unterweger [3], C. Fürst [3], D. Stifter [1]
[1]Center of Surface and Nanoanalytics, Johannes Kepler University - Linz (Austria), [2]CEST Centre of Electrochemical Surface Technology - Wiener Neustadt (Austria), [3]Kompetenzzentrum Holz GmbH - Linz (Austria)

Lignin is the second most abundant bio-polymer after cellulose. Being a by-product of paper industry, it is mainly used as a fuel in paper mills. However, lignin has a great potential as an alternative to petroleum-based precursor chemicals. One promising application is the production of carbon fibers (CF) from lignin in a process consisting of spinning, followed by oxidation and carbonization [1]. A better understanding of the physical mechanisms underlying these processes is required to optimize the production of lignin based CF and to make them competitive in the CF market. To this end, we studied the change of surface chemistry during the initial stages of carbonization of non-oxidized as well as oxidized films of wheat straw lignin by X-ray photoelectron spectroscopy (XPS).

The C1s spectra of non-oxidized lignin samples showed only ether and hydroxyl groups as oxygen functionalities, which is consistent with the reported structure of wheat straw lignin (hydroxyphenyl, guaiacyl and syringyl units linked mainly by ether bridges [2]). After heating of non-oxidized lignin in air, the concentration of oxygen increased and a new carboxyl peak in the C1s spectra (see figure, left). A different behavior was observed for the oxidized lignin samples. Significant amounts of carbonyl and carboxyl groups introduced by oxidation were removed during heating to temperatures between 100 °C and 200 °C (see figure, right). Moreover, above 250 °C a strong asymmetry emerged in the aliphatic/aromatic peak for both non-oxidized and oxidized lignin samples, which indicated the formation of amorphous or graphite-like carbon. In order to gain complementary information on the effect of heat treatment, a thermogravimetric analysis was performed. Furthermore, thermal changes in the surface topography of non-oxidized as well as oxidized lignin films were studied by atomic force microscopy.

Thanks/Acknowledgement

This work was carried out within the IWB/EFRE programme, cofinanced by the European Regional Development Fund and the State of Upper Austria.

References

[1] Maink, H.; Täger, O., Körner, E.; Hilfert, L.; Busse, S.; Edelmann, F. T. Journal of Materials Research and Technology 2015, 4, 283–296.

[2] Zeng, J.; Helms, G. L.; Gao, X.; Chen, S. Journal of Agricultural and Food Chemistry 2013, 61, 10848−10857.

BIO1.1-2O221

ULTRASOUND ASSISTED DEPOSITION OF CALCIUM PHOSPHATE LAYERS ON MAGNESIUM ALLOY AZ31

C-N. Liu [1], I. Giner [1], F. Böke [2], M. Gebhard [3], A. Devi [3], H. Fischer [2], A. Keller [1], G. Grundmeier [1]

[1]Technical and Macromolecular Chemistry, Department of Chemistry, University of Paderborn - Paderborn (Germany), [2]Dental Materials and Biomaterials Research, RWTH Aachen University Hospital - Aachen (Germany), [3]Chemistry of Inorganic Materials, Ruhr-University Bochum - Bochum (Germany)

Magnesium alloys have attracted great interest among the biomaterials community as they present biocompatibility and mechanical properties close to human bones. Therefore AZ31 is considered to be good candidate material for biodegradable implants. Unfortunately, these alloys experience a fast and uncontrollable corrosion rate when they are exposed to physiological media, which in turn leads to a critical hydrogen evolution.

The coating of implants with inorganic calcium phosphates structures is a common approach for controlling the degradation rate of magnesium based alloys. In addition, these coatings provide additional biocompatibility and bioactivity. Among the most used calcium phosphate coatings is octacalcium phosphate (OCP) which is the precursor of biological hydroxyapatite (HAp). HAp is one of the major constituents of bones and teeth. OCP coatings are able to regulate the growth and degradation of the new bone related material.[1]

Consequently, synthesis, deposition and characterization of HAp is a field of high interest. However, to date the correlation of the structures of the deposited calcium phosphates with their biofunctionality is incomplete due to the challenging characterization of the deposited layers.

This contribution reports on the synthesis of related calcium phosphates species (OCP and nanocrystalline Apatite) by means of ultrasound assisted deposition.[2] The deposited coatings were characterized by means of X-ray photoelectron spectroscopy, FTIR spectroscopy, Raman spectroscopy and X-ray diffraction. The correlation between the deposition parameters and the coating composition and structure will be illustrated. Additionally, electrochemical impedance spectroscopy and cytocompatibility tests with human mesenchymal stem cells demonstrate the suitability of the coatings for biomedical applications.

Thanks/Acknowledgement

The authors gratefully acknowledge the financial support of the German Federation of Industrial

Research Associations (AiF) within the IGF project No 18267 N.

References

(1) Suzuki, O.; Kamakura, S.; Katagiri, T.; Nakamura, M.; Zhao, B.; Honda, Y.; Kamijo, R. Bone formation enhanced by implanted octacalcium phosphate involving conversion into Ca-deficient hydroxyapatite. Biomaterials 2006, 27, 2671–2681.

(2) Liu, C.-N.; Wiesener, M.; Giner, I.; Grundmeier, G. Structure and corrosion resistance of cerium-oxide films on AZ31 as deposited by high-power ultrasound supported conversion chemistry. Front. Mater. 2015, 2.

BIO1.1-4O248

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) FOR BIOMATERIALS CHARACTERISATION

J. Counsell [1], W. Boxford [1], C. Blomfield [1], J. Hardy [2], M. Firlak [2], A. Roberts [2]
[1]Kratos Analytical, [2]Lancaster University

Electromagnetic fields affect a variety of tissues (e.g. bone, muscle, nerve and skin) and play important roles in a multitude of biological processes. This has inspired the development of electrically conducting devices for biomedical applications, including: biosensors, drug delivery devices, cardiac/neural electrodes, and tissue scaffolds. It is noteworthy that there are a number of clinically approved devices capable of electrical stimulation of the body, all of which are designed for long term implantation. The first examples of which (cardiac pacemakers) were developed in Europe; other examples include bionic eyes, bionic ears and electrodes for deep brain stimulation (DBS). It is also notable that many companies have recently established new research, development and commercialisation of bioelectronic medicines. Bioelectronics is an emerging area of technology that promises broad impact in healthcare, the potential market for which is worth billions of Euros.

The detailed analysis of biomaterials and biomedical devices offers valuable insight into the underlying function of the products, and we demonstrate the application of state of the art X-ray photoelectron spectroscopy (XPS) to characterize the surface and interfaces of biomaterials.

Here we demonstrate the use of XPS to analyse bioelectronic materials in various morphologies (e.g. films and foams). The materials are composites of electroactive polymers (e.g. polypyrrole) and biopolymers (e.g. polysaccharides and proteins) that can be used for various applications (e.g. drug delivery, tissue scaffolds).

References

J. Rivnay, et al. Review on bioelectronics: Chem. Mater. 2014, 26, 679−685

G. G. Wallace, et al. Review on bioelectronics: Nanoscale. 2012, 4, 4327–4347

J. G. Hardy, et al. Article on bioelectronic drug delivery devices: J. Mater. Chem. B, 2014, 2(39), 6809-6822.

J. G. Hardy, et al. Article on instructive bioelectronic tissue scaffolds: Macromol. Biosci., 2015, 15, 1490-1496.

BIO2.1-2O294

STABILIZATION OF DRY PROTEIN COATINGS WITH COMPATIBLE SOLUTES

M. Killian
Friedrich-Alexander-University - Erlangen

Storage of protein modified surfaces in air can become necessary for several applications, e.g. during the implantation of biomedical devices or for sensor applications. Protein coatings are very sensitive to dehydration and can undergo significant and irreversible alterations of their conformations if exposed to air. Xia et al.[1] previously investigated the stabilizing effects of trehalose on protein self-assembled monolayers (SAMs) and could retain the protein activity for 2h.

With the use of compatible solutes from extremophilic bacteria, ectoine and hydroxyectoine, we were able to preserve the activity of dried protein SAMs up to 24h. The protective effect can be explained by the "preffered exclusion model"[2] (cf. figure below), i.e., the solutes trap a thin water layer around the protein, retaining an aqueous environment and thus prevent unfolding of the protein. Horseradish peroxidase immobilized on compact TiO_2 was used as a model system. Structural differences between compatible solute stabilized and unstabilized protein films were analyzed with static time-of-flight secondary ion mass spectrometry (ToF-SIMS). The biological activity difference observed in a colorimetric activity assay was correlated to changes in protein conformation by application of principle component analysis (PCA) to the static ToF-SIMS spectra.

Thanks/Acknowledgement

We would like to thank the DFG research unit FOR1718 FunCOS "Functional Molecular Structures on Complex Oxide Surfaces" for funding, Prof. D.G. Castner for providing the opportunity to conduct parts of the research at NESAC/BIO, Seattle, USA, and Dr. A.J. Taylor, NPL, UK, for discussion of PCA data.

References

[1] N. Xia, C.J. May, S.L. McArthur, D.G. Castner, Langmuir 2002, 18, 4090.

[2] T. Arakawa, S.N. Timasheff, Biophys. J. 1985, 47, 411

BIO1.1-3O320

ENZYME AND POLYELECTROLYTE FUNCTIONALIZED LAYERED NANOMATERIALS: TOWARDS PROCESSABLE BIONANOMATERIALS FOR ANTIOXIDANT APPLICATIONS

P. Rouster, M. Pavlovic, I. Szilagyi
Department of Inorganic and Analytical Chemistry, University of Geneva - Geneva (Switzerland)

In our days, antioxidant enzymes are commonly used in various fields such as biomedical treatment or chemical manufacturing in order to convert reactive oxygen species (ROS) into water and oxygen[1,2]. During the degradation process of the ROS, several enzymes are involved like superoxide dismutase (SOD) and horseradish peroxidase (HRP). However, these enzymes are sensitive to the external medium (pH, temperature and ionic strength) which can significantly affect their properties. Furthermore, the recyclability of native enzymes is often limited as they can hardly be separated from their reaction medium. In order to improve the reusability and the functional stability of the enzymes, their immobilization on solid supports appear to be a promising approach[3].

Here, we investigated the immobilization of enzymes (native or enzyme mimic) on layered nanomaterials such as titania nanosheets (TNS) or layered double hydroxides (LDH). The immobilization of the antioxidant enzymes or their mimics on the nanomaterials occurred through electrostatic and hydrophobic interactions. As the bare materials possessed a limited stability at low/moderate salt concentration, they were functionalized with polyelectrolytes in order to improve the colloidal stability and to protect and prevent the leakage of enzymes from the surface. Depending on the polyelectrolyte dose applied, charge neutralization (aggregating system) and overcharging (stable suspension) of the nanomaterials could be observed due to polyelectrolyte adsorption on oppositely charged surfaces. The fully coated nanomaterials resulted in stable dispersions where primary particles were observed (Figure 1A). Finally, the enzymatic activity (Figure 1B) of the immobilized and embedded enzymes were measured and compared to the native one.

References

[1]: Mateo, C.; Palomo, J. M.; Fernandez-Lorente, G.; Guisan, J. M.; Fernandez-Lafuente, R. Enzyme and Microbial Technology 2007, 40, 1451.

[2]: Louzao, I.; van Hest, J. C. M. Biomacromolecules 2013, 14, 2364.

[3]: Pavlovic, M.; Rouster, P.; Szilagyi, I. Nanoscale 2017, 9, 369.

BIO1.2-5O379

MICROBIOLOGICALLY INFLUENCED CORROSION MECHANISMS OF DX2304 DUPLEX STAINLESS STEEL DURING THE FORMATION OF PSEUDOALTEROMONAS NCIMB 2021 BIOFILM: A TOF-SIMS, XPS AND ELECTROCHEMICAL CHARACTERIZATION

E. Gardin [1], S. Zanna [1], A. Seyeux [1], A. Allion [2], P. Marcus [1]

[1]CNRS – Chimie ParisTech, PSL Research University, Institut de Recherche de Chimie Paris, Physical Chemistry of Surfaces Group - Paris (France), *[2]Aperam Isbergues, Research Center – Solutions Dept. - Isbergues* (France)

Microbiologically Influenced Corrosion (MIC), also known as biocorrosion, refers to the accelerated corrosion of metallic materials induced by adhesion of microorganisms at the surface and subsequent biofilm formation [1]. This biofilm consists in the microorganisms embedded in a self-produced matrix of Extracellular Polymeric Substances (EPS) composed of polysaccharides, proteins, lipids and debris of DNA and RNA [2]. In the case of stainless steels, the presence of an aerobic biofilm at the surface is often found to promote localized corrosion [3]. The evolution of the surface oxide film (passive film) during biofilm formation is therefore a key parameter in MIC of stainless steels. In this work, oxide film/biofilm interactions were studied in the case of DX2304 Duplex Stainless Steel (DSS), a complex alloy with a two-phase microstructure composed of austenite and ferrite. Biofilm formation was performed in aerated artificial seawater inoculated with the marine aerobic *Pseudoalteromonas* NCIMB 2021 bacterial strain for 1h, 24h and 1 week. Control experiments were conducted in an equivalent abiotic medium. In order to investigate the effect of biofilm on the surface oxide film, an innovative methodology based on the coupling of Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) was developed. This methodology allowed to characterize locally the oxide film formed on austenite and ferrite phases of DX2304 DSS. Electrochemical behavior was studied by Open Circuit Potential (OCP) monitoring, Electrochemical Impedance Spectroscopy (EIS) and polarization curves. In the first step of biofilm formation (1h), the composition of the surface oxide film was unchanged and the electrochemical behavior remained stable, apart from a decrease in the level of cathodic oxygen reduction. For longer exposures times (24h and 1 week), a significant decrease in the OCP associated with a further decrease in the level of cathodic oxygen reduction were observed and will be discussed with regard to surface characterization.

References

[1] F. Mansfeld, “The interaction of bacteria and metal surfaces”, Electrochimica Acta, vol. 52, pp. 7670-7680, 2007.

[2] H. C. Flemming, J. Wingender, U. Szewzyk, P. Steinberg, S. A. Rice, S. Kjelleberg, “Biofilms: an emergent form of life”, Nature Reviews Microbiology, vol. 14, pp. 563-575, 2016.

[3] I. B. Beech, V. Zinkevich, L. Hanjangsit ,R. Gubner, R. Avci, “The effect of *Pseudomonas* NCIMB 2021 biofilm on AISI 316 stainless steel”, Biofouling, vol. 15, pp. 3-12, 2000.

BIO2.1-5O413

TITANIUM SURFACES FUNCTIONALIZED WITH CHITOSAN MOLECULES AS ENGINEERED BIOMATERIALS FOR OSTEOPROSTHETIC IMPLANTS.

G. Iucci [1], M. Santi [1], V. Secchi [1], M. Monetti [1], M. Orsini [2], S. Concolato [2], C. Battocchio [1]
[1]Roma Tre University, Dept. of Sciences - Rome (Italy), [2]Roma Tre University, Dept. of Engineering - Rome (Italy)

Titanium is a biocompatible material widely used in orthopedic/dental medicine; furthermore, this substrate is well known for its ability to promote osteointegration. Recently, a great research effort was devolved to the development of bioactive coatings on titanium implants, with the aim to obtain engineered biomaterials most appropriate for long-term treatment of critical-sized bone defects. The quest for developing the most suitable bioactive prosthetic surface has been addressed from different perspectives: the composition of the bioactive material, the structure of the coating in terms of being monolithic or composite, the surface topography features, and the fabrication techniques used to prepare the desirable coating [1]. However, bacterial infection following surgical implantation of biomaterials and devices poses a risk to implant successful osteointegration.

Recently, it was shown that, among the different bioactive inorganic materials being investigated, titanium surfaces functionalized with chitosan molecules are able to prevent bacterial adhesion [2] through a mechanism involving the interaction between the oppositely charged bacterial cell wall and the chitosan. This interaction results in a change in bacterial membrane permeability, leading to the fatal leakage of cellular contents. In this work, chitosan-grafted Ti surfaces were investigated by surface-sensitive spectroscopic techniques such as XPS (X-ray photoelectron spectroscopy) and RAIRS (Reflection Absorption Infrared Spectroscopy), with the aim of determining the structure of the immobilized carbohydrates overlayer. XPS analysis allows checking the chemical structure of the system, ascertaining the successfulness of the grafting procedure and determining the overlayer thickness. RAIRS investigations yield information on the adlayer molecular structure.

References

[1] F.Pishbin, V. Mouriño, S. Flor, S.Kreppel, V. Salih, M. P. Ryan, and A.R. Boccaccini ACS Appl. Mater. Interfaces 2014, 6, 8796−8806

[2] Tee Yong Lim, W. Wang, Zhilong Shi, Chye Khoon Poh, K. G. Neoh J Mater Sci: Mater Med (2009) 20:1–10

BIO2.1-4O422

IMPACT OF HYDROPHILIC AND HYDROPHOBIC FUNCTIONALIZATION OF MODEL TIO2/TI SURFACES ON PROTEINS ADSORPTION

A. Galtayries [1], H. Fabre [2], D. Mercier [1], D. Portet [3], N. Delorme [2], J.F. Bardeau [2]
[1]IRCP, Chimie ParisTech - Paris (France), [2]Université du Maine - Le Mans (France), [3]Surfactis Technologies - Angers (France)

Controlling adsorption of proteins onto medical devices is a key issue for implant-related infections. As self-assembled monolayers (SAMs) on titanium oxide represent a good model to study the surface-protein interactions, TiO_2 surface properties were modified by grafting bisphosphonate molecules terminated with hydrophilic poly(ethylene glycol) groups and hydrophobic perfluoropolyether ones, respectively. Characterization of the surface chemistry and surface topography of the modified surfaces was performed using XPS and atomic force microscopy (AFM). Quartz-crystal microbalance with dissipation (QCM-D) was used to determine the mass of adsorbed proteins as well as its kinetics. Poly(ethylene glycol)-terminated SAMs were the most effective surfaces to limit the adsorption of both BSA and fibrinogen in comparison to perfluorinated terminated SAMs and pristine TiO_2 surfaces, as expected. The adsorption was not reversible in the case of BSA, while a partial reversibility was observed with Fg, most probably due to multilayers of proteins. The grafted surfaces adsorbed about the same quantity of proteins in terms of molecules per surface area, most probably in island-like groups. The proteins interaction on pristine TiO_2 reveals a more important, non-specific adsorption of proteins.[1]

These differences observed in the adsorption of the proteins on the functionalized Ti surfaces reveal the importance to further study bacterial and yeasts adherence.

References

[1] H. Fabre, D. Mercier, A. Galtayries, D. Portet, N. Delorme, J.- F. Bardeau, Applied Surface Science, accepted 2017.

CAT - Catalytic materials

CAT2-3O088
REDOX PROPERTIES OF CU IONS IN MOLECULAR SIEVES

J. Radnik [1], T.T.H. Dang [2], S. Gatla [3], V.S. Raghuwanshi [4], A. Hoell [5]
[1]Bundesanstalt für Materialforschung und -prüfung (BAM) - Berlin (Germany), [2]Vietnam Institute of Industrial Chemistry - Hanoi (Vietnam), [3]Johnson Matthey Chemicals India - Raigad (India), [4]Monash University - Clayton (Australia), [5]Helmholtz-Zentrum für Energie und Materialien - Berlin (Germany)

Molecular sieves as materials with defined pores are nanostructured materials which can applied in chemistry, medicine and biology. Typical examples for such materials are zeolites, porous glass, mesoporous silica and active carbon. Introducing transition metal ions in such materials can widen the possibilities of these materials. Especially, by varying the location of these ions in the sieves the redox properties can be tailored which is a promising way to obtain catalysts with the desired properties.[1,2]

For this purpose, Cu^{2+} ions were introduced into a SAPO-5 (silicoaluminaphosphate) with the zeolite framework type AFI by a hydrothermal method and by impregnation. As expected, the different preparation methods led to different locations of the Cu^{2+} ions which was confirmed by Extended X-ray Absorption Fine Structure and Anomalous Small-Angle X-ray Scattering: by the hydrothermal method the ions were incorporated in the SAPO-5 framework, by impregnation mononuclear Cu species or CuO nanoparticles were formed depending on the Cu amount. For investigating the redox properties of the Cu^{2+} ions the differently prepared sample were treated in an inert Ar atmosphere until 550°C. X-ray Photoelectron Spectroscopy was performed to study the valence states of Cu after this treatment. For a definite determination of the valence states, both Cu2p photoelectron and *Cu LMM* Auger spectra had to be recorded. Cu^{2+} exhibited a clear chemical shift and a typical satellite structure in the Cu2p spectra, but between mono- and zerovalent Cu it could not distinguish. On the other hand, these two species showed a clear shift in the Auger spectra. It was shwon, that Cu^{2+} incorporated in the framework could not be reduced in Ar atmosphere. In contrast, the mononuclear Cu^{2+} species were reduced to stable Cu^{+}. Likewise, the CuO nanoparticles were reduced to the monovalent species, but they could be much more easily reoxidized in air (see Figure). The consequences for the catalytic properties will be discussed.

Thanks/Acknowledgement

We thanks D.L Hoang and A.Martin for the scientific discussions and ESRF and BESSY II for providing beamtime.

References

(1) P.J.Smeets, J.S.Woertnik, B.F.Sels, E.I.Solomon, R.A.Schoonheydt, *Inorg.Chem.* **2010,** 49, 3573-3583

(2) J.Cejka, G.Centi, J.Perez-Pariente, W.J.Roth, *Catal.Today* **2012**, 179, 2-15

CAT2-4O121

COMBINED XPS AND LEIS SPECTROSCOPIC STUDY OF MODEL LAFEO3 PEROVSKITES-BASED THREE-WAY CATALYSTS

S. Nandi, E. Berrier, A.S. Mamede, J.F. Paul
Unité de Catalyse et Chimie du Solide UCCS UMR CNRS 8181 - Villeneuve D'ascq (France)

INTRODUCTION

Perovskite materials like $LaFeO_3$ possessing the so-called self-regenerating properties [1] have the potential to be used as heterogeneous bulk catalysts for application as three-way catalysts in automotive exhausts for the removal of pollutants like NOx, CO and unburnt hydrocarbons, simultaneously. Besides the fact that the catalytic reactions occur essentially at the surface, it has been also seen that La-containing perovskite surface is subjected to variations from the bulk formulation by formation of amorphous carbonate phase [2]. Recent work has highlighted the role of the reversible mobility of "bulk" species towards the surface in perovskites [3], a phenomenon at the origin of self-regenerating properties. We are interested in understanding how the perovskite formulation affects its surface composition and structure by the combination of surface analysis techniques for the investigation of conventional and model $LaFeO_3$ catalysts.

RESULTS

The $LaFeO_3$ powders were prepared by varying the formulation ($La_{1-x}FeO_3$, $0 \leq x \leq 4$) by the citrate method. In parallel, the nature (composition and thickness) of thin films by adjusting the citrate solution concentration and the spin rate has been investigated in order to obtain homogeneously covered films on Si(100) wafers. The structure (Raman and grazing XRD) of the thin films showed that they are relevant models for the powdered $LaFeO_3$ catalysts. The thin films surface compositions were investigated by XPS (Table 1). Adjusting the bulk formulation allows obtaining a surface atomic La/Fe ratio finally close to 1. Moreover, LEIS analyses (Figure 1) confirm that the Fe coverage is higher in $La_{0.8}FeO_3$(1b) than in $LaFeO_3$(1a). Finally, decreasing the precursor concentration allows dispersing perovskite as an atomic layer on SiO_2/Si(100)(1c). Finally, the evolution of the XPS intensities (La 3d, Fe 2p and Si 2p) combined with morphological models allowed us to estimate the thickness of the $LaFeO_3$ coatings in function of preparation parameters, coverage being estimated from LEIS data.

Formula	La/Fe ratio (XPS)
$LaFeO_3$	3.0
$La_{0,9}FeO_3$	2.6
$La_{0,8}FeO_3$	2.2
$La_{0,6}FeO_3$	1.3

Thanks/Acknowledgement

The present work is part of the PARTIAL-PGMs project funded by the European Commission (Horizon 2020) under grant agreement 686086.

References

[1] Nishihata et al. Nature, 418 (2002) 164-167
[2] Schoen et al. Catalysis Today, 258 (2015) 543-548
[3] Blanck et al. Catalysis Today, 283 (2017) 151-157

CAT1-2O209

PT DOPED TUNGSTEN OXIDE – FROM MODEL STUDIES TO CATALYTIC AND GAS SENSING APPLICATIONS

K. Mašek, R. Šedivá, V. Johánek, A. Ostroverkh, M. Václavu, R. Fiala, N. Tsud, J. Vojík, O. Leiko, V. Matolín
Charles University, Faculty of Mathematics and Physics - Prague (Czech republic)

Tungsten oxide is a reducible oxide and it serves as an important material in the fields of heterogeneous catalysis and gas sensing. Chemical properties of tungsten oxide can be changed by its doping by any active metal like Pt. Complex structure of the real devices are not suitable for fundamental research. The investigation is performed on well-defined model systems based generally on well-ordered layers prepared by physical methods under UHV conditions. Model systems are studied by a variety of surface techniques to relate the physical properties of the system to its chemical reactivity.

In this contribution we will present the structure of the epitaxial and nanostructured platinum - tungsten oxide model system. Strong metal substrate interaction (MSI) led to the modification of electronic state and chemical properties of the base material. Chemical reactivity of the model system will be demonstrated by adsorption of methanol at low temperature and its decomposition. Chemical properties and structure were studied using synchrotron and laboratory x-ray photoelectron spectroscopy and electron diffraction under UHV conditions. Methanol dehydrogenation process was observed during step by step increase of the temperature up to 500 K. The formation of methoxy and methyl groups was found in dependence on the temperature annealing.

Practical use of Pt – tungsten oxide system in the gas sensing and catalytic applications under operando conditions will be shown. These nanostructured layers were prepared by radiofrequency magnetron sputtering using a composite Pt – tungsten oxide target. The structure, morphology and chemical composition including metal-oxide interaction were characterized by photoelectron spectroscopy and scanning electron microscope. The efficiency and stability of the system during catalytic reaction and gas sensing process were investigated. The chemical properties of nanostructured Pt-tungsten oxide will be demonstrated by its use as catalyst for partial methanol oxidation reaction and as conductivity gas sensor for detection of hydrogen at low concentrations.

The last presented application of nanostructured Pt-tungsten oxide will be its testing as catalyst in proton exchange membrane fuel cell (PEMFC). This system exhibit promising similarity with Pt-CeOx system: atomically dispersed ionic platinum and very high fuel cell specific power (wats per gram of Pt). This important observation makes definitely worthy further deep studies of the Pt-WOx catalysts for hydrogen oxidation reaction.

CAT1-1O327

STRUCTURAL CHARACTERIZATION OF THE CEOX/PT (111) BY SURFACE X-RAY DIFFRACTION

R. Znaiguia
ESRF - The European Synchrotron - Grenoble (France)

X-rays capability to penetrate into the matter allows investigating surface structures in a variety of environments. ID03 is the dedicated SXRD beamline at ESRF, which offers ideal conditions for the fast characterization of surfaces and interfaces in different environments. Cerium oxide is a material with unique physical and chemical properties. It is used in catalysis and fuel cells, due to its ability to store, and release oxygen. We wanted during this experiment to investigate the evolution of the cerium oxide ultrathin epitaxial films during reduction and oxidation processes using SXRD at different temperature and gas composition. Platinum is the mostly used element in catalysts for fuel cell technology, but its high price limits large-scale applications.

Platinum doped cerium oxide represents an alternative solution. Our goal is to investigate the structural properties of CeOx thin film on Pt(111) to better understand its catalytic properties. Thermal treatment in UHV (Ultra High Vacuum) and in oxygen partial pressure induce a controlled and reversible reduction in the CeO2 film [1]: CeO2 (Ce4+) à Ce2O3 (Ce3+)

The As-Prepared sample shows the presence of Pt(111) and the most stable cerium oxide CeO2 (Fig.1). After reduction of the sample at 750°C, we observe a partial rearrangement of the CeOx thin film atomic and electronic structure leading to the formation of PtxCe alloys and/or to the oxygen vacancy formation.

Indication of the presence of a Pt/Ce alloy can be found in the Pt CTRs comparison (Fig.2) before and after reduction (750°C).

We have observed that for different CeOx films thickness, thermal treatments in vacuum and in O2 partial pressure induces rearrangement in the surface of the and interface of the film.

Thanks/Acknowledgement

Co-Authors: Francesco Carla, Lucia Amidani, Francesco Benedetti, Jacopo Stefano PelliI Cresi, Federico Boscherini and Paola Luches.

References

[1]Luches P. et al. J. Phys. Chem. C 2011, 115, 10718–10726.

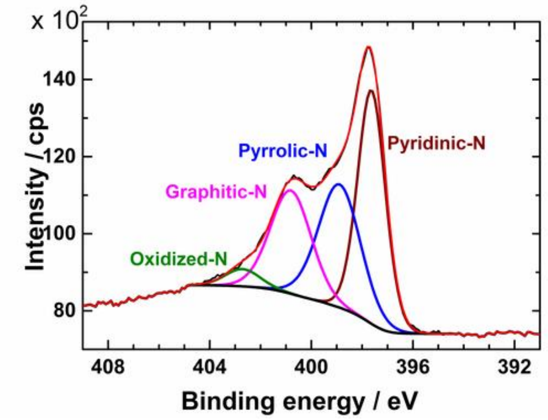
CAT2-2O381

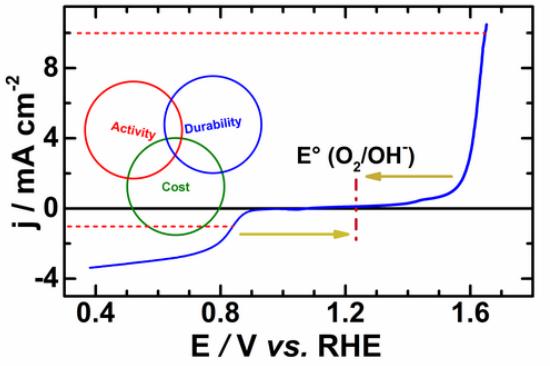
NOBLE METAL FREE ELECTROCATALYSTS FOR ORR AND OER : DOPED GRAPHENE BASED MATERIALS

C. Canaff, K. Kumar, I. Abidat, T. Napporn, A. Habrioux, B. Kokoh

CNRS UMR 7285 IC2MP Université de Poitiers 4 rue Michel Brunet-B27 86073 POITIERS - Poitiers (France)

The challenging large-scale production of regenerative fuel cells requires the development of highly stable reversible air electrodes which are able to catalyze both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Recently, numerous studies were dedicated to the activation of ORR and/or OER in alkaline medium on heteroatom-doped graphene supported transition metal oxides (TMO) [1]. The development of electrode materials, free from precious group metals and capable of decreasing overpotentials in fuel cells and water electrolyzer, requires stable supporting and conducting substrates in order to deposit low metal oxide loadings (ca. 30 wt.%). This challenging approach led us to prepare Co3O4 materials on graphene-based substrates known to be more stable than the commonly used carbon supports. Co3O4 particles synthesized from a solvothermal method were thereby deposited onto reduced graphene oxide (RGO) and N-doped reduced graphene oxide (NRGO). The electronic properties and surface composition of the different materials were characterized by X-ray induced photoelectron spectroscopy measurements. N1s photopeak has been scrutinized and discriminated by binding energy: Pyridinic N, pyrrolic or amino N and graphitic N [2-3] (Figure 1). These measurements were combined to cyclic voltammetry experiments in order to unveil charge transfer from cobalt to nitrogen. This latter phenomenon greatly affects the charge acceptance of the surface Co atoms in cobalt oxide particles, thus enhancing catalytic performances of the composite electrode materials towards the ORR and OER (Figure 2).





References

[1] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, Nat Mater, 10 (2011) 780-786.

[2] H. B. Yang, J. Miao, S-F. Hung, J. Chen, H. B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao, Hao M. Chen, L. Dai, B. Liu, Sci. Adv. (2016) 2, e1501122.

[3] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, J. Am. Chem. Soc., 136 (2014) 4394-4403

CAT2-1O384

WHAT CAN ELECTROCHEMICAL SCANNING TUNNELING MICROSCOPY REVEAL FOR HETEROGENEOUS CATALYSIS?

Y. Liang [1], J.H.K. Pfisterer [1], O. Schneider [2], A.S. Bandarenka [1]
[1]Physik-Department, Physics of Energy Conversion and Storage, Technische Universität München, James-Franck-Str. 1 - 85748 Garching (Germany), [2]Institut für Informatik VI, Technische Universität München, Schleißheimerstraße 90a - 85748 Garching (Germany)

Scanning tunneling microscopy (STM)[1] has been utilized as a sufficient surface topographic tool for the past decades. Additionally, it was reported that the tunneling current which depends on several factors (tip-sample distance, surface electronic structure, tunneling medium, etc.) can locally reveal events undergoing on the surface or at the interface, especially for heterogeneous catalytic reactions (participate in more than 90% of chemical industrial processes)[2,3,4,5]. The catalytic activity of a heterogeneous catalyst is determined by the electronic structure of specific surface sites with optimal adsorption properties for the corresponding reaction intermediates. It is one of the key factors of fundamental understanding and design of heterogeneous catalyst materials. Currently, there is no direct instrumental method capable of locating the catalytic active sites on the sub-nanometer scale under reaction conditions.

Here we demonstrate that during given reactions electrochemical STM can capture non-uniformly distributed 'unexpected' tunneling current disturbances while scanning over the electrode surfaces, which indicating the location of optimal active sites. The disturbances are expected to be originated by the catalytic reactions that are taking place at the active sites, where the relatively stronger disturbances should appear consequently. Hydrogen evolution and oxygen reduction reactions at various catalyst electrodes in contact with aqueous electrolytes, involved in the future energy provision, are chosen as the model systems.

Thanks/Acknowledgement

Financial support from the DFG project BA 5795/3-1 and the cluster of excellence Nanosystems Initiative Munich (NIM), is gratefully acknowledged. O.S. acknowledges funding from Toyota Motor Europe.

References

1, Binnig, G., Rohrer, H., Gerber, C. & Weibel, E. Surface studies by scanning tunneling microscopy. Phys. Rev. Lett. 49, 57-61 (1982).

2, Möller, R., Esslinger, A. & Koslowski, B. Noise in vacuum tunneling: application for a novel scanning microscope. Appl. Phys. Lett. 55, 2360-2362 (1989).

3, Zambelli, T., Wintterlin, J., Trost, J. & Ertl, G. Identification of the" active sites" of a surface-catalyzed reaction. Science 273, 1688 (1996).

4, Nørskov, J. K. Surface chemistry: Catalysis frozen in time. Nature 414, 405-406 (2001).

5, Hahn, J. & Ho, W. Oxidation of a single carbon monoxide molecule manipulated and induced with a scanning tunneling microscope. Phys. Rev. Lett. 87, 166102 (2001).

CAT1-3O391

ANALYSIS OF CHEMICAL SURFACE PROPERTIES IN CHROMIUM-VANADIUM SOLID SOLUTIONS

J. Alvarez-Rodriguez [1], I. Pirrotta [2], A. Guerrero-Ruiz [1], E. Moran [2], M.A. Alario [2]

[1]Dpto. Química Inorgánica y Química Técnica (UNED) - Madrid (Spain), [2]Dpto. Química Inorgánica (UCM) - Madrid (Spain)

1. **Introduction /** Among first row transition metal elements, chromium has been identifyed in prolific oxidation states in mixed metallic oxides as II, III, IV, V and VI in metal oxides with unusual electronic and magnetic properties which technological behaviors of practical interest as high-Tc, spintronic materials, spin Peierls material, Mott insulators, heavy fermion materials... The crystal structures of these chromium and chromium mixed oxides can be fully listed as: rutile and rutile-like materials (CrO_2, Cr_nO_{2n-2}, $Cr_{1-x}V_xO_2$ solid solution); perovskite structure ($MCrO_3$, M=Ca,Sr or Pb; $Bi_{0,5}M_{0,5}CrO_3$, M=Sr or Pb) and hollandite ($K_2Cr_8O_{16}$). Among them, the study of Cr(IV) oxides is particularly attractive to rise knowledge to its peculiar physico-chemical properties like: half-metallicity (CrO_2 and $K_2Cr_8O_{16}$), frustrated order or spin glass systems ($Bi_{0,5}Sr_{0,5}CrO_3$ and $Bi_{0,5}Pb_{0,5}CrO_3$), ferromagnetic order ($K_{1,2}Cr_8O_{16}$), antiferromagnetic order($Cr_{1-x}V_xO_2$). Focus in last one, in order to complement the detailed characterization of the solid V-Cr solution by powder X-ray diffraction, electron diffraction, magnetic susceptibility and magnetization this work is developed with the aim to reveal with confidence necesary the oxidation state of V and Cr.

2. **Experimental /** The data were registered by using an ESCAPROBE P (Omnicron) spectrometer where had been integrated modules for XPS, AES and SIMS techniques. Available XPS non-monochromatized by MgKα (1253.6 eV) and Al Kα X-ray (1486.6 eV) source operated at 75-250 W. The residual pressure was lower than 10^{-7} Pa during the spectra collection. The Hemispherical Analyser EA 125 operated in Constant Analyser Energy mode and the pass energy was switched to 20 eV. Under these conditions the FWHM of the Ag3d5/2 peak at 368.1 was 1.0 eV. Data analysis of core level XPS spectra was conducted with Casa-XPS software.

3. **Discussion /** Several samples of solid solution $Cr_{1-x}V_xO_2$ (with x=0,3-0,7) synthetized using α-CrO_2 and VO_2 at 1173K and 40kbar were analyzed in comparative data. Analysis of V2p region employing as reference V_2O_3, VO_2, V_2O_5 for V(III), V(IV) and V(V); while Cr2p region is analyzed using as reference CrO_2 and Cr_2O_3 for Cr(IV) and Cr(III), respectively. Binding energy of V 2p3/2 peaks registered among 521.5-523eV, Cr 2p3/2 peak positions among 574.9-576.2 eV and chromium energy separation ΔE (2p3/2 to 2p1/2) between 9.5-10.0 is discussed.

Thanks/Acknowledgement

We acknowledge financial support from the Spanish Government (projects CTQ2014-52956-C3-2-R and CTQ2014-52956-C3-3-R).

References

[1] Driving Curie temperature towards room temperature in the half-metallic ferromagnet K2Cr8O16 by soft redox chemistry. Dalton Trans.,41 (2012) 1840-1847.

[2] The preparation of ultra-thin chromium-vanadium oxides on Cu(100) sutided by XPS and LEED. Surf.Sci., 445 (2000) 80-88.

CAT2-5O417

THE INFLUENCE OF SC,V DOPING AND CODOPING ON PHOTOCATALYTIC ACTIVITY OF TIO$_2$

P. Murzin, A. Murashkina, A. Emeline, A. Rudakova

St. Petersburg State University, Laboratory "Photoactive Nanocomposite Materials" - Saint-Petersburg (Russian federation)

TiO$_2$ is a very widely used material. A branch of its' applications is based on its' photocatalytic activity. Thus understanding the mechanism and enhancing the activity is a desirable aim. Doping by different impurities is one of the way to achieve it since one can intentionally alter TiO2s' properties such as morphology, surface area, optical response and photocatalytic activity.

Regarding nonmetal impurities, metals of transition and platinum groups, many researches have been done over the last 15 years [1] [2]. As for codoping of TiO2 by transition metals not so many studies are presented [2] [3]. Since Sc and V have comparable radii and close charge to titanium their incorporation into the material can give extra active sites and thus enhance the photoactivity.

A series of Sc and V doped and co-doped samples with concentrations range 0.1 wt% to 1.1 wt% and different Sc to V ratio was synthesized. Surface characterization was carried out by SEM, X-ray phase analysis and BET. Photoactivity was evaluated as phenol decomposition in aqueous suspension.

The results show that the photoactivity of samples is changed in the same way regardless of which dopant is incorporated. The variance of Sc to V ratio leads to activity increase for low active samples and to activity decrease for active samples. The fundamental mechanism of this change is still under discussion though it has a correlation with work function of the materials.

Thanks/Acknowledgement

Supported by Mega-grant of the Government of the Russian Federation no. 14.Z50.31.0016. With the help of to RC "Nanophotonics", RC"Chemical Analysis and Materials Research Centre",RC"X-ray Diffraction Studies" of the Research Park at the Saint-Petersburg State University.

References

[1] J. Choi, H. Park, and M. R. Hoffmann, J. Phys. Chem. C, vol. 114, no. 2, 2010.
[2] Y. G. Yonghong Gu, et al., Chinese Opt. Lett., vol. 12, no. 9, 2014.
[3] V. Jabbari, et al., RSC Adv., vol. 5, no. 95, 2015.

CER - Ceramics

CER-1O106

INVESTIGATION BY XPS, XRD, AES OF CAVITIES OF POROUS CERAMIC MATERIALS

E. Beche [1], V. Flaud [2], J. Esvan [3], Y. Gorand [4], D. Perarnau [1]

[1]PROMES Odeillo, CNRS UPR 8521, 7 rue du Four Solaire, 66120 - Font-Romeu (France), [2]ICGM, UMR 5253, Place Eugène Bataillon, CC1701, 34095 - Montpellier (France), [3]CIRIMAT-ENSIACET, 31030 - Toulouse (France), [4]UPVD-PROMES-C2M, Tecnosud, Rembla de la thermodynamique, 66100 - Perpignan (France)

Introduction : Porous materials are promising materials for CSP (Concentrating Solar Power) applications with high surface exchange area in a given volume. However, due to their porosity and shape, they offer challenges to determine the surface properties required to evaluate their performance and behavior at high temperature. Adaptation of analytical methods (XPS, AES, XRD, Raman spectroscopy) was necessary to characterize the microstructure inside the cavities and to determine the oxidation kinetics and the modifications of the material after use in CSP applications.

Experimental : The foam samples were heated in a 6 kW solar reactor for about 30 min. at the focus of the concentrated solar radiation. The experimental setup and the sample testing device were fully detailed in ref [1]. The XRD and SEM analyses were first carried out in order to complete informations about microstructure provided by the manufacturer and write the identification card of foams. The XPS and AES analyses were mainly carried out in order to determine the chemical composition from the surface to the substrate for ZrB_2 and SiC heated samples.

Results and discussion : For Si-ZrB_2 foams, the surface chemical composition showed a SiO_2-rich layer. The B_2O_3 compound must be preferentially evaporated. Si species moved through the Si-ZrB_2 ceramic to form a mixed ZrO_2-SiO_2 layer. SiO_2(l) compound would be above the mixed layer and was crystallized in a SiO_2(s) compound on the surface during the cooling process. Mixed SiOB and BN coumpounds were also detected. These results led to select appropriate techniques to analyze oxidized foams in one cavity of porous material (surface and bulk informations) and to qualify relevant candidates used in high temperature volumetric solar absorbers.

Conclusions : Experimental methods (XRD, XPS, AES...) were optimized (source size, surface, bulk, geometric and sources effects) in order to characterize the microstructure of the pore walls. After a heating treatment with solar energy, the microstructure and the oxidation behavior of the ZrB_2 and SiC ceramic foams were determined [2].

Thanks/Acknowledgement

This work was supported by the European SFERA II program (FP7-INFRA, Grant Agreement N° 312643, WP13-T3A). The authors want to thank S. Mey-Cloutier and C. Caliot for providing heated ceramic foams with solar energy.

References

1. S. Mey-Cloutier, C. Caliot, A. Kribus, Y. Gray, G. Flamant. Solar Energy. 2016, Vol. 136, pp. pp. 226-235.
2. E. Beche, Characterization of the physical and chemical properties of the surface of cavities of porous materials, 2016-08, Deliverable D13.6, SFERAII-WP13-T3A. http://sfera2.sollab.eu/downloads

COR - Corrosion

COR2-5O027

LOCAL DEGRADATION MECHANISM BY TARNISHING OF PROTECTED SILVER MIRROR LAYERS FOR SPACE APPLICATION STUDIED BY SURFACE ANALYSIS

V. Maurice [1], E. Limam [1], A. Seyeux [1], S. Zanna [1], L. Klein [1], C. Grezès-Besset [2], I. Savin De Larclause [3], P. Marcus [4]

[1]*CNRS - Chimie ParisTech - Paris* (France), [2]*CILAS Marseille - Aubagne* (France), [3]*CNES - Toulouse* (France), [4]*CNRS - Chimie ParisTech - Toulouse* (France)

Satellites assigned to earth observation missions embark space telescopes equipped with mirrors consisting of thin layered stacks including a reflecting metallic layer made of silver. Despite the necessary presence of a protection layer, local degradation (i.e. tarnishing) of these silver mirrors has been observed during qualification and storage phases limiting their long-term durability in earth atmosphere before satellite launching.

Our study addressed the local initiation and propagation of tarnishing of model stack samples of space silver mirrors deposited by cathodic magnetron sputtering and consisting of thin silver layers supported on light-weight SiC substrates and protected by thin SiO_2 oxide films, each with an adhesion interfacial layer. Combined surface and interface analysis using Time-of Flight Secondary Ion Mass Spectrometry, X-ray Photoelectron Spectroscopy and Atomic Force Microscopy was performed before and after accelerated aging in gaseous H_2S selected as most corrosive atmospheric agent.

The results show that substrate surface pores, resulting from the SiC material processing, promote the local initiation of tarnishing. Silver sulfide columns, identified as Ag_2S by XPS, grow locally with the same density as the SiC surface pores as a result from a defective protection by the SiO_2 barrier layer as shown by AFM and ToF-SIMS. Channels most likely connect the silver layer to its environment through the deposited protection layer, which enables local H2S entry and Ag_2S growth as columns until emergence at the stack surface above the protection layer as observed by AFM, ToF-SIMS and XPS. Preferential emergence of sulfide columns observed by AFM above the walls of the SiC surface pores shows that substrate sites of high aspect ratio are more defectively protected after silver deposition and thus more susceptible to the initiation of tarnishing.

Aging causes the sulfide spots to grow in number and size, eventually leading to coalescence of nearby sulfide columns. In more advanced stages, tarnishing gets slower owing to saturation of all pre-existing defect sites (surface pores) for preferential sulfidation. However, sulfidation still progresses laterally underneath the protection layer, consuming the silver layer and deteriorating the protection layer as revealed by ToF-SIMS depth profile imaging. The mechanical stress induced by volume expansion related to Ag_2S formation from metallic silver is thought to crack the covering SiO_2 barrier layer, thus opening new pathways for H_2S ingress and enabling lateral progress of local tarnishing underneath the protection layer.

Thanks/Acknowledgement

Region Ile-de-France is acknowledged for partial financial support for the XPS and ToF-SIMS equipments.

COR2-1O051

DECOMPOSITION OF POLYTETRAFLUOROETHYLENE IN PROTON EXCHANGE FUEL CELLS - A SPECTROSCOPICAL STUDY

I. Biswas, J. Florenski, M. Schulze
German Aerospace Centre (DLR) - Stuttgart (Germany)

The degradation of perfluorinated sulfonic acid (PFSA) membranes, e.g. Nafion™, as solid electrolytes of proton exchange membrane fuel cells (PEMFC) is a well-studied problem. Fluoride emission rate has been extensively used to measure in operando membrane decomposition and thinning [1], and radical attack of the polymer is postulated as the dominant factor for decomposition [2, 3]. Furthermore, the influence of catalyst deposits on the membrane decomposition has been investigated [4].

Another component, the gas diffusion layer (GDL) of the fuel cell is also prone to a similar degradation phenomenon. It provides electrical contact of the electrochemically active layer while maintaining the supply of reaction gases and managing the delicate balance of humidity – under dynamic operation with varying amounts of product water. It typically consists of a carbon-based conductive medium and a hydrophobicity impregnation agent like polytetrafluoroethylene (PTFE). The ratio determines the hydrophobicity and thus influences performance.

Accelerated stress tests revealed that also the PTFE of the GDLs is decomposed. The loss of hydrophobicity is responsible for a disturbance of the delicate PTFE humidity balance. In this work, the decomposition of PTFE in the PEMFC environment was shown to be similar to that of PFSA. Photoemission spectroscopy data of artificially aged samples, reference polymers and GDL samples after operation (displayed in Fig. 1) were compared.

A distinct correlation between condensing humidity in local areas and PTFE decomposition suggests that the underlying mechanism includes the transport of radicals from the catalyst to the GDL by means of liquid water.

References

[1] R. Baldwin, M. Pham, A. Leonida, J. McElroy, T. Nalette, J. Pow. Sourc. 29 (1990) 399.

[2] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umebayashi, A. Tasaka, Y. Iriyama, T. Abe, Z. Ogumi, J. Pow. Sourc. 158 (2006) 1222.

[3] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, J. Pow. Sourc. 131 (2004) 41.

[4] S. Helmly, B. Ohnmacht, P. Gazdzicki, R. Hiesgen, E. Gülzow, K. A. Friedrich, J. Electrochem. Soc. 161 (2014) F1416.B.

COR1.1-1O064

H2O ADSORPTION AND DISSOCIATION ON OXIDIZED PU METAL

<u>L. Jolly</u>, B. Ravat, B. Oudot, F. Delaunay
CEA, Centre de Valduc - Is-Sur-Tille (France)

Plutonium metal is particularly sensitive to corrosion even at ambient temperature. Corrosion during storage is industrially under control, however the fine mechanisms are not well known, not to say controverted especially with presence of H_2O [1,2].

The goal of this study is to describe first stages of corrosion mechanisms of plutonium metal under water vapor at room temperature. The knowledge of these first stages is important because they tend to control the corrosion way. Photoelectron spectroscopy (PES) is a powerful technique for the purposes of studying various properties of surfaces, e.g. their composition, oxidation state, chemical and electronic properties.

The plutonium alloy surface was prepared by following a defined procedure (electropolished, cleaned by Argon ions sputtering and annealed) in order to produce a clean surface of a multilayer composed of a PuO_2 thin film on Pu_2O_3 film on Pu metal bulk easily repeatable in terms of nature and thickness [3]. These initial surfaces were exposed to water vapor at different pressures (from 5.10^{-7} mbar to 1 mbar) at ambient temperature [4].

The X-ray photoelectron spectroscopy (XPS) measurements were obtained on an EscaLab 250® from ThermoFisher Scientific connected to a glove box, using monochromatic Al-Ka X-rays. Pu4f and O1s transitions fitting (performed by CasaXPS [4,5]) gave respectively the proportions of oxides (PuO_2 and Pu_2O_3) and the proportion and nature of chemisorbed species on the surface. XPS spectra extrinsic loss structures modelling (performed by QUASES Generate [6]) allowed determining the structure and the thickness of PuO_2 film grown on Pu_2O_3.

These new analytic results enable to suggest mechanisms of H_2O adsorption/dissociation as a function of the nature, the thickness and defects of the formed PuO_2 oxide.

References

[1] J.M. Haschke, T.H. Allen, L.A. Morales (2000), Science 287 285.

[2] T. Gouder, A. Seibert, L. Havela, J. Rebizant (2007) Surf. Sci., 601, L77-L80

[3] L. Jolly, P. Berthou, F. Delaunay (2013), Poster P2-18, ECASIA'13, Cagliari, Sardinia, Italy

[4] L. Jolly, B. Oudot, B. Ravat, F. Delaunay (2015), Poster P1-TR/C-01, ECASIA'15, Granada, Spain

[5] N. Fairley, CasaXPS®, www.casaxps.com; Casa Software LTD, UK

[6] S. Tougaard, QUASES®, Version 5.3, Software for Quantitative XPS/AES of Surface Nano-Structures by Analysis of the Peak Shape and Background, Quases Tougaard: Odense, 2000.

COR2-3O153

THE EFFECT OF FLAVINS ON THE CORROSION PROPERTIES OF STAINLESS STEELS DURING INITIAL STAGES OF MICROBIOLOGICALLY INFLUENCED CORROSION

N. Wurzler, J. Radnik, W. Unger, O. Ozcan Sandikcioglu
BAM Federal Institute for Materials Research and Testing - Berlin (Germany)

Microbiologically influenced corrosion (MIC) on steel occurs where the presence and activity of microbes change the localized conditions on the surface of a metal substrate [1]. For instance, metal reducing bacteria (MRB) are capable of utilizing metal compounds in the passive layer on stainless steel as electron acceptors during their metabolism. This weakening of the passive film not only leads to an acceleration of the general corrosion processes, but also increases the susceptibility of stainless steels to pitting corrosion [2]. Even though the electron transfer mechanisms are not yet fully understood, recent research shows that the secretion of electron shuttles like flavins contribute significantly to the extracellular electron transfer (EET) [3, 4]. Electron shuttle molecules like riboflavin (RB) or flavin mononucleotide (FMN) are secreted by MRB after the transition from planktonic to sessile mode and exist in the biofilm at low concentrations. Therefore, they are precise early phase indicators of bacterial settlement.

This project aims at clarifying the electrochemical interaction mechanisms of MRB with stainless steel surfaces, with a special focus on the role of the extracellular redox molecules. The analysis of corrosion processes as a function of chloride and flavin concentration have been performed by means of electrochemical methods. Due to the differences in their chemical structure, FMN and RB have shown significant differences in terms of their adsorption behavior and the stability of the formed films, which directly influences the electron transfer processes. Therefore, Electrochemical Quartz Crystal Microbalance (eQCM) studies have been performed on sputtered FeCr electrodes to investigate the adsorption/desorption kinetics of flavins.

The results of electrochemical studies are complemented by the analysis of the changes in the passive film chemistry and the chemical composition of the adsorbed films by means of Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRRAS) and X-ray photoelectron spectroscopy (XPS). Changes in surface morphology have been investigated by means of Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).The presentation will summarize our results on the degradation mechanisms of passive films on stainless steel surfaces in the presence of flavins and provide useful insights from a fundamental aspect for the understanding of the initial stages of microbiologically influenced corrosion.

References

1. Liao, J., et al., 2010. 52(4): p. 1393-1403.
2. Coetser, S.E. and T.E. Cloete, Critical Reviews in Microbiology, 2005. 31(4): p. 213-32.
3. Marsili, E., et al., PNAS, 2008. 105(10): p. 3968-73.
4. von Canstein, H., et al., Applied and Environmental Microbiology, 2008. 74(3): p. 615-23.

COR2-4O173

COMBINED XPS, TOF-SIMS AND PHOTOCURRENT SPECTROSCOPY PHYSICO-CHEMICAL CHARACTERIZATION OF SURFACE OXIDE FILMS ON BRIGHT ANNEALED FERRITIC STAINLESS STEEL

F. Di Franco, A. Seyeux, S. Zanna, V. Maurice, P. Marcus
CNRS - Chimie ParisTech, Institut de Recherche de Chimie Paris, Research Group Physical Chemistry of Surfaces - Paris (France)

The corrosion resistance of stainless steels is determined by the thickness, structure, composition and electronic properties of the oxide layers grown on their surface and isolating the metallic substrate from the environment. Surface analytical techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) have been and still are widely applied to characterize thickness, chemical structure and composition of thin and ultrathin surface oxide films. In contrast, PhotoCurrent Spectroscopy (PCS) is a technique more seldom applied, to obtain direct information on the electronic properties of thin photoconducting surface films on metals and alloys.

In the present work, XPS and ToF-SIMS have been combined to PCS in order to perform an integrated physico-chemical characterization of surface oxide films grown on bright annealed ferritic stainless steel in different conditions. Ferritic stainless steels are a nickel-free (i.e. cheaper) alternative to austenitic stainless steels. They are process-annealed to high temperature (~ 1000 °C) in order to reduce hardness and achieve the ductility required for mechanical machining. Bright annealing, is performed under inert gas atmosphere (a mixture of hydrogen and nitrogen) in order to minimize the reaction with oxygen and to avoid the growth of oxide scales and preserve a bright appearance.

Our results show that on as-received bright annealed samples the surface oxide film is ~ 2.0 nm thick and has a bilayer structure with an inner layer close to pure Cr(III) oxide and an outer layer of mixed Fe(III) and Cr(III) oxide as shown by XPS and ToF-SIMS. By PCS electronic band gaps of the inner and outer layers are measured close to 3.4 eV and 2.8 eV, respectively, and the oxide films behave as an insulator with an inversion potential of ~ - 0.7 V vs. Ag/AgCl at $\lambda = 309$ nm and at pH ~ 9.5. After thermal treatment in air between 350°C and 550 °C, the surface oxide films thickens and the outer layer is enriched in Fe(III) as shown by XPS and ToF-SIMS. PCS confirms iron enrichment of the outer layer with a band gap reduced to 2.0 eV; photocurrent intensity increases according to thickening and iron enrichment. Complementary linear voltammetry and electrochemical impedance spectroscopy analysis evidence a decrease of the polarization resistance and a cathodic shift of the corrosion potential after thermal treatment. The knowledge of the structure, composition and electronic properties of these surface films will be discussed to rationalise their corrosion behaviour.

COR2-2O199

COMPOSITIONAL STUDY OF A CORROSION PROTECTIVE LAYER FORMED BY LEACHABLE LITHIUM SALTS IN A COATING DEFECT ON AA2024-T3 ALUMINIUM ALLOYS

K. Marcoen [1], P. Visser [2], M.L. Abel [3], J.F. Watts [3], J.M.C. Mol [4], H. Terryn [1], T. Hauffman [1]

[1]Vrije Universiteit Brussel, Department of Materials and Chemistry, Research Group Electrochemical and Surface Engineering, Pleinlaan 2, 1050 - Brussels (Belgium), [2]AkzoNobel, Specialty Coatings, Rijksstraatweg 31, 2171 AJ - Sassenheim (Netherlands), [3]University of Surrey, Department of Mechanical Engineering Sciences, GU2 7XH - Guildford (United kingdom), [4]Delft University of Technology, Department of Materials Science and Engineering, Mekelweg 2, 2628 CD - Delft (Netherlands)

AA2024-T3 aluminium alloys are widely used in the aerospace industry because of their remarkably high strength-to-weight ratio. However, as these alloys are highly susceptible to localized corrosion, they require an advanced corrosion protection scheme. International restrictions on the use of toxic and environmentally harmful Cr(VI) corrosion inhibitors have triggered the development of alternative metal surface pretreatments for many years now. Nevertheless, it remains a major challenge to fully replace chromate inhibitor pigments by systems that show sufficient effectiveness. A promising alternative is found by incorporation of lithium-based corrosion inhibitors in polymer coatings. Under exposure to neutral salt spray conditions, these lithium salts are shown to leach out of the organic coating to form a protective layer in an artificial defect [1,2].

In this work the composition and growth of a lithium-based protective layer is investigated by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Unlike EDX, XPS and AES, ToF-SIMS is a technique that shows a high sensitivity towards lithium in combination with a high lateral resolution. ToF-SIMS mappings are used to monitor the lateral spread of the protective layer in artificial 1mm-wide scribes in function of exposure time to a neutral salt spray. The composition of the protective layer is studied as well, by comparing the mass spectra of exposed scribe areas to the mass spectra of pseudoboehmite and Li-Al layered double hydroxide reference samples.

This work contributes to a better understanding of the growth mechanism of the protective layer and provides structural information which can be linked to corrosion protection behaviour.

References

(1) Visser, P.; Liu, Y.; Zhou, X.; Hashimoto, T.; Thompson, G. E.; Lyon, S. B.; van der Ven, L. G. J.; Mol, A. J. M. C.; Terryn, H. A. The Corrosion Protection of AA2024-T3 Aluminium Alloy by Leaching of Lithium-Containing Salts from Organic Coatings. Faraday Discuss. 2015, 180, 1–16.

(2) Visser, P.; Lutz, A.; Mol, J. M. C.; Terryn, H. Study of the Formation of a Protective Layer in a Defect from Lithium-Leaching Organic Coatings. Prog. Org. Coatings 2016, 99, 80–90.

COR1.2-3O203

DEVELOPMENT AND CHARACTERIZATION OF HYDROPHOBIC ALUMINUM ANODIZED TO ACT AS A LONG-LASTING PROTECTIVE FILM IN CORROSION SALINE MEDIA

R. Jaimes Ramírez [1], A. Covelo [1], S. Rodil [2], P. Corona Lira [3], A. Ramírez Reivich [3], M. Hernández [1]

[1]Centro de Ingeniería de Superficies y Acabados (CENISA), Dpto. de Materiales y Manufactura, Facultad de Ingeniería, UNAM, 04510, México - México (Mexico), [2]Instituto de Investigaciones en Materiales, UNAM, 04510, México - México (Mexico), [3]División de Ingeniería Mecánica e Industrial (DIMEI), Dpto. Ingeniería Mecánica, Facultad de Ingeniería, UNAM, 04510, México - México (Mexico)

Anodizing is an electrochemical process that is used to increase corrosion resistance and improve the surface properties of aluminum. For decades this process has been used for multiple applications, however it is necessary to generate anodized layers that are more resistant to corrosive environments [1]. This work focuses on the development of a novel hydrophobic process for anodized aluminum AA2024-T3 consisting of combining a corrosion inhibitor, sodium metavanadate, with a γ-irradiated fluoropolymer. The anodizing films formed in sulphuric acid media were sealed by using different aqueous solutions such as boiling water, potassium dichromate and cerium nitrate. The corrosion resistance was measured with electrochemical impedance spectroscopy (EIS). These results showed that samples sealed with Ce(NO3)3 had a higher average value of impedance around 105 ohm-cm2 at high frequencies, whereas values of total impedance of 109 ohm-cm2 were obtained at low frequencies after 100 h of testing in a NaCl solution 0.1 M as seen in Fig. 1. Contact angle measurements revealed best results of 128.8°. X-ray photoelectron microscopy (XPS) in conjunction with scanning electron microscopy (SEM) indicated the formation of a thick layer of fluoro-compound above the anodized aluminum with variable composition depending on the sealed solution used (Fig. 2). The fluoropolymer compound modified the aluminum oxide and thus, it promoted a chemical bonding between them. On the other hand, the g-irradiation did not modify the organic groups of the fluropolymer; however, the fluropolymer network became stiffer and more amorphous since X-ray diffraction, infrared spectroscopy and differential scanning calorimetry demonstrated structural and thermal modifications; therefore the g-irradiation promoted higher hydrophobic properties on the anodized aluminum.

Thanks/Acknowledgement

Rebecca Jaimes Ramírez acknowledges Programa de Becas Posdoctorales from DGAPA, Universidad Nacional Autónoma de México 2016-2017, México.

References

[1] A. Covelo, M. Hernández, R. Jaimes-Ramírez, J. Uruchurtu. Hydrophobic Coatings for Corrosion Control. In press, Ed. INTECH, 2017.

COR1.1-4O235

INVESTIGATION OF THE CORROSION BEHAVIOUR OF A RARE-EARTH MAGNESIUM ALLOY FOR SHORT IMMERSION TIMES IN A SODIUM SULPHATE SOLUTION

N. Pebere [1], S. Leleu [1], N. Causse [1], N. Pebere [1], B. Rives [2]
[1]CIRIMAT - ENSIACET - Toulouse (France), [2]IRT Saint-Exupery - Toulouse (France)

Magnesium alloys containing rare-earth elements have low density, good mechanical properties and improved fire resistance compared to Mg-Al-Zn series [1]. Numerous studies have been published on the corrosion of pure magnesium or aluminium-magnesium-zinc alloys, but the influence of rare-earth alloying elements on their corrosion behaviour is still under discussion [2]. Südholz et al. found that an increase in the Y content in Mg-Y alloys increased their corrosion rate in NaCl solutions [3]. Furthermore, Liu et al. showed that particles in a Mg-Y-Gd-Nd-Zr were anodic for short immersion times [4], contrary to the general agreement on the cathodic role of intermetallic particles in Mg alloys.

In the present work, the corrosion behaviour of a Mg-Nd-Gd-Zn-Zr commercial alloy (Elektron 21) was investigated during short immersion times (less than 1 h) in a Na2SO4 solution. Electrochemical impedance spectroscopy was used to follow the modifications at the Mg alloy/ electrolyte interface as a function of immersion time. The results were compared with those obtained on pure Mg (99.95 wt%). The impedance diagrams obtained at the corrosion potential for the Mg alloy presented the same phenomenology as that obtained for pure Mg. However, from the analysis of impedance diagrams, it was observed that for the Elektron 21, the charge transfer resistance (RCT) decreased at the beginning of exposure to 0.1 M Na2SO4 (5 and 25 min) and then increased. This behaviour was not observed for pure magnesium for which a progressive increase of RCT was observed and explained by the decrease of the active surface area due to the formation of a protective film (MgO) [5].

Complementary optical, scanning electron microscopy and atomic force microscopy observations (ex situ and in situ) were performed on the alloy surface to find correlation between the electrochemical behaviour of the alloy and the reactivity of the intermetallic particles.

Thanks/Acknowledgement

This work is supported by the Companies Mapaero (Pamiers, France) and Prodem (Cornebarrieu, France) within the SURFINNOV IRT Saint Exupéry project.

References

[1] F. Czerwinski, Corros. Sci. 86 (2014) 1–16.

[2] F. Cao, G.L. Song, A. Atrens, Corros. Sci. 111 (2016) 835–845.

[3] A.D. Südholz, K. Gusieva, X.B. Chen, B.C. Muddle, M.A. Gibson, N. Birbilis, Corros. Sci. 53 (2011) 2277–2282.

[4] J. Liu, Y. Song, J. Chen, P. Chen, D. Shan, E.-H. Han, Electrochim. Acta. 189 (2016) 190–195.

[5] G. Baril, G. Galicia, C. Deslouis, N. Pébère, B. Tribollet, V. Vivier, J. Electrochem. Soc. 154 (2007) C108–C113.

COR1.2-1O259

TOWARDS AN ATOMISTIC UNDERSTANDING OF ACID CORROSION INHIBITION OF STEEL: DFT STUDY OF INHIBITOR SUBUNIT ADSORPTION ON FE{110}

B. Provost [1], M.Y. Ho [2], T. Hughes [2], J.M. Goodman [1], S.J. Jenkins [1]
[1]Department of Chemistry, University of Cambridge - Cambridge (United kingdom), [2]Schlumberger Gould Research - Cambridge (United kingdom)

Acid corrosion of steels represents an unavoidable and important problem for the oil and gas industry due to the strong acidising fluids used to maximise oil and gas production. To reduce the economic impact associated with corrosion-induced deterioration of steel, an appropriate corrosion mitigation strategy must be used. Corrosion control is most cost-effectively achieved through use of acid corrosion inhibitor (ACI) molecules, which tend to be aromatic and include heteroatoms (usually N, O, P or S). [1] Although the activity of a wide variety of known ACI has been studied, their protection mechanism is still poorly understood. Our work aims to better understand these processes at an atomistic level by studying the adsorption behaviour of three different molecular subunits common to many ACI molecules (benzene, naphthalene and quinolinium) on a flat Fe surface (the {110} facet) using density functional theory (DFT) calculations. The results, including adsorption geometries and energies, charge and spin transfer analyses as well as adsorption-induced work function changes, have been compared for the three adsorbates. We have also studied the effect of van der Waals corrected DFT on binding site energetics and geometries as such corrections have been shown to provide results in better agreement with experiment for similar systems. [2] In comparing the adsorption behaviour for these three ACI subunits, we aim to advance the atomistic understanding of acid corrosion inhibition on metal and steel surfaces.

References

[1] M. Finšgar, J. Jackson, *Corr. Sci.* **2014**, 86, 17-41

[2] J. Carrasco, W. Liu, A. Michaelides, A. Tkatchenko, *J. Chem. Phys.* **2014**, 140, 084704

COR1.2-2O271

HARD CHROMIUM COATINGS FROM TRIVALENT CHROMIUM SALTS: RELATIONSHIP BETWEEN CHEMICAL COMPOSITION AND MORPHOLOGY.

D. Del Pianta
IPREM UMR-5254 - Pau (France)

Industrial hard chromium process is commonly applied to enhance anti-wear or anti-corrosion properties on iron-based substrate whatever its intrinsic specificities. The plating process generally consists in the electrochemical reduction of hexavalent chromium salts in the presence of a small quantity of sulfuric acid (H2SO4) [1].

Nowadays, the process will no longer be used as the REACH European regulation suggests to forbid the utilization of hexavalent chromium salts (CMR agent) by the end of the 2017 year. The HCTC consortium from French IRT M2P intends to find an alternative plating process with a trivalent chromium bath developed by COVENTYA Company. The use of a Cr(III) solution requires to understand the associated chemical mechanisms and to release the organic complexing agents initially present in the bath to favor the cations reduction [2].

First results show, on the contrary of well-known coatings built-up from Cr(VI) solution, the appearance of crossing microcracks (Figure 1a) which are well-known to decrease the general anti-corrosion coating properties [3]. The XPS chemical analysis of the deposit reports the presence of some amorphous carbides, chromium oxides and residual traces of electrolyte which would be the starting point of understanding the structural weakness of such coating. For 30mm thick deposit (Figure 1b), the crossing microcracks density is quite small when the bath temperature is high and the current density of the electrochemical reduction process is low. XPS results highlight a direct evolution of carbides (+13%at increase) and oxides (-8%at decrease) contents in relation with the final morphology of the deposit.

References

[1] Hoare, J.P. Journal of electrochemistry society, 1979, 126, 190–199.

[2] Zeng, Z.; Liang, A; Zhang, J., Recent patent on materials science, 2009, 2, 50–57.

[3] Zeng, Z.; Zhang, J., Surface Coating Technology, 2008, 202, 2725–2730.

COR1.1-5O339

TOF-SIMS WITH ISOTOPIC TRACERS FOR THE STUDY OF NICKEL-BASE ALLOY SURFACES: OXIDE LAYER GROWTH MECHANISMS AND ABSORPTION OF HYDROGEN

P. Marcus, S. Voyshnis, X. Wu, A. Seyeux
Chimie ParisTech - CNRS, PSL Research University, Institut de Recherche de Chimie Paris, Physical Chemistry of Surfaces Group - Paris (France)

Surface oxide growth and entry of hydrogen in NiCrFe alloys exposed to water at high temperature and high pressure water have been investigated by ToF-SIMS.

The ionic transport is a key factor in the growth of passive film on metals and alloys. In this work a method has been developed to investigate the ionic transport in oxide films, based on a two step process. Firstly the passive film is formed in aqueous solution, then the sample is further oxidized under oxygen 18 in a ToF-SIMS instrument.

This in situ oxidation step with an isotopic tracer allows us to locate the growing oxide, at the surface of the passive film or at the oxide-metal interface. This technique was applied to passive films formed in high temperature water (300°C) on the surface of a nickel-base alloy (Alloy 600) of composition Ni-15Cr-8Fe (wt%).

The data clearly show that upon further oxidation in oxygen 18, 18O is found at the oxide-alloy interface, giving direct evidence of inward oxygen anions transport in the oxide. The in-depth profiles measured by ToF-SIMS allowed us to determine the diffusion coefficient of oxygen anions in the oxide layer. An apparent diffusion coefficient = ~3.10-19 cm2.s-1 was found.

The next part of the work was focused on the key question of the fate of the hydrogen produced by the cathodic reaction associated to anodic oxidation of the alloy (water reduction). This was studied by exposing the alloy to deuterated water (D2O). The signal of deuterium ions was then followed by in-depth profiles measured by ToF-SIMS. The data clearly show that deuterium produced by the cathodic reaction is present in the oxide layer. Calibration of the deuterium amount in the material was performed by ERDA (Elastic Recoil Detection Analysis).

COR1.1-2O348

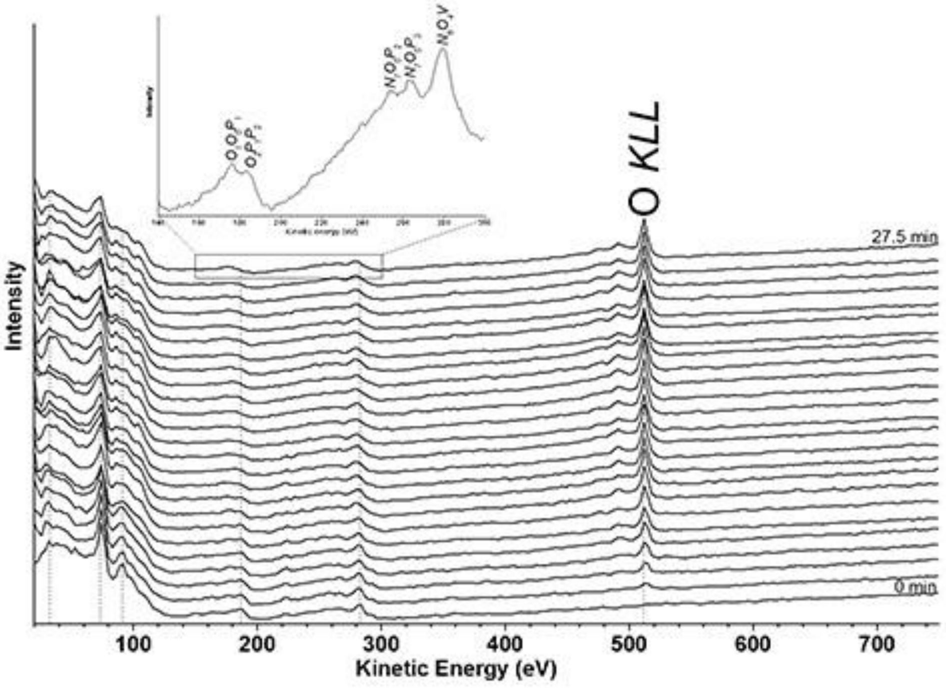
A COMPARATIVE STUDY OF THE OXIDATION OF A DEPLETED URANIUM-MOLYBDENUM ALLOY (DU-5MO) IN UHV CONDITIONS BY AES AND XPS

S. Bacon [1], M. Brierley [2], J. Watts [1]
[1]*University of Surrey - Guildford (United kingdom)*, [2]*AWE - Aldermaston (United kingdom)*

The oxidation of uranium in atmospheric conditions is a primary cause of corrosive attack of the metal and therefore a significant engineering concern. There is a long history of surface analysis studies, utilising techniques including XPS and AES, to characterise the pure metal oxide [1,2]. More recent examples in the literature, however, are relatively rare and primarily focus on niobium alloys [3,4]. Here we report the oxidation kinetics of a DU-5Mo alloy using AES (Figure 1). Quantification and chemical shift information by XPS is being used in parallel to inform similar information by AES and compare with existing niobium data.

References

1. Allen, G. C. & Tucker, P. M. Surface oxidation of uranium metal as studied by X-ray photoelectron spectroscopy. J. Chem. Soc. Dalt. Trans. 470–474 (1973). doi:10.1039/dt9730000470
2. Allen, G. C. & Wild, R. K. Auger Spectroscopy of Uranium. J. Chem. Soc. Dalt. Trans. 493–498 (1974).
3. Younes, C. M., Allen, G. C. & Embong, Z. Auger electron spectroscopic study of the surface oxidation of uranium-niobium alloy {U-6 wt.% Nb} in a UHV environment containing primarily H2, H2O and CO. Surf. Sci. 601, 3207–3214 (2007).
4. Fu, X., Liu, K., Wang, X., Zhao, Z. & Yu, Y. X-Ray Photoelectron Spectroscopic Study of the Surface Reaction of Uranium–Niobium Alloy with O2. Surf. Rev. Lett. 10, 381–386 (2012).



COR1.1-3O360

CHEMICAL SURFACE ANALYSING BY XPS AND TOF-SIMS: HOW METALLIC IMPURITIES AFFECT MAGNESIUM CORROSION

D. Mercier, A. Seyeux, S. Zanna, J. Swiatowska, P. Marcus
Institut de Recherche de Chimie Paris - Paris (France)

Magnesium and Mg based alloys corrosion has been widely studied, and it is well known that under open circuit potential conditions, Mg corrosion is accompanied by H2 evolution. Under anodic potential polarization, an increase of the H2 evolution rate is observed, often called negative difference effect (NDE), This observation is in contradiction with the expected electrochemical kinetic (Butler Volmer equation) which predicts an exponential decrease of H2 evolution as a function of applied anodic potential. Different mechanisms have been suggested to explain the NDE, including the formation of monovalent Mg(I) or a catalytic effect induced by surface enrichment of metallic impurities such as iron. Up to now, none of the proposed mechanisms has been firmly demonstrated.

In this work, we have compared the corrosion evolution of high purity (HP, 99.99%) and ultra-high purity (UHP, 99.9999%) Mg, with iron contents of 60ppm and 0.01ppm respectively. The Mg oxide growth has been followed by chronoamperometry (+0.5V/Eocp, 250mC/cm^2) in NaCl electrolyte. The surfaces were analysed by XPS and ToF-SIMS.

HP Mg exhibits strong H2 evolution accompanied by the formation of non-homogeneous “dark spots” on the Mg surface, which forms at grain boundaries. This is observed for the UHP Mg and which H2 evolution was very limited. Optical microscopy observations revealed the presence of few circular craters of approximatively 15µm size at the UHP Mg surfaces.

Using 3D chemical ToF-SIMS profiling, we were able to observe that the localized corrosion process is initiated by segregated iron at grain boundaries. Iron was also detected outside the dark spots indicating an iron redeposition on the surface.

Measurements provide direct evidence of a catalytic effect induced by iron at the Mg surface, and bring with new insight the localized action of iron segregated at grain boundaries.

CUL - Cultural heritage

CUL2-1O243

MULTI-TECHNIQUE INVESTIGATION OF SULFUR PHASES IN THE CORROSION PRODUCT OF IRON CORRODED IN LONG TERM ANOXIC CONDITIONS: FROM MICROMETRIC TO NANOMETRIC SCALE

M. Bouttemy [1], F. Mercier [2], S. Grousset [3], A. Etcheberry [1], P. Dillmann [2], D. Neff[2]
[1]Institut Lavoisier de Versailles, UVSQ, CNRS, Université Paris-Saclay - Versailles (France), [2]LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay - Gif Sur Yvette (France), [3]LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay - IRSN, PRP-DGE/SRTG/LETIS - ANDRA - Gif Sur Yvette (France)

The study of anoxic corrosion process of ferrous metals is a matter of concern for industrial sector (pipelines, container for nuclear waste storage….) but also for cultural heritage objects conservation. Indeed, the formation and the presence of sulfide compounds in the corrosion products of buried objects, either in terrestrial or marine environments, can drastically change the corrosion mechanisms and, so, the conservation strategies for these objects. Particularly, in natural environment, the presence of micro-organisms such as Sulfate-Reducing Bacteria (SRB) may influence the corrosion rate of ferrous objects by favoring the precipitation of iron sulfide phases and modifying then the initial corrosion process [1].

The determination of the iron sulfides nature and their distribution in the corrosion product layer is a crucial issue to address in order to anticipate the degradation of ferrous object during extraction, storage or conservation operations. In the present work, archeological ferrous samples, representative of long term corrosion systems, have been considered. A multi-technique approach was developed to achieve an overall physico-chemical characterization and to cover the dimensions requirement of the corrosion systems.

First, FE-SEM imaging coupled with EDS and µ-Raman spectroscopy were performed on the archeological ferrous samples enabling the localization and identification of the natural corrosion products. Mix of phases of greigite (Fe_3S_4) and mackinawite (FeS) in a corrosion layer mainly constituted of iron carbonates were observed at a sub-micrometric scale, in consistency with the literature [2], showing the precipitation of greigite, mackinawite and/or pyrite (FeS_2) in the presence of bacteria or in sulfur environment. Then, Nano-Auger spectroscopy, owing to its local chemical characterization capability, was investigated to obtain a chemical diagnostic at a nanometric scale. Scanning Auger Microscopy (SAM) was performed to evaluate the ability of this technique to spatially discriminate different phases (iron sulfides, oxides and carbonates) at a local scale and extreme surface sensitivity (5nm escape depth). Then, thanks to µ-Raman mappings, specific areas presenting only one component were selected and identified for the acquisition of reference Auger spectra, and especially high energy resolution spectra of Fe-MVV and S-LVV regions. Finally, the spatial distribution of the different phases obtained with SAM could be compared with nano-SIMS experiments informing about the sulfur isotopic composition variations and the bio-origin of the sulfur phases.

References

[1] H.A. Videla et al., Int. Biodeterior. Biodegrad. 63 (2009) 896–900.
[2] S. Grousset et al., Corrosion Science 112 (2016) 264–275.

CUL1-1O314

A STUDY OF PARCHMENTS USING TOF-SIMS AND CHEMOMETRICS

M-L. Abel, **J. Watts, O. Kirkham**
University of Surrey - Guildford (United kingdom)

In this study we present the application of ToF-SIMS to the analysis of parchment in order to provide scientists, conservators and historians with information that may be obtained from surface analysis. Such materials are usually studied using DNA analysis or proteomics [1] but results are not always conclusive. A series of parchments have been studied in order to further ascertain whether it is possible to determine properties of said parchments such as the side examined or the species. This has been paired with a multivariate analysis approach in order to extract information from spectra, which on the first approach are very similar, such as principal component analysis (PCA) or non-negative matrix factorisation (NMF). In this work we can show that species and sometimes side of the parchment (skin versus flesh) can be determined using the above approach. In previous work, one of the stumbling blocks has been to ascertain why the chemometrics behaviour is different for different species and in order to resolve this matter, various specimens of different ages were used in this study and particular attention has been given to the provenance of the samples with acquisition of freshly manufactured specimens of three different species: goat, calf and sheep. The main problem encountered resides into avoiding the bias introduced via presence of contamination resulting from either the fabrication or the handling of the parchments.

References

[1] M. D. Teasdale, N. L. van Doorn, S. Fiddyment, C. C. Webb, T. O'Connor, M. Hofreiter, D. G. Bradley, Phil Trans Royal Soc London B 2015, 370 (1660, 20130379).

CUL1-3O390

EXPLOITING XPS AND XAES FOR THE QUANTITATIVE ANALYSIS OF NANOMETRIC THICK FILMS FORMED ON BRASS ALLOYS

A. Rossi [1], F. Cocco [1], M. Fantauzzi [1], B. Elsener [2]
[1]Università degli Studi di Cagliari - Cagliari (Italy), [2]ETH Zurich - Zurich (Switzerland)

Copper-zinc alloys are interesting materials for their applications in many fields of technology including the production of brass wind musical instruments. From the surface analytical viewpoint brass alloys represent a challenging system since the most intense photoelectron lines of both, copper and zinc, exhibit a small chemical shift when trying to distinguishing Cu (0) from Cu (I) and Zn (0) from Zn (II). XAES was recognized as analytical method for identifying the chemical state of Cu and Zn in presence of thick surface films. Their identification and quantification is more difficult for films only few nanometer due simultaneous presence of signals from the surface and from the bulk.

The aim of this investigation was to establish an analytical approach for the calculation of thickness and composition of thin layers formed on brass alloys. A curve fitting procedure of the Cu $L_3M_{4,5}M_{4,5}$ and Zn $L_3M_{4,5}M_{4,5}$ Auger signals was first carried out, based on the parameters obtained on reference compounds. This allowed the identification of the different chemical state contributions to both copper and zinc signals. The ratios R between the intensity of the photoelectron I_{2p} and the correspondent Auger intensity, I_{LMM}, were calculated for a series of reference compounds so that a correction factor was determined. This approach was tested on CuZn37 brass following mechanical polishing [1]. It allowed us to determine the oxide film thickness, taking into account the contamination layer, and the composition of the surface film as well as that of the interface bulk/ surface film. The good agreement between the compositions of the alloy measured by XRF with the one obtained by this approach is substantiating its validity.

Results from the application of this analytical approach on a series of mechanical polished brass alloys and on brass alloys exposed to phosphate buffer solution will be presented and discussed in order to shed a light on the growth mechanism of the surface layers formed on brass.

Thanks/Acknowledgement

MIUR (I) and SNF (CH) are thanked for financing the project.

References

[1] F. Cocco, B. Elsener, M. Fantauzzi, D. Atzei and A. Rossi, RSC Advances, 2016, 6, 31277; doi: 10.1039/C5RA23135C

CUL1-2O420

AN XPS SURFACE ANALYTICAL INVESTIGATION TO RATIONALIZE CORROSION RATE MEASUREMENTS IN HISTORICAL BRASS WIND INSTRUMENTS

F. Cocco [1], B. Elsener [2], M. Fantauzzi [1], A. Rossi [1]
[1]Dipartimento di Scienze Chimiche e Geologiche - Università di Cagliari - Cagliari (Italy), *[2]Institut für Baustoffe (IfB) - ETHZ - Zurich* (Switzerland)

Brass instruments of the 19th and early 20th centuries get more and more used to be played in historically informed performance practice. During and after playing the musician's hot, wet breath could worsen the instrument's interior corrosion, but little is known about this danger. For this reason, the corrosion state inside these historical brass instruments before and after being played was monitored by electrochemical methods and the efficiency of preventive conservation by air ventilation has been checked. Except endoscope images nothing is known on the surface state and surface composition at the point of measurements. In order to correlate the results of electrochemical measurements with the surface state and composition, information from surface analytical experiments on brass model alloys in controlled environments are required.

In this work, results of x-ray photoelectron spectroscopy (XPS/XAES) surface analysis of brass (Cu-Zn alloy) model samples in various surface state (mechanically polished, as received) and exposed to a mild environment (phosphate buffer pH 7) and to a quite aggressive solution (artificial saliva), that represent the two extremes regarding liquids possibly present in the tuning slides after playing, are reported. Brass alloys exposed to the phosphate buffer solution showed a rapid formation of a thin film composed of copper and zinc oxide that is not protective. In the artificial saliva solution the corrosion rate of brass was initially very high but decreased rapidly to values below 1 µm/year. XPS surface analysis has shown the formation of a thick protective film of CuSCN (thiocyanate) and zinc phosphate.

The combination of electrochemical and surface analytical data obtained on model brass alloys allows rationalizing the different corrosion behaviour found in the tuning slides of the brass wind instruments.

Thanks/Acknowledgement

The Italian Ministry of University and Research (MIUR) is thanked for financing the PRIN project prot. 2010329WPF_005 “Sustainability in cultural heritage: from diagnosis to the development of innovative systems for consolidation, cleaning and protection”. SNF is also aknowledged for the financing the project "Brass instruments of the 19th and early 20th centuries between long-term conservation and use in historically informed performance practice”.

References

B. Elsener, M. Alter, T. Lombardo, M. Ledergerber, M. Wörle, F. Cocco, M. Fantauzzi, S. Palomba, A. Rossi; Microchemical Journal, 2016, 124, 757-764, doi:10.1016/j.microc.2015.10.027

B. Elsener, F. Cocco, M. Fantauzzi, S. Palomba, A. Rossi, Materials and Corrosion, 2016, 67, (12), 1336-1343

ELC - Micro- and optoelectronics

ELC-2O030

NEW APPROACH FOR PHYSICO-CHEMICAL CONTROL OF SENSIBLE SURFACES DURING TRANSFER AND STORAGE BETWEEN STEPS IN MICROELECTRONIC

B. Pelissier [1], **S. Labau** [1], **J. Moeyaert** [1], **M. Martin** [1], **C. Beitia** [2], **T. Baron** [1]
[1]CNRS-LTM, MINATEC Campus, Univ. Grenoble Alpes - Grenoble (France), [2]CEA-LETI, MINATEC Campus, Univ. Grenoble Alpes - Grenoble (France)

In the actual microelectronic chip’s production chain, wafer’s queue time and storage conditions are becoming more and more critical, especially for materials and surfaces sensible to oxidation and Airborn Molecular Contamination (AMC).

Beyond the problematic of steps between processes, preserving the physico-chemical integrity of those surfaces is also a key point for advanced characterization studies. “Quasi insitu” analyses, based on the concept of using a specific carrier under high quality static vacuum [1] has been been demonstrated to be a key advantage for process understanding and development when considering highly air-reactive surfaces [2] [3] [4].

The presented study will detail and explain the capabilities of the existing septup with regards to AMC and then propose a new approach, based on a low gas partial pressure, allowing to increase furthermore the system performances. Thus, using an industrial transfer chain between an industrial 300mm surface preparation tool (Siconi® process) and a pARXPS Theta 300 customized spectrometer, and considering significant queue times inside the carrier, the results will highlight and explain the differences obtained on AMC contamination with regards to transfer conditions inside the carrier (fig. 1).

Moreover, the effect of carrier pre-outgazing and/or bakeout will be investigated. Other surface treatments leading to higher surface sensitivity to AMC will be considered too.

Thanks/Acknowledgement

This work has been supported by the French ANR program "Investissements d’Avenir” contract number ANR-10-EQPX-33

References

[1] XPS analysis with an ultra clean vacuum substrate carrier for Oxydation and AMC prevention B.Pelissier, H.Kambara, & al. Microelectronic Engineering 85 (2008) 151-155

[2] Impact of Oxidation on Ge2Sb2Te5 and GeTe Phase-Change Properties E.Gourvest, B.Pelissier, & al. Journal of The Electrochemical Society, 159 (4) H373-H377 (2012)

[3] Control of carbon content in amorphous GeTe films deposited by PE-MOCVD for PCRAM applications" M.Aoukar, P.Szkutnik, & al. Journal of Physics D: Applied Physics, 48 (26), (2015)

[4] Dry efficient cleaning of PMMA residues from graphene with highdensity H2 and H2-N2 plasmas G.Cunges, D.Ferrah, & al. Journal of Applied Physics 118, 123302 (2015)

[5] HF contamination of 200mm Al wafers: a pARXPS study B.Pelissier, H.Fontaine & al. Microelectronic Engineering 88 (2011), pp. 861-866

ELC-4O077

NANOSCALE ELEMENTAL ANALYSIS OF GESN NANOWIRES BY SCANNING AUGER MICROSCOPY

E. Martinez [1], **T. Haffner** [2], **A. Gassenq** [3], **E. Robin** [3], **J. Aubin** [1], **J.M. Hartmann** [1], **P. Gentile** [3], **T. Baron** [2], **F. Bassani** [2], **B. Salem** [2]

[1]*CEA,LETI,Minatec campus,Université Grenoble Alpes - Grenoble (France)*, [2]*CNRS,LTM,Université Grenoble Alpes - Grenoble (France)*, [3]*CEA,INAC,Université Grenoble Alpes - Grenoble (France)*

GexSn1-x nanowires (NWs) can improve the performances of metal-oxide-semiconductor field effect transistors (MOSFETs). Their integration is considered in future sub-11 nm pFETs operating with reduced power dissipation [1]. The carrier mobility is boosted by the strain and the lower direct bandgap of GexSn1-x. However, high Sn contents (~10 at.%) are needed far in excess of the equilibrium Sn solubility in bulk Ge [2]. A precise control of the Sn content is thus crucial from the transistors integration point of view.

Reaching higher insertion of Sn needs developing adequate vapour-liquid-solid growth methods using Au-based catalysts. In this work, a surface technique such as scanning Auger microscopy (SAM) is used to optimize the growth of such NWs and maximize the Sn incorporation. SAM is a valuable technique combining high spatial resolution (~10 nm) and quantitative elemental analysis [3] to highlight chemical composition heterogeneities in the NWs [4]. Compared to electronic microscopy, SAM offers the advantage that no complex sample preparation is needed.

We will show that the chemical characterization of individual NWs can be done at the nanoscale through local spectroscopy and linescan imaging. Specific protocols are developed for a detailed analysis of the Sn incorporation according to the growth conditions. The chemical composition is obtained after adequate surface preparation. Elemental in-depth information is also obtained combining Auger electron spectroscopy with argon sputtering. Both axial and radial composition heterogeneities are thus highlighted.

Reliable Sn quantification is obtained, on the basis of reference samples such as GexSn1-x 2D epi-layers grown on Ge strain relaxed buffers by chemical vapor deposition (CVD) [5]. We will show that Auger depth profiling and cross-sectional analyses gives valuable depth sensitive chemical information. The Auger results are checked by comparison with complementary X-ray diffraction (XRD) and transmission electron microscopy combined with electron dispersive spectroscopy (TEM-EDS).

Thanks/Acknowledgement

The Auger, XRD and TEM analyses were performed at the NanoCharacterization Platform of the MINATEC campus (PFNC). The authors are thankful to the French "Recherche Technologique de Base" program for the measurements performed on state-of-the-art characterization tools.

References

[1] X. Gong et al., Symposium on VLSI Technology Digest of Technical Papers (2013).

[2] S. Biswas et al., Nature Communications, 7, 11405 (2016).

[3] E. Martinez et al., J. Electron Spectrosc. Relat. Phenom., 191, 86 (2013).

[4] W. Hourani et al., Nanoscale 7, 8544 (2015).

[5] A. Gassenq et al., Appl. Phys. Let. 109, 242107 (2016).

ELC-3O188

LIGHT ELEMENTS DEPTH PROFILING WITH PLASMA PROFILING TIME-OF-FLIGHT MASS SPECTROMETRY

Y. Mazel [1], E. Nolot [1], J.P. Barnes [1], A. Tempez [2], S. Legendre [2]
[1]CEA-LETI / Université Grenoble Alpes - Grenoble (France), [2]Horiba Scientific - Palaiseau (France)

Plasma Profiling Time-Of-Flight Mass Spectrometry (PP-TOFMS) is a sputtering-based elemental depth profiling technique combining a pulsed radio-frequency argon plasma source for sample sputtering and ionization with an orthogonal time-of-flight mass spectrometer. Previous studies showed nanometer depth resolution on NiPt-silicides for advanced contacts, calibration-free semi-quantitative profiling on MEMS magnetic stacks and the capacity to simply identify unexpected contaminant [1].

A PP-TOFMS (Horiba Scientific) has recently been installed in the clean room of the CEA-LETI in close proximity with deposition tools to allow fast feedback on material development. In this paper, we'll first use complementary Time-Of-Flight Secondary Ion Mass Spectrometry analyses to highlight: (i) the very low surface mixing induced by PP-TOFMS plasma and (ii) the need to fine tune plasma conditions for the thin layered materials to optimize the crater shape, thereby improving the depth resolution. Such measurement strategies lead to rather sharp interfaces and fast and reliable semi-quantitative analysis, even for ultrathin films. However, PP-TOFMS operated with argon plasma does not feature optimal sensitivity to light elements, which restricts its application range in microelectronics. We'll comment on improved PP-TOFMS protocols using Ar/He mixtures to improve the sensitivity of the technique for light elements. The main ionization process in pulsed glow discharge plasmas is known to be Penning ionization involving carrier gas metastables. While the energy of argon metastables (11.5 eV) is too low for efficient ionization of light elements, helium metastables (20 eV) provide enough energy for most elements [2]. We'll compare the effect of Helium addition on both the signal level and the depth resolution for technologically relevant samples. As illustrated on the figure, compared with pure argon, 10 and 20 vol% He addition significantly increases the sensitivity for all species and especially for light elements. Lower sputter rates were observed, as expected as He is lighter than Ar, suggesting better ionization yields. Sensitivity improvement is seen for monoatomic ions while signal from molecular ions often decreases indicating that more efficient dissociation processes occur in the plasma.

References

[1] A. Tempez et al., J. Vac. Sci. Technol. B (2016) 34
[2] B. Lange et al., Anal. Bioanal. Chem. (2007) 389

ELC-1O296

IMPROVED 3D IMAGING OF MICROELECTRONIC SAMPLES BY CORRELATING TOF-SIMS WITH X-RAY TOMOGRAPHY OR AFM

J-P. Barnes [1], A. Priebe [1], G. Goret [1], M.A. Moreno Villavicencio [1], I. Mouton [1], N. Chevalier [1], G. Audoit [1], P. Bleuet [1], B. Gautier [2]

[1]Univ. Grenoble Alpes, F-38000 Grenoble, France CEA, LETI, MINATEC Campus, F-38054 - Grenoble (France), *[2]Institut des Nanotechnologies de Lyon, INSA de Lyon, Université de Lyon, UMR CNRS 5270, 7, avenue Capelle, F-69621 - Villeurbanne* (France)

The characterization of heterogeneous or porous structures in the micron-scale range can be particularly challenging. Examples of such structures can be found in the through-silicon via (TSV) and copper pillars used in 3-D integration and in selectively grown III-V structures in oxide masks. To measure both morphology and composition at this length scale it is often necessary to combine several characterization techniques on the same sample.

For samples that can be analyzed by more conventional dual-beam TOF-SIMS depth profiling, the correlation with AFM is pertinent. Performing several AFM scans at different points in a TOF-SIMS depth profile enables the local sputter rate and roughness to be measured leading ultimately to a pixel by pixel depth scale correction in the TOF-SIMS data.

For larger samples in the tens of micron range that are not suited for conventional profiling, we have developed a method to analyse the same sample first by X-ray computed nano-tomography (CNT) in a SEM and then by time-of-flight secondary ion mass spectrometry in an instrument equipped with a gallium focused ion beam (FIB-TOF-SIMS) [1,2]. Serial FIB slicing combined with the chemical TOF-SIMS imaging is used to build up a 3-D picture of sample composition. The morphological sample reconstruction from the CNT is combined with the compositional information from the TOF-SIMS, using suitable algorithms in one unique multimodal, hyperspectral 3-D volume. Figure 1(a) X-ray CNT image of a copper pillar and (b), FIB-TOF-SIMS tomography analysis overlaid with the X-ray CNT data showing Ag and Ni rich zones shows how the combination of the two techniques is essential if the morphology and the presence of Ag rich phases is to be investigated. The presence of a TOF-SIMS mass spectra at each voxel in the volume means that both major elements and contaminants can be visualized. This approach is also applied to TSV samples.

Thanks/Acknowledgement

This work was performed on the nanocharacterisation plateform at the CEA Grenoble and was financed by the CARNOT ATRIµM project and H2020 project 688225 METRO4-3D.

References

[1] A. Priebe et al. Ultramicroscopy. 173 (2017):10-13. [2] A. Priebe et al. J. of Microscopy 264(2) (2016) 247-251).

GEO - Geology and geochemistry

GEO-1O325
PYRITE SURFACE PRE-TREATMENT DRIVES AMINO-ACIDS ADSORPTION

E. Mateo-Marti, **S. Gálvez-Martínez, M. Sánchez-Arenillas**
Centro de Astrobiologia - Madrid (Spain)

We have demonstrated that the annealing process for cleaning pyrite surfaces is a critical parameter in promoting ordering on the surface and driving surface reactivity. Furthermore, we describe a spectroscopic surface characterization of the presence or absence of the surface ordering, as indicated by the Low Energy Electron Diffraction (LEED) pattern, as a function of the surface annealing process. Complementary X-ray photoemission spectroscopy (XPS) results provide evidence that longer annealing processes of over 3 hours repair the sulfur vacancies in the pyrite, making FeS species partially disappear in favor of FeS2 species[1]. These features play an important role in molecular adsorption. We show that in the case of the cystine amino acid on the (100) pyrite surface, the substrate structure is responsible for the chemical adsorption form. The presence of an ordered structure on the surface, as indicated by the LEED pattern, favors the cystine NH3+ chemical form, whereas the absence of the surface ordering promotes cystine NH2 adsorption due to the sulfur-deficient surface. The cystine molecule could then act by changing its chemical functionalities to compensate for the iron surface coordination. The chemical molecular adsorption form can be selected by the surface annealing conditions, implying that environmental [2] conditions could drive molecular adsorption on mineral surfaces. These findings are relevant in several surface processes, and they could play a possible role in prebiotic chemistry surface reactions and iron–sulfur scenarios[3].

Thanks/Acknowledgement

MINECO is gratefully acknowledged for the PhD grant BES-2011-044395 of M.S.A and funding through Spanish research project ESP2014-55811.

References

[1] M. Sánchez-Arenillas, E. Mateo-Martí, Phys.Chem.Chem.Phys, 18 (2016) 27219-27225.

[2] M. Sanchez-Arenillas, E. Mateo-Martí, Chemical Physics, 458 (2015) 92-98.

[3] C. Huber, G. Wachtershauser, Science, 281 (1998) 670–672.

GLA - Glass

GLA-2O133

ELECTRODIFFUSION VS CHEMICAL DIFFUSION IN ALKALI CALCIUM PHOSPHATE GLASSES – IMPLICATION OF STRUCTURAL CHANGES

K-M. Weitzel, A. Hein, M. Schäfer
Philipps-Universität Marburg - Marburg

A long term transport experiment has been performed on a bioactive calcium phosphate glass of the molar composition 30 CaO *25 NaO *45 P_2O_5 using the technique of bombardment induced ion transport (BIIT) with potassium as foreign bombarder ion [1]. Ion transport due to gradients of the electrical potential and the concentration lead to incorporation of K^+ and depletion of both Na^+ and Ca^{++} by electrodiffusion in forward direction. The resulting concentration profiles have been quantitatively analyzed by the time-of-flight secondary ion mass spectrometry (ToF-SIMS). The concentration profiles of the P^+ and PO_x^+ signals (x = 1…4) resemble those of the K^+, Na^+ and Ca^{++} signals, indicating a characteristic change of the local bonding situation. This is interpreted as an indirect hint of a change of local structure of the glass network. Since the concentration profiles imprinted by the BIIT constitute pronounced concentration gradients, these depletion profiles further evolve on a much longer time scale due to chemical diffusion (absence of electric potential gradients). The former depletion zone is partially refilled by chemical diffusion. At the same time the structural changes of the glass network are demonstrated to be reversible. Numerical simulations on the basis of the coupled Nernst-Planck-Poisson equations allow deriving the diffusion coefficients of sodium, potassium and calcium for both cases, i.e. electrodiffusion and chemical diffusion. The two experiments are sensitive to different aspects of the diffusion coefficients and thus are complementary. The analysis is sensitive to the concentration dependence of $D(Na^+)$ and $D(Ca^{++})$ for the electrodiffusion and of $D(K^+)$ for the chemical diffusion. For the chemical diffusion of Na^+ and Ca^{++} in backward direction $D(Ca^{++})$ is larger than $D(Na^+)$ indicating that the extra sites occupied by Ca^{++} in the preceding electrodiffusion are energetically high-lying.

Thanks/Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG We 1330/17-1) is gratefully acknowledged.

References

[1] A. Hein, J. Martin, M. Schäfer, K.-M. Weitzel, Journal of Physical Chemistry C, in press (2017)

GLA-1O196

GLASS SURFACE CHARACTERIZATION AND ATOMISTIC MODELLING TO DETERMINE THE DRIVERS OF WATER TRANSPORT IN GLASS

D. Rebiscoul [1], C. Mansas [1], J.M. Delaye [2], T. Charpentier [2], F. Bruguier [2], O. Bouty [2], B. Penelon [2]

[1]*ICSM - Bagnols-Sur-Cèze* (France), [2]*CEA - Bagnols-Sur-Cèze* (France)

Exposed to atmosphere or to solution, glass surface is modified. The first stage of this modification is driven by two concomitant processes: (i) the water hydration/interdiffusion consisting of water diffusion through glass network[1,2] and ion-exchange between alkali ions from glass and positively charged water species from the solution[2,3] and (ii) the hydrolysis of the matrix. In this study, the relation existing between water transport in glass, glass topology, chemical elements (network former and charge compensator) and their structural role in glass were investigated through glass surface characterization during alteration and topology modelling of glass.

Three series of glasses with and without boron and having various ratios of charge compensators CaO/Na_2O were used ($73SiO_2–5Al_2O_3–(22−x)Na_2O–xCaO$; $63SiO_2–15B_2O_3–4Al_2O_3$ or $2ZrO_2–(18−x)Na_2O–xCaO$ where $x = 0, 6, 9$).The glass structure was characterized using Raman spectroscopy and NMR. Their topologies i.e. the density of bottlenecks Ns were obtained by molecular dynamics. Water transport was characterized by X-Ray Reflectivity and FTIR-ATR[4]. From these data, the duration of the predominance of the hydration/interdiffusion processes τ_H, the apparent water diffusion coefficient DH2O and the water structure in the hydrated glass were determined.

The results show that τ_H is driven by the ability of Si-O-X bonds to be hydrolyzed as much as the fraction of free water clusters in hydrated glass. Moreover, for aluminosilicate glasses, water transport is mainly driven by glass topology through the role of Ca in glass strengthening the glass network by decreasing the density of bottleneck. When boron is added to the glass, the results are similar for glasses without boron except if the amount of Na is not sufficient a part of Ca is required as a charge compensator for AlO_4 and BO_4 units. In that case, water transport is mainly driven by the chemical interactions between the water molecules, Ca and the network former of glass matrix. The Figure 1 illustrates this phenomenology.

Thanks/Acknowledgement

We are grateful to Bruno Corso for XRR maintenance and M. Moskura for the MAS NMR spectra.

References

1.Doremus, R. H, 1975
2.Bunker, B. C., 1994
3.Boksay, Z. et al; 1967
4.Rébiscoul, D.; et al, 2012

LIF - Life science

LIF-1O052

RAPID 100 NM-SCALE TANDEM MS IMAGING AND IDENTIFICATION OF ENDOGENOUS BOTANICAL METABOLITES IN SEXTONIA RUBRA AMAZONIAN SPECIES

G. Fisher [1], T. Fu [2], D. Touboul [2], S. Della-Negra [3], E. Houël [4], N. Amusant [5], C. Duplais [4], A. Brunelle [6]

[1]Physical Electronics - Chanhassen (United States of America), [2]Institut de Chimie des Substances Naturelles, CNRS - Gif-Sur-Yvette (France), [3]Institut de Physique Nucléaire, CNRS - Orsay (France), [4]CNRS, UMR EcoFoG, AgroParisTech, Cirad, INRA - Cayenne (France), [5]Cirad, UMR EcoFoG, AgroParisTech, CNRS, INRA - Kourou (France), [6]CNRS, UMR EcoFoG, AgroParisTech, Cirad, INRA - Gif-Sur-Yvette (France)

We have explored the botanical synthesis of bioactive molecules in the wood of *S. rubra* (Figure 1) via TOF-SIMS Parallel Imaging MS/MS as part of an effort to develop a new strategy for investigating natural product formation. The TOF-TOF tandem mass spectrometer of the PHI *nanoTOF* II enabled, for the first time in botanical analysis and natural product biosynthesis, simultaneous surface screening of the botanical matrix chemistry by TOF-SIMS (MS^1) imaging and targeted identification of matrix components by MS/MS (MS^2) imaging.[1] Imaging of molecules with unambiguous identification occurred in minutes without observable degradation of the specimen. Hence, the botanical chemistry was broadly profiled while multiple tandem MS imaging analyses were performed for discovery. Fragmentation of molecular precursor ions within a monoisotopic window was accomplished by keV-CID, and the lateral resolution produced in both MS^1 and MS^2 images was found to be ≤ 500 nm.

The botanical metabolites of rubrynolide and rubrenolide, having significant xylophage repellant and antifungal properties[2], are produced in oil cells that are found in close proximity to both vessels and parenchyma cells. Moreover, there are thought to be several bio-molecular precursors en route to these bioactive metabolites. Our goal was to identify known and potential biosynthetic precursors using tandem MS, and to verify their coincidence with rubrynolide and rubrenolide by MS imaging. We were able to demonstrate the presence of numerous precursors and to confirm or derive their structure, thus contributing in the exploration of natural product biosynthesis.

References

[1] (a) G.L. Fisher, A.L. Bruinen, N. Ogrinc Potočnik, J.S. Hammond, S.R. Bryan, P.E. Larson, R.M.A. Heeren, *Anal. Chem*. **2016**, DOI: 10.1021/acs.analchem.6b01022. (b) G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren in *SIMS XX Proceedings* (Ed.: D. Castner), Wiley, New Jersey, **2016**, DOI: 10.1116/1.4943568. (c) P.E. Larson, J.S. Hammond, R.M.A. Heeren, G.L. Fisher, Method and Apparatus to Provide Parallel Acquisition of MS/MS Data, U.S. Patent 20150090874, **2015**.

[2] A.M.S. Rodriguez, P.N.E.T. Theodoro, V. Eparvier, C. Basset, M.R.R. Silva, J. Beauchêne, L.S. Espíndola, D. Stein, *J. Nat. Prod*. **2011**, DOI: 10.1021/np1001412.

LIF-2O223

INFRARED NEAR-FIELD SPECTROSCOPY OF NANOSCALE SUGAR PARTICLES WITH ATTOGRAM SENSITIVITY

A. Huber
neaspec GmbH - Munich (Germany)

We demonstrate measurement of material-specific infrared near-field absorption spectra at spatial resolution of ca. 10-20 nm. Measurements are ased on the integration of a novel broadband mid-IR laser source into a commercial scattering-type Scanning Near-field Optical Microscopy (s-SNOM) system with standard FTIR interferometric detection.

s-SNOM [1] employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically tip-scattered light simultaneous to AFM imaging yields nanoscale resolved near-field images [2,3]. Utilizing broadband laser sources like a THz-TDS system or mid-IR supercontinuum laser for tip illumination enables near-field spectroscopic measurements at nanoscale spatial resolution. Figure 1 shows the absorption spectrum in the mid-IR spectral range measured for isolated sugar particles with nanoscale dimensions on a Silicon substrate, revealing characteristic absorption spectra for Glucose and Fructose that are in excellent agreement with conventional FTIR spectra. Insets: AFM scans of the investigated nanoparticles on a Si substrate outlining sizes of investigated objects. Particularly, the size of the Glucose particle allows to determine the mass of the measured object to be only ca. 100 attogram.

Besides nanoscale resolved material identification infrared nanoscopy enables quantitative measurements of dielectric values for polymers [4] or the determination of free carrier concentration and mobility in low-dimensional structures [5,6].

References

[1] F. Keilmann, R. Hillenbrand, Phil. Trans. R. Soc. Lond. A 362, 787 (2004)

[2] F. Huth, et al., Nano Lett. 12, 3973 (2012)

[3] C. Westermeier, et al., Nature Comm. 5, 4102 (2014)

[4] A. A. Govyadinov, et al., J. Phys. Chem. Lett. 4, 1526 (2013)

[5] J. M. Stiegler, et al., Nature Comm. 3, 1131 (2012)

[6] Z. Fei, et al., Nature Nanotech. 8, 821 (2013)

MET - Metals

MET1-4O031

INFLUENCE OF CR ADDITION ON HOT-DIP GALVANIZING BEHAVIOUR OF MN CONTAINING SHEET STEEL

T. Kawano [1], Y. Fushiwaki [2], Y. Nagataki [3], M. Nagoshi [1]

[1]Steel Research Laboratory, JFE Steel Corporation - Kawasaki (Japan), [2]Steel Research Laboratory, JFE Steel Corporation - Fukuyama (Japan), [3]Steel Research Laboratory, JFE Steel Corporation - Chiba (Japan)

Hot-dip galvanizing is a widely used process for automotive application of steel products. Concerns about reducing automotive body weight and improving collision safety encourages active use of high strength sheet steels. For this, various alloying elements such as Si, Mn are added to the steels. However, some of those elements are selectively oxidized on the surface through the recrystallization annealing process and impact on wettability or reactivity in the following galvanizing process. Therefore, it is important to clarify the influences of the alloying elements on galvanizing behavior from the viewpoint of the active utilization of galvanizing on high strength steels.

The present study focused on the influence of Cr on the galvanizing behavior of a sheet steel containing Mn. A 0.6mass%Cr-1.6mass%Mn steel and 1.9mass%Mn steel were compared in terms of selective surface oxidation and interfacial reaction during galvanizing. The galvanizing was conducted by dipping into a molten Zn bath containing 0.13mass%Al.

The selective surface oxides on the Cr-added steel were identified by means of EPMA and XRD as Mn-Cr spinel in addition to MnO, whereas only MnO was found on the Cr-free steel. SEM and TEM-TED analyses of the coating interface of the galvanized samples revealed that a columnar ζ-phase Fe-Zn IMC (Inter Metallic Compound) was formed on both of the Cr-added and Cr-free steels. In addition, a granular Fe-Zn IMC was found on the Cr-added steel, which was Γ_1-phase containing a higher Fe content compared to the ζ-phase.

Furthermore, on the Cr-free steel, a Fe-Al IMC formed along the interface between the Fe-Zn IMC and the substrate steel. On the other hand, there was a slight formation of Fe-Al IMC on the Cr-added steel and Al was detected in the Mn-Cr spinel surface oxide whereas the Al was not detected in the MnO.

These facts suggest that the Al from the molten Zn preferentially reacted with the Mn-Cr spinel more than the Fe of the substrate steel on the Cr-added steel. As a consequence, the Fe-Al IMC formed slightly and instead the formation reaction of the Fe-Zn IMC proceeded to make the Fe content higher to form Γ_1-phase.

It is concluded that Cr addition to a Mn steel modified the surface oxide from MnO to Mn-Cr spinel and the reactivity of the Mn-Cr spinel influenced the galvanizing behavior. This result suggests that the performance in the galvanizing process could be controlled by modification of the surface oxides.

MET1-2O048

INTERPHASE CREATION INMETAL MATRIX COMPOSITE MATERIALS

J-F. Silvain [1], C. Azina [1], I. Cornu [1], B. Mortaigne [2], Y. Lu [3]
[1]*ICMCB-CNRS - Pessac* (France), [2]*DGA - Paris* (France), [3]*UNL - Lincoln* (France)

High thermal conductivities and low thermal expansion coefficients (CTE) are required for heat-sink materials as they promote rapid heat dissipation and allow controlled thermo-mechanical strains upon thermal cycling. Currently, Cu or Al are being used for heat sinks. However, they are not suitable due to the large CTE mismatch with the ceramic and silicon parts of components.

To overcome this issue, we propose to replace the Cu and Al in heat sinks by metal matrix composites (MMCs), more particularly Cu matrix composites reinforced with carbon. The proper transfer of thermomechanical properties in MMCs is often compromised by the absence of effective interfaces, especially in non-reactive systems such as Cu/C. However, for a thermally efficient assembly, the interfaces should allow proper transfer of thermo-mechanical loads between the materials, which is only possible in the presence of chemical bonding.

The synthesis of composite materials by alloying the matrix with carbide forming elements has been investigated using a well-known process used for Al-based composites. The solid-liquid coexistent process allows the formation of a liquid phase which enhances the reactivity between the carbide forming element and the carbon reinforcement.

Ti- or Zr-alloyed Cu powders were introduced in the Cu/C mixture and sintered under a mechanical load. Fully dense materials were obtained. With the addition of the Ti-alloyed Cu powders, the creation of uniform and homogeneous TiC interphases was observed (see Fig. 1) whereas the Zr-alloyed Cu leads to the creation of a non-regular ZrC interphases instead. Chemical analyses have shown that both Ti and Zr react with carbon. Microstructural and chemical characterization of both interfacial zones were performed. Thermal properties have been enhanced with respect to the Cu/C composites without interphases.

Figure 1: EDS analysis of the Cu(Cu-Ti)/C interfacial zones

MET1-3O068

ON QUANTITATIVE COMPARISON OF EXPERIMENTAL RESULTS WITH CALCULATED ENERGIES IN INTERFACIAL NANOSEGREGATION

P. Lejcek [1], M. Sob [2]
[1]Institute of Physics, AS CR - Prague (Czech republic), *[2]CEITEC, MU - Brno* (Czech republic)

Segregation of alloying or trace elements at interfaces – grain boundaries and free surfaces – of poly- and nanocrystalline metallic materials is often controlling the properties of the functional parts. The most known consequences of the grain boundary segregation are temper embrittlement, increased ability to intergranular corrosion or deceleration of grain boundary migration. Presently, there are quite extended databases of quantitative experimental data on segregation enthalpies of various solutes at individual grain boundaries as well as of segregation energies obtained by theoretical approaches. However, the comparison of the results obtained in these two ways meets some problems due to mutual misunderstanding among the experts in both fields; surprisingly the crucial problem consists in definitions of individual energetic characteristics. In this contribution, a detail analysis of the thermodynamic parameters of grain boundary segregation is given. Individual sets of thermodynamic parameters of segregation are defined which can be obtained from experiments and their properties are discussed. It is shown that for a comparison of experimental and calculated results, the standard molar enthalpy and the segregation energy are the most representative quantities. Their comparison will be shown and discussed [1].

Thanks/Acknowledgement

This work was supported by the Czech Science Foundation [GA P108/12/0144 (PL), GA 14-22490S and GA 16-24711S (MS)], by the Academy of Sciences of the Czech Republic [Institutional Project RVO:68081723 (MS)], and by the Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020 (LQ1601) (MS).

References

[1] P. Lejcek, M. Sob, V. Paidar: Interfacial segregation and grain boundary embrittlement: An overview and critical assessment of experimental data and calculated results. Progress in Materials Science 87 (2017) 83–139.

MET1-1O099

DIFFUSION EXPERIMENTS AND PHASE FORMATION IN THE ALUMINIUM-COPPER-SYSTEM WITH TOF-SIMS AND XRD

A. Amsüss [1], W. Robl [2], H. Hutter [1]
[1]Technische Universität Wien (Vienna), Institute of Chemical Technologies and Analytics - Vienna (Austria), [2]Infineon Technologies AG - Regensburg (Germany)

Modern semiconductors consist of multiple metal layers. Junctions of Cu and Al are very common. Due to annealing steps and operational heating different migration phenomena can be expected. Miniaturisation of devices consequently leads to a reduction of sizes in all dimensions.

With a time-lag method [1] diffusion coefficients as well as activation energies were obtained in thin-film geometries. For that reason, a buried Al layer below Cu was heated in-situ under UHV conditions in a highly sensitive time of flight secondary ion mass spectrometer (ToF-SIMS) while the surface was observed for Al enrichment. The point in time, when this happens, is called first arrival time (t_{fa}). Variation of the thickness of the underlying Al layer showed great influence on the first arrival time (see figure). A major part of literature concentrates on bulk diffusion and phase formation in massive samples at relatively high temperatures. Our main focus were thin layers at moderate temperatures up to 300 °C for the diffusion experiments. This is where Harrison's diffusion model comes into play. [2]

It is also obvious that the mixing of two species implicates another important topic, the phase formation. This has already been the topic of many studies, e.g. in [3]. In contrast to these findings, our access to this topic was the direct observation of phase formation with an experimental setup of in-situ measurements in a thin-film geometry in our XRD instrument. The emergence and disappearance of selected reflexes in the present thin layer system were investigated.

Diffusion can have great influence on mechanical as well as on electrical properties. Therefore, it is of utmost interest to gain information on the basic diffusion properties and to be able to predict the evolution of different phases.

References

[1] J. Crank, The Mathematics of Diffusion. Oxford Science Publications (1990)

[2] L.G. Harrison, Trans. Faraday Soc. 57, 1191–1199 (1961)

[3] H. Koerner, S. Ananiev, R. Bauer, et al. Interconnect Technol Conf / Adv Met Conf (IITC/AMC), 2014 IEEE Int. 109-112 (2014)

MET2-2O251

SURFACE ANALYSIS OF FINE WATER-ATOMIZED IRON POWDER AND SINTERED COMPACTS

J. Wendel, R. Shvab, E. Hryha, L. Nyborg
Chalmers University of Technology - Gothenburg (Sweden)

Press and sinter is a core technology in powder metallurgy (PM) in which a metal powder is mixed with a lubricant and other additives and compacted at large mechanical pressures to create the desired shape. The component is then delubricated and finally sintered in order to strengthen the material. The end result of the sintering depends on both the physical properties of the powder such as particle size, morphology and size distribution, as well as chemical properties like surface chemical composition and presence of surface oxides. In this study, the surface characteristics of two fractions of water-atomized iron powder, sieved to -45 and -75 µm, were investigated. This was done using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and high-resolution scanning electron microscopy (HR SEM) equipped with energy dispersive X-ray spectroscopy (EDX). Powder mixed with lubricant, and with and without graphite as carbon source, were subsequently compacted at three different pressure levels of 400, 600, and 800 MPa. The compacts were then sintered in a dilatometer using a hydrogen-nitrogen based atmosphere. Fracture surfaces and metallographic cross-sections of the sintered components were analyzed with XPS, AES, and HR SEM+EDX. Results showed that both types of powder are mainly covered by a thin iron oxide layer but with the presence of submicron-sized oxide particles. The sintering behavior of the compacts was related to the surface properties, indicating a connection between the surface quality of the powder, its size fraction, and the sinterability.

Thanks/Acknowledgement

The authors would like to thank Höganäs AB for scientific cooperation. Funding from the Swedish Foundation for Strategic Research is gratefully acknowledged.

MET2-1O304

ELECTRONIC STRUCTURE AND PHASE COMPOSITION OF NI ROD ARRAYS FORMED IN SILICON DIOXIDE MATRIX BY TRACKING TECHNOLOGY AND ELECTROCHEMICAL DEPOSITION

E. Parinova [1], S. Turishchev [1], R. Ovsyannikov [2], J. Fedotova [3], E. Streltsov [3], A. Mazanik [3], F. Kronast [4], D. Marchenko [4], A. Fedotov [3]

[1]Voronezh State University - Voronezh (Russian federation), *[2]Helmholtz Zentrum Berlin - Berlin* (Germany), *[3]Belarusian State University - Minsk* (Belarus), *[4]Helmholtz Zentrum BerlinBelarusian State University - Berlin* (Germany)

Arrays of Ni particles embedded in a dielectric matrix of silicon dioxide with the enhanced magnetoresistance effect tunable by electric field can be a perspective structure for modern electronic applications (e.g. magnetic tomography) and novel electronic devices. Non-destructive techniques sensitive to the local atomic environment are really demanded for the characterization of such structures.

Swift heavy ion tracks formation with different doses were applied followed by chemical etching of SiO2 layers aimed at pores formation. Subsequent electrochemical filling of pores by nickel allowed to form massives of rods with different geometry and surface distribution. A complex of techniques were applied to characterize the morphology, atomic and electronic structure of the submicron Ni rods distributed inside SiO2 layer on Si substrate. We used SEM and AFM to study the morphology and surface distribution of Ni rods. Synchrotron X-ray absorption near edge structure (XANES) in total electron yield and fluorescence modes allowed to study specificity of local atomic surrounding of Ni, Si and O atoms in formed structures. These techniques combination made it possible to perform analysis of electronic structure and phase composition of surface and interfaces (bulk) of the formed structures. Further high energy and spatial resolution PhotoEmission Electron Microscopy (PEEM) technique were applied to investigate simultaneously morphology and electronic structure at microscopic level. Low nickel oxides residuals were found at the surface between metallic Ni rods while no interatomic interactions were detected even if rods concentration led to small surface Ni islands formation. It is shown that further increase of rods amount (island coverage) may lead to low silicide formation. The proposed technological approach allows to effectively form magnetic Ni rods arrays having relatively sharp interphase boundaries with silicon dioxide wide gap matrix.

Figure. Left: PEEM image at Si $L_{2,3}$ XANES edge of not filled pores structure. Right: XANES Si $L_{2,3}$ spectra indicating sharp pores edges and its Si bottom.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh.

NAMA – Nanomaterials

NAMA3-5O019

OPTICAL CHARACTERIZATION OF PEROVSKITE MATERIALS USING SPECTROSCOPIC ELLIPSOMETRY

J-P. Gaston, C. Eypert, M. Stchakovsky
HORIBA Scientific - Palaiseau (France)

Hybrid organic-inorganic perovskite materials have emerged over the past five years as absorber layers for new high-efficiency yet low-cost solar cells that combine the advantages of organic and inorganic semiconductors. In despite this significance evolution, the physics behind the electronic transport in these materials is still poorly understood.

A suitable technique for characterizing thin films of perovskites is spectroscopic ellipsometry, which is a surface sensitive, non-destructive, non-intrusive optical technique that measures the change in the polarization state of light reflected from the surface of a sample.

It provides significant advantages for nano-material characterization such as determination of film thickness with Ångstrom resolution and determination of optical constants that allow the deduction of a wide range of physical properties.

We performed ellipsometry measurements (together with Tauc-Lorentz modeling) in order to validate the dielectric properties obtained in the visible spectrum (high-frequency regime).

The analyzed samples consist of layers of glass, ITO, PEDOT: PSS and MAPbI3 (thus the first four layers of a fully constituted “inverted” PSC) which are made and maintained in a nitrogen environment during the entire measurement process.

NAMA1.1-1O021

INVESTIGATION OF CORE@SHELL NANOPARTICLES USING SYNCHROTRON RADIATION BASED TECHNIQUES (XPS, NEXAFS, STXM)

A. Hermanns [1], B. Ritter [1], E. Kemnitz [1], K. Sparnacci [2], S. Swaraj [3], A. Lippitz [4], J. Radnik [4], W. Unger [4]

[1]Humboldt-Universität zu Berlin - Berlin (Germany), [2]Università del Piemonte Orientale - Alessandria (Italy), [3]SOLEIL Synchrotron - Saint-Aubin (France), [4]Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany)

Engineered core@shell nanoparticles have become indispensable in various industrial applications.[1] Although material, shape and size of the particles vary strongly depending on the specific application, they have one thing in common: Their surface chemistry determines their performance. Therefore, we aim to develop a valid methodology to study the surface chemistry and shell thickness of core@shell nanoparticles in an accurate and quantitative manner using Energy-Resolved X-Ray Photoelectron Spectroscopy (ER-XPS). In contrast to Angle-Resolved XPS (AR-XPS) which is only suitable for flat samples, ER-XPS can be applied to nanoparticles with for example spherical geometry.

Two particle systems were investigated: Firstly, Hyflon cores with PMMA shell (total diameter 52 nm) and, secondly, SrF_2 cores with CaF_2 shell (total diameter 9 nm). The first system is used to grow colloidal photonic crystals with applications like sensors, switches and photovoltaic devices.[2] The second system can be doped with lanthanides to create luminescent nanoparticles which can be applied as biological labels, displays or fluorescent ceramics.[3]

Both systems were investigated by ER-XPS at the HE-SGM beamline of the Synchrotron source BESSY II (Berlin). By varying the excitation energy between 200 and 849 eV and the consequent adjustment of the XPS information depth (z_{95}) between 2 and 6 nm, depth profiles of the composition (elements and chemical species) of the nanoparticle surface were measured. Figure 1 contains the C1s XPS high-resolution spectrum of the Hyflon@PMMA nanoparticles at different excitation energies. A continuous transformation of the spectrum is observed which corresponds to an increasing contribution of the core to the XPS intensity with increasing information depths.

Additionally, Near Edge X-Ray Absorption Spectroscopy (NEXAFS) revealed a very different absorption behavior of core and shell material for the Hyflon@PMMA particles. Therefore, they were investigated by Scanning Transmission X-Ray Microscopy (STXM) at the HERMES beamline of the Synchrotron source SOLEIL (Saint-Aubin).

Thanks/Acknowledgement

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 and innovation programme.

References

[1] N. Belsey, *J. Phys. Chem.* **2016**, *120*, 24070-24079.

[2] D. Antonioli, *Polym. Int* **2012**, *61*, 1294-1301.

[3] B. Ritter, *J. Phys. Chem.* **2016**, *120*, 8992-8999.

NAMA2.3-3O059

REDUCTION OF GRAPHENE OXIDE BY UHV ANNEALING

S. Kaciulis [1], A. Mezzi [1], P. Soltani [1], H. Xia [2], M. Lavorgna [3], Y. Wang [4], T. Zhai [5]
[1]ISMN - CNR - Rome (Italy), [2]Sichuan University - Chengdu (China), [3]IMCB - CNR - Naples (Italy), [4]Modern Chemistry Research Institute - Shaanxi (China), [5]Building Material Quality Supervision Testing Center - Guiyang (China)

The reduction of graphene oxide (GO) is widely used for production of graphene and composite materials with graphene, which are very promising due to their extraordinary electrical and mechanical properties [1]. Nevertheless, the major research attention was given to the chemical reduction, whereas the possibility to reduce GO by annealing in ultra-high vacuum (UHV) environment still has not been thoroughly investigated.

In addition to the mostly used analytical techniques, such as Raman spectroscopy and electron microscopy, also Auger electron spectroscopy (AES) can be employed for the identification of graphene. As it was recently demonstrated, from the shape of C KVV spectra excited by electron beam (AES) and X-ray photons (XAES) it is possible to recognize the presence of 2D carbon on different supports [2,3] and in various composites [1,4].

In present study, was investigated the influence of UHV annealing till 600 °C on the chemical composition of GO. The thermal reduction of GO was compared with the chemical effect of various reducing agents, such as chitosan, mercapto and sulfur used for the preparation of several composites. In particular, the GO reduction was investigated in the following polymeric materials: chitosan-based aerogel and composites and bromo-butyl rubber-based composites. For sake of comparison, the control samples were prepared by using only the reducing agents dispersed with the GO, and submitting them to the same thermal treatments adopted for the preparation of the composites. Different preparation procedures [1,5] were adopted for the films and aerogels, by using suitable thermal treatments for the thermal stability of the polymers.

All the samples were analyzed by XPS and AES techniques, paying a particular attention to the shape of C KVV spectra described by the D parameter values [2]. The successful reduction of GO to graphene at T= 600 °C was also verified by Raman spectroscopy.

References

[1] N. Yan, G. Buonocore, M. Lavorgna, et al., Composites Sci. Technol. 102 (2014) 74.

[2] S. Kaciulis, A. Mezzi, P. Calvani, D.M. Trucchi, Surf. Interface Anal. 46 (2014) 966.

[3] L. Nobili, L. Magagnin, R. Bernasconi, et al., Surf. Interface Anal. 48 (2016) 456.

[4] S. Kaciulis, A. Mezzi, S.K. Balijepalli, et al., Thin Solid Films 581 (2015) 80.

[5] F. He, G. Mensitieri, M. Lavorgna, et al., Composites Part B, in press, DOI: 10.1016/j.compositesb.2016.10.076

NAMA3-1O063

THE PHASE COMPOSITION OF BURIED DIELECTRIC INTERLAYERS AND INTERATOMIC INTERACTIONS IN THE AMORPHOUS MULTILAYER NANOSTRUCTURES [(COFEB)60C40/SIO2]200 BY USXES AND IR DATA.

E. Domashevskaya, N. Builov, V. Terekhov, K. Barkov
Voronezh State University - Voronezh (Russian federation)

Magnetic properties of heterophase systems depend on many parameters of the atomic and electronic structure. The main concerns volume ratio of the ferromagnetic and nonmagnetic phase, which affects the distance between the nanoparticles of the metal alloy, and hence the magnitude of the magnetic interaction between the magnetic moments of the granules.

Multilayer nanostructures (MLNS) $[(CoFeB)_{60}C_{40}/SiO_2]_{200}$ obtained by ion-beam sputering two targets on a rotating pyroceramics substrate, are amorphous. Dimensions of metal particles in the composite layers $(CoFeB)_{60}C_{40}$ are around 2-4 nm. The thickness of the MLNS bilayers are ~ 6 nm, and consist of sum thickness of a composite layers (~ 4 nm) and of the dielectric interlayers (~ 2 nm), according to small-angle diffraction data. Investigated samples 1,2,3 of №1462 serie slightly differ in bilayers thickness.

For determination of the phase composition of the buried amorphous dielectric interlayers produced by ion-beam sputtering quartz target, we used the ultrasoft X-ray emission spectroscopy (USXES) method by registering the silicon Si $L_{2,3}$ -spectra reflecting the distribution of the density of states (s + d) in the valence band. Varying the X-ray tube accelerating voltage of RSM-500 spectrometer in the range of 1 kV to 6 kV allows to investigate the samples without destroying by increasing the investigated layers thickness from 10 nm to 120 nm.

According to the simulation of the experimental ultrasoft X-ray Si $L_{2,3}$- spectra (Fig.1a) using reference spectra, amorphous dielectric interlayers consist of silica SiO_2 and suboxide $SiO_{1.3}$ which ensures the presence of localized states in the forbidden band of a dielectric for the realization of hopping conductivity in addition to tunneling through the dielectric interlayers.

At the infrared (IR) spectra of MLNS, in addition to the Fe-O, Co-O modes, there are

intensive B-C modes relating to the composite layers, a intensive Si-O- Si interlayer modes and very weak Si-C interface mode (Fig.1b).

Fig.1 (a) - Experimental and simulated (thin line) USXES Si $L_{2,3}$ –spectra and (b)- IR spectra of MLNS $[(CoFeB)_{60}C_{40}/SiO_2]_{200}$.

NAMA3-2O066

DEPOSITION OF NANOPARTICLES BY ELECTROSPRAY FOR IMPROVED ANALYSIS BY SEM/TEM AND EDX

V-D. Hodoroaba [1], **J. Mielke** [1], **P. Dohányosová** [2], **P. Müller** [3], **S. López-Vidal** [2]
[1]Federal Institute for Materials Research and Testing (BAM) - Berlin (Germany), [2]RAMEM Ltd. - Madrid (Spain), [3]BASF SE, Material Physics Research - Ludwigshafen (Germany)

Of many experimental techniques for measuring particle sizes and size distributions, electron microscopy (EM) is still considered as the gold standard, especially in the nano range (1–100 nm). Furthermore, high-resolution X-ray spectroscopy (EDX) in conjunction with EM can be applied to individul NPs.

Preparation of an EM sample for generic particulate materials is a difficult task. Usually the particles in a suspension are deposited on a support. However, this procedure includes the drying of larger solvent amounts on the substrate itself, and this can affect the spatial distribution of the deposited particles. One possibility to overcome this is the use of an electrospray system, where the suspension of particles is sprayed onto the substrate in charged droplets that are so small that they either dry off on the substrate immediately without affecting the position of particles, or even already during their flight time to the substrate (Figure 1). Additionally, the charging of particles minimizes agglomeration and aggregation, maximizing the collection of the EM grids.

The prototype of an electrospray deposition system from RAMEM under its trademark IONER (www.ioner.eu) was tested. Electrospray is theoretically described since a long time [1], but no dedicated commercial instruments are available for the preparation of TEM grids yet, apart from electrostatic deposition of aerosols [2].

Several materials have been sprayed onto TEM grids and the resulting particle distributions were evaluated. Operation parameters such as the sample flow-rate, capillary – substrate distance, electric field strength and sampling period length have been optimized. It was found that the particles deposited by electrospray generally show a much more homogeneous spatial distribution on the substrate and a substantial increase of the number of single particles (suited to automatic analysis).

Thanks/Acknowledgement

This work has received funding from the European Union's Seventh Programme for research, technological development and demonstration under grant agreement no. 604347-2 (NanoDefine).

References

[1] Taylor G, Proc. Royal Soc. London. Series A, Math. and Phys. Sci., **280** (1964), p. 383

[2] M Fierz et al., *Aerosol Sci Technol* 2007 **41** 520

Fig. 1 The principle of electrospray (left) versus the common "drop on grid" technique (right)

NAMA1.1-4O079

SULFUR-CONTAINING NANOPARTICLES: MONITORING CHEMICAL EVOLUTION BY NAP-XPS AND IN SITU XAS

S. Carenco [1], C. Larquet [1], A.M. Nguyen [1], J.J. Gallet [2], F. Bournel [2], B. Lassalle [3], C. Sanchez [1]

[1]Sorbonne Universités, UPMC, CNRS, Laboratoire de Chimie de la Matière Condensée de Paris, - Paris (France), [2]Sorbonne Universités, UPMC & Synchrotron SOLEIL - Paris (France), [3]Synchrotron SOLEIL - Gif-Sur-Yvette (France)

Inorganic nanoparticles with a reduced diameter (5-20 nm) exhibit a large surface-to-volume ratio: as a consequence, their nature, stability, and properties are as much defined by their surface than by the structure of their core. In the last decade, NAP-XPS was extensively used to characterize the chemical evolution of nanoparticles submitted to reactive gases (H_2, CO_2,[1] CO,[2] NO, etc.), eg. in the context of heterogeneous catalysis.[3–5] Humidity and even aqueous conditions are however often encountered in wider circumstances: in aqueous electrocatalytic processes (fuel cells, etc.), in biological media (nano-medicine) or in day-to-day use of nanomaterials (ambient humidity, corrosion).

Here, we will discuss the behavior of nanoparticles exposed to water vapor. The example of metal oxysulfides will be selected because of the recent advances made in our group for their synthesis. In contrast with more common metal sulfate phases, metal oxysulfides exhibit reduced sulfur atoms that provide a covalent character to the compound and a unique set of electronic and chemical properties: eg. absorption can be adjusted in the visible range that is more favorable for photocatalysis. Stability of the nanoparticles toward water and humid conditions will be cross-examined, first with XPS under a background pressure of H_2O and/or O_2 (TEMPO beamline at SOLEIL), second, with XAS at Sulfur K-edge under dry or humid conditions (LUCIA beamline at SOLEIL). By combining these techniques, we will show that, depending on the nature of the metal cation, the nanoparticles are prone to form metal sulfates on their surface, resulting in an increased band-gap. The reversibility of this process will also be discussed. These findings highlight the relevance of in situ monitoring of nanoparticles to develop applications such as photocatalysis.

Thanks/Acknowledgement

Cluster of Excellence (LABEX) MATISSE, UPMC, CNRS and Collège de France are acknowledged for financial support. SOLEIL synchrotron is acknowledged for beamtime and support.

References

[1] S. Carenco et al., Small 2015, 11, 3045.
[2] S. Carenco, Chemistry 2014, 20, 10616.
[3] F. Tao et al., J. Am. Chem. Soc. 2010, 132, 8697.
[4] V. Papaefthimiou et al., Chem. Mater. 2014, 26, 1553.
[5] S. Carenco et al., J. Phys. Chem. C 2013, 117, 6259.

NAMA1.1-5O081

LINKING NANOSILVER (AGNP) TOXICITY TO THE PHYSICOCHEMICAL PROPERTIES OF THE PARTICLES WHICH CAN CHANGE AS A FUNCTION OF EXPERIMENTAL AND BIOLOGICAL CONDITIONS

D. Baer [1], J. Brown [2], A. Porter [3], B. Thrall [1], T. Tetley [4], L. Van Winkle [5], T. Xia [6]

[1]Earth and Biological Sciences Directorate, Pacific Northwest National Laboratory - Richland (United States of America), [2]Department of Pharmaceutical Sciences, University of Colorado - Denver (United States of America), [3]Department of Materials and London Centre for Nanotechnology, Imperial College London - London (United kingdom), [4]Lung Cell Biology, Airways Disease, National Heart & Lung Institute, Imperial College London - London (United kingdom), [5]School of Veterinary Medicine, University of California at Davis - Davis (United States of America), [6]David Geffen School of Medicine, University of California at Los Angeles - Los Angeles (United States of America)

Although colloidal Ag is generally considered safe for humans, use of nanosilver in consumer products has dramatically increased both the amount of Ag exposure and possible exposure pathways. To fill knowledge gaps for nano-Ag safety assessment, the National Institute of Environmental Health Sciences (NIEHS) supported a consortium of investigators to examine how physical and chemical characteristics of Ag nanoparticles (AgNPs) can lead to adverse health outcomes. Here we report a consortium perspective linking physicochemical properties of the particles to Ag biodistribution and toxicity. It is necessary to recognize the dynamic nature of AgNPs. They can change in response to handling and variations in their environment and such changes can influence Ag biodistribution and biological responses. Consortium studies identified the critical relationships among AgNP properties, environmental effects, and the biodistribution and fate of Ag associated with the particles. Three critical regions of interactions were identified: i) effect of exposure medium and biological environment on particle properties and transformations; ii) processes occurring at the cellular surface impacting particle attachment, uptake, accumulation and clearance; and iii) particle fate and transformations within a cell. The nature of AgNPs during biological exposure is influenced by the initial characteristics of the particles including size, structure and the presence of designed or inadvertent coatings. These initial properties are usually altered by exposure to artificial or natural media [1, 2]. These physicochemical properties are often time dependent and such changes, including often ignored effects due to handling or storage[3], can influence biological outcomes. Ag can be transported into cells as both ions and particles. While ions are known to impact cytotoxicity, AgNPs within cells often have greater toxicity. Intercellular processes are similar to those in extracellular media except that the Ag is located within specific microenvironments within a cell. It appears that intracellular dissolution of Ag is a major cause of toxicity.

Thanks/Acknowledgement

This work was supported by the National Institutes of Environmental Health Sciences Centers for Nanotechnology Health Implications Research Consortium under Center grant U19 ES019544.

References

[1] R. Behra, et al., "Bioavailability of silver nanoparticles and ions: from a chemical and biochemical perspective," Journal of The Royal Society Interface, 10 (2013) 20130396.

[2]B. F. Leo, et al., "The Stability of Silver Nanoparticles in a Model of Pulmonary Surfactant," Environmental Science & Technology, 47(2013)11232-11240.

[3] D. R. Baer, P. Munusamy, and B. D. Thrall, "Provenance information as a tool for addressing engineered nanoparticle reproducibility challenges," Biointerphases, 11(2016) 04B401.

NAMA1.2-5O096

AN INVESTIGATION ON ELECTROCATALYTIC PROPERTIES OF N-DOPED TITANIUM DIOXIDE NANOTUBE ARRAYS DECORATED WITH NICKEL NANOPARTICLES

S. Khameneh-Asl, N.S. Peighambardoust, M. Sarbazeh
Department of Mechanics, Materials Science and Engineering group, University of Tabriz, Tabriz, Iran - Tabriz (Iran, islamic republic of)

Fuel cells are known as one of the most important energy resources, but because of their expensive electrodes they are not economical for many applications. Nanomaterials can be very useful for increasing the efficiency of these cells. Between synthesized nanostructures, TiO2 nanotubes have a special value because of their high chemical resistance, suitable band gap for specific applications, photocatalytic properties and being non-toxic. In this study, it has tried to create a non-expensive electrode compared with Pt electrodes and investigate electrocatalytic properties of it. The conditions of TiO2 nanotubes synthesis and their coating with nickel nanoparticles have been optimized. To synthesize TiO2 nanotubes, anodization method in potentiostat condition in the non-aqueous solution based on ethylene glycol (EG, 2 Vol. % H2O and 3 wt % NH4F) was used. The anodizing temperature has been optimized with current-time diagram during anodization and annealing temperature has been optimized using FESEM images and current-time diagram during coating process. The results showed that, optimized anodizing temperature is 25oC and optimized annealing temperature of nanotubes is 450oC. To dope nitrogen ion substitutional into TiO2 nanotubes structure, the samples have been floated in ammonia solution for 10 hrs and EDX analysis results showed that doping has been done completely and resulted in a reduction of the band gap of these nanotubes. For coating the nickel nanoparticles, pulse electroplating has been used. The results of FESEM images, EDX analysis and cyclic voltammetry tests taken from the samples Ti-NT, Ti/N-NT, Ti/Ni-NT, Ti/N/Ni-NT showed that although presence of nitrogen ion and nickel nanoparticles have separately a positive effect on TiO2 nanotubes electrocatalytic properties up to 800 µA/cm2 or 22%, nitrogen doping and nickel nanoparticles decorating have simultaneously a better effect on this property of TiO2 nanotubes up to 2000 µA/cm2 or 57% as which were shown in Fig. 1.

Figure 1: CV curves of TiO2 Nanotube sample (Ti-NT) and TiO2 nanotube Nitrogen-doped and Ni coated sample (Ti/N/Ni-NT) in 1 M H2SO4 + 0.5 M CH3OH at a scan rate of 100 mV s-1

NAMA2.4-3O105

REACTION KINETICS OF ULTRA THIN ALKALI-HALIDE FILMS UPON ELECTRON IRRADIATION

A. Husseen, S. Le Moal, H. Oughaddou, G. Dujardin, A. Mayne, E. Le Moal
Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Université Paris-Sud - Orsay (France)

Electron-induced modification of alkali-halide bulk crystals has been widely investigated, mostly using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and scanning tunneling microscopy [1,2]. At primary electron energies typically less than 10 keV, electron irradiation is known to induce layer-by-layer alkali halide desorption, through a mechanism that involves the creation of halogen atom vacancies in the bulk, followed by their migration to the crystal surface, and the agglomeration of alkali metal atoms at step edges. Comparatively, the effects of electron irradiation on thin alkali-halide films have rarely been considered; in particular, the case of *ultra-thin* alkali-halide films composed of one or two monolayers, grown on fcc metals has never been addressed. This is all the more surprising since such alkali-halide films are increasingly used as spacers to electronically decouple organic molecules from metallic substrates in atomically controlled systems for single molecule spectroscopy measurements [3].

In the ultra-thin film case, the limited amount of reactants and the interactions with the substrate are crucial, leading to different reaction kinetics, compared to the bulk crystal or thick film case. The outcomes may be different too, since the products of alkali-halide dissociation may adsorb or even react with the metallic substrate, whereas on bulk crystals and thick films the dissociation products inevitably adsorb on the same alkali-halide material.

Here, we report on the desorption of ultra-thin NaCl films grown on Ag(001) upon electron irradiation using LEED and AES, with primary electron energies of 52-60 eV and 3 keV, respectively. LEED and AES are used both to modify the NaCl films and to investigate the reaction kinetics and the outcome of any modification. We observe that Cl depletion follows first-order reaction kinetics, in contrast with previous studies on thick NaCl films and bulk crystals. Na atoms produced from NaCl dissociation diffuse to bare areas of the Ag(001) surface, where they form Na-Ag superstructures that are known for the Na/Ag(001) system [4]. A model for electron-induced desorption of ultra-thin alkali-halide films from metallic surfaces is proposed, and future applications in the production of nanoscale chemical templates are discussed [5].

References

[1] H. Tokutaka *et al*, Surf. Sci. 21, 233 (1970).
[2] M. Szymonski *et al*, Prog. Surf. Sci. 67, 123 (2001).
[3] B. Doppagne *et al*, Phys. Rev. Lett. 118, 127401 (2017).
[4] H. Tochihara and S. Mizuno, Prog. Surf. Sci. 58, 1 (1998).
[5] A. Husseen *et al*, Phys. Rev. B, submitted.

NAMA2.4-1O114

PLASMON AND PHONON EXCITATIONS AND HEAT TRANSPORT IN NANOLAMINATE ALUMINA/SILVER MULTILAYER COATINGS

D. Wainstein [1], V. Vakhrushev [2], A. Kovalev [1], R. Gago [3]

[1]Surface Phenomena Researches Group, I.P. Bardin Central Research Institute for Ferrous Metallurgy - Moscow (Russian federation), [2]Surface Phenomena Researches Group, I.P. Bardin Central Research Institute for Ferrous Metallurgy; Moscow Technological University (MIREA) - Moscow (Russian federation), [3]Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas - Madrid (Spain)

The multilayer Al_2O_3/Ag coatings with different numbers and thicknesses of individual layers were fabricated by DC magnetron sputtering. The Ag layers thicknesses were from 1 to 5 nm, oxide layers were varied from 8 to 40 nm. All samples had the 200 nm Al_2O_3 overlayer to avoid silver layer oxidation up to electron spectroscopy experiments. Heat conductivity of coatings was measured by a pulsed photothermal reflectance (PPR) technique. The electron spectroscopy investigations (XPS, plasmon electron microscopy, HREELS of intraband transitions and phonon losses) were performed using electron spectrometer ESCALAB MK2 (VG). Nanostructuring influences on the electronic structure of metal and insulator. Binding energies of electrons in atoms are growing, and localization of electrons reduces metallic interatomic bonds while layers thickness decreased. Al_2O_3 band gap evolves differently in Γ and X reciprocal space points with oxide layers thinning. Size effect of nanostructuring leads to widening effective band gap together with its flattening. Phonon heat transport in Ag/Al_2O_3 nanocomposite has some specific features. It corresponds to classic description when layers thinning below phonon MFP embarrasses heat transport by phonon propagation. Anisotropy of acoustic phonon propagation grows with nanostructuring of MIM coatings. Simultaneously phonons transmittance probability from Ag to Al_2O_3 interface significantly decreases with layer thinning. At the same time the probability of opposite phonon transportation raises. Generally input of transboundary heat transfer by phonons is very small but its role grows in thin layers. Plasmons are exciting in thin metal layers surrounded by alumina with symmetric or anti-symmetric intensity profile depending on their energy and thickness of the layer. This non-uniform resonance structure is a consequence of confinement of electromagnetic density of states in thin planar nanocomposite. Surface plasmon-polariton (SPP) interactions are propagating on 5.0 - 2.0 nm into the oxide boundary layer directly proportionally to intensities of plasmon excitation in Ag. SPP propagation is the prevailing electronic mechanism of heat transfer. It is driven by Ag conducting electrons. As electronic DOS at EF in alumina is too low to transfer electrons to conducting band through a wide band gap, the SPP resonance injects Ag 5s electrons into the oxide conducting band by electromagnetic field near the interface. All these synergistically acting features of phonons and plasmons propagation in layers and on interfaces decrease sharply heat conductivity of nanolaminate MIM coatings.

Thanks/Acknowledgement

The research was carried out with partial financial support of RSF project No. 14-12-00170 and RFBR project No. 16-08-00527.

NAMA1.1-3O127

IN-SITU AND EX-SITU COMPLEMENTARY ANALYSIS OF COATED NANOPARTICLES

C. Minelli, N. Belsey, D. Cant, A. Shard
National Physical Laboratory - Teddington (United kingdom)

Reliable and reproducible measurement methods for nanoparticles will significantly accelerate the uptake of these materials in commercial applications and allow industry to comply with regulation. However, there remain significant challenges in the analysis of nanomaterials due to, among other factors, the interdisciplinary nature of the field, the lack of adequate reference materials to calibrate analytical tools and the difficulties associated both with sample preparation for analysis and the interpretation of data.

The coatings of nanoparticles, both intentional and unintentional, play a crucial role in determining their properties and directing their behavior. For the effective commercial exploitation of these innovative materials, it is essential to achieve a detailed understanding of their interfaces and therefore establish sound sample preparation and measurement protocols for quantitative analysis. We use a combination of techniques which can be employed directly to colloidal suspensions and on the dried particles to ensure a meaningful interpretation.

We applied this approach to the analysis of organic coatings on nanoparticles in liquid media (in-situ) using techniques such as analytical centrifugation and dynamic light scattering and ex-situ with X-ray photoelectron spectroscopy (XPS). Examples of these systems include protein coated gold nanoparticles and polymeric core/shell nanoparticles. The main outcomes of a VAMAS inter-laboratory study whose aims included to assess the inter-laboratory variability in the measurement of nanoparticle coatings using XPS and LEIS will also be discussed.

We will show how the different techniques produce complementary information, validate and support the measurement methods and ultimately provide the analyst with a flexible toolkit for the analysis of a broad spectrum of nanoparticle systems.

Thanks/Acknowledgement

This work was funded by the UK Department of Energy, Business & Industrial Strategy and with funding from the 14IND12 Innanopart project by the European Union through the European Metrology Programme for Innovation and Research (EMPIR). EMPIR is jointly funded by the EMPIR participating countries within EURAMET and the European Union.

References

C. Minelli and A. G. Shard, Chemical measurements of polyethylene glycol shells on gold nanoparticles in the presence of aggregation, Biointerphases, 11 (2016) 04B306.

N. A. Belsey, D. J. H. Cant, C. Minelli et al, VAMAS Inter-Laboratory Study on Measuring the Thickness and Chemistry of Nanoparticle Coatings Using XPS and LEIS, Journal of Physical Chemistry C, 120 (2016) 24070.

N.A. Belsey, A.G. Shard and C. Minelli, Analysis of protein coatings on gold nanoparticles by XPS and liquid-based particle sizing techniques, Biointerphases 10 (2015) 019012.

NAMA2.3-1O158

THE DESIGN OF AN INTEGRATED XPS/ RAMAN SPECTROSCOPY INSTRUMENT FOR CO-INCIDENT ANALYSIS

T. Nunney [1], **C. Glenister** [1], **N. Hibbard** [2], **M. Meyer** [2]
[1]*Thermo Fisher Scientific - East Grinstead* (United kingdom), [2]*Thermo Fisher Scientific - Madison* (United States of America)

Advanced materials present ever increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample, removing the need for additional registration or processing to ensure that the data is being collected from the same position. Often in surface analysis many related techniques are integrated onto the same system. These can include such practices as Ultraviolet Photoelectron Spectroscopy (UPS) for valence band and work function measurements. Ion Scattering Spectroscopy (ISS) is often used to give much more elemental surface information compared to XPS alone. Reflected Electron Energy Loss Spectroscopy (REELS) can also give information on hydrogen in samples which cannot be detected by any of the previously named techniques, allowing full elemental analysis of samples with these combined.

An integrated system that has a Raman spectrometer with a micro-focused, monochromated XPS system can be used for even further analysis. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. This combined approach is particularly powerful when analyzing carbon nanomaterials. Chemical modifications of the material can be easily determined and quantified with XPS, and Raman offers a fast way of determining the quality and conformity of the material. Vibrational structure can also give more precise chemical information in some cases. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will discuss the design of this combined, in-situ approach to multi-modal analysis, illustrated with analysis examples from applications including carbon nanomaterials and mineralogy.

NAMA2.4-2O161

MOLECULAR DYNAMICS SIMULATION OF NANOSTRUCTURED NI/AL FILMS

O. Politano, V. Turlo, F. Baras
Laboratoire ICB, UMR 6303 CNRS-Universite de Bourgogne Franche Comté - Dijon (France)

Nanometric metallic multilayers (N2M) are structured as a succession of interfaces separated by a few nanometers. N2Ms are made of thin layers (4-100 nm) of metals deposited alternately. The many areas of contact should promote mixing between pure metals and alloying processes. In most cases, it is observed that the ignition temperature of the reaction coincides with the melting temperature of the less refractory metal. The mixing is then associated with the dissolution of the solid phase into the liquid one. The Ni-Al reactive foil was chosen as the representative system. By igniting locally one edge of the sample, a self-sustaining reactive front propagates along the foil, without any further supply of heat. The exothermic processes are the interdiffusion of the two metals together with the formation of new phases such as intermetallics.

We studied by means of molecular dynamics (MD) simulations the products formed after the reaction that occurs in N2M. MD is a valuable tool to study those systems, since the typical length scale (a few nanometers) corresponds precisely to the scale accessible in the simulation.

The formation of the new phase, here the NiAl intermetallic compound, develops in non-equilibrium conditions. Underlying microscopic processes and some specific properties such as nucleation and growth of the new intermetallic phase are revealed, while well-established experimental characteristics are observed. Depending on the stoichiometry and initial temperature, several types of nucleation and growth are observed: grain formed at the solid-liquid interfaces or crystallization directly from the melt. In the first case, we will show how the crystallographic orientations of the Ni/Al interfaces influence the kinetic and microstructure during the subsequent grain formation.

NAMA2.3-5O171

AG MIGRATION IN METAL/CERAMIC NANO-MULTILAYERS: CONFINEMENT,STRESS-RELAXATION AND OXYGEN-MEDIATED MASS TRANSPORT

M. Chiodi, C. Cancellieri, F. Moszner, M. Andrzejczuk, J. Janczak-Rusch, L.P.H. Jeurgens

Empa, Swiss Federal Laboratories for Materials Science and Technology, Lab. for Joining Technologies & Corrosion - Dübendorf (Switzerland)

Industry faces the technological challenge of fabricating multi-material nanosized assemblies joined at ever-lower temperatures keeping a high throughput and offering enhanced durability at higher service temperatures.These contradictory requirements can be fulfilled with novel types of nanostructured brazing fillers with an exceptionally high interface-to-volume ratio, constituted of Nano-MultiLayers (NMLs) of a brazing filler and a chemically inert barrier. The interplay between spatial confinement, internal stress and the processing environment can stimulate phase-transitions and/or enhanced kinetics associated with a significant outflow of the confined metallic brazing filler to the surface. This phenomenon could be exploited for joining materials below the constituents bulk melting point [1].

In this work, we present a comprehensive combinatorial SEM/TEM, XPS and XRD investigation of the evolution of $(Ag/AlN)_{5nm/10nm}$ NMLs upon heating in air [2]. SEM/TEM evidence a strong Ag migration from the NML to its surface. Silver particles are found after heating in air up to 420°C. XRD and pole figures confirm that Ag and AlN are initially textured. Such ordering is partially lost upon heating, due to the Ag migration and the oxidation of AlN. The microstructural evolution of the Ag/AlN NML during annealing was monitored by real-time XRD. Beyond 250°C, the Ag coherency domain strongly increases, which correlates with the particles appearing/coarsening on the surface. The Ag nano-layers show an accumulation of stress between 200-280°C which is then released at higher temperatures, triggering the massive Ag migration. Identical experiments carried out in vacuum or in absence of multilayered structure show no Ag migration. A systematic XPS surface and depth profile analysis (carried out on samples heated at different temperatures: from RT to 420°C) allows to elucidate the crucial role of oxygen in dramatically enhancing Ag mobility at low temperature. In fact, oxygen penetrates through the NML and (partially) reacts with both AlN (forming AlOx) and Ag (incorporated in Ag layers sub-surface). The adsorption and dilution of oxygen in Ag strongly enhances its surface self-mobility, kinetically enhancing its migration to the surface.

References

[1] J. Janczak-Rusch et al., Phys. Chem. Chem. Phys. 17 (2015) 28228-28238.

[2] M. Chiodi et al., J. Mater. Chem. C 4 (2016) 4927-4938.

NAMA1.2-3O193

DETERMINATION OF THE INPUT PARAMETERS FOR INELASTIC BACKGROUND ANALYSIS COMBINED WITH HAXPES USING A REFERENCE SAMPLE

C. Zborowski [1], O. Renault [1], A. Torres [1], Y. Yamashita[2], G. Grenet[3], S. Tougaard[4]

[1]Université Grenoble Alpes & CEA, LETI, Minatec Campus - Grenoble (France), [2]Nationale Institute for Materials Science (NIMS) - Tsukuba (Japan), [3]Institut desNanotechnologies de Lyon, Ecole Centrale de Lyon - Ecully (France), [4]Department of Physics, Chemistry and Pharmacy, University of Southern Denmark - Odense (Denmark)

Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1]. It was shown that by combining HAXPES with inelastic background analysis [2], structures at a depth >50 nm can be studied. This study was performed on technologically relevant High Electron Mobility Transistors presenting different thicknesses of the Ta/Al electrode on an $Al_{0.25}Ga_{0.75}N/AlN/GaN$ heterostructure [Fig. 1a]. HAXPES was performed at the Spring-8 synchrotron using 8 keV photons. Here, we present a non-destructive solution to get information on deeply buried layers and interfaces. This is a refined analytical method, based on the use of a reference spectrum, for determining the required input parameters, i.e. the inelastic mean free path calculated using the TPP-2M formula and the inelastic scattering cross-section. As the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic scattering cross-sections [3], K, which can be determined from Reflection Electron Energy-Loss Spectra. The use of a reference sample gives extra constraints which make the analysis faster to converge towards a more accurate result. The figure shows the best Ta $3p_{3/2}$ corrected spectra calculated with different cross-sections and the resulting in-depth distribution, which are in good agreement with the TEM results. We have also successfully used this technique to study structures at a depth >70 nm.

Thanks/Acknowledgement

Part of this work was performed at the Nanocharacterization Platform of CEA-MINATEC. NIMS and Spring-8 are acknowledged for providing beamtime and the staff of the BL15-XU beamline for their assistance during the experiment.

References

[1] P. Risteruci et al., Applied Physics Letters, 104, (2014).

[2] S. Tougaard, Journal of Electron Spectroscopy and Related Phenomena, 178–179 (2010).

[3] P. Risterucci et al., Applied Surface Science, 402, (2017).

NAMA2.3-4O205

PREPARATION, INTERCALATION AND CHARACTERIZATION OF NANO STRUCTURED (ZN, AL) LAYERED DOUBLE HYDROXIDES

M. Richetta [1], V. Alessandra [1], A. Mattoccia [1], P.G. Medaglia [1], M. Roberto [1], K. Saulius [2], M. Alessio [2], S. Peyman [2], R. Pizzoferrato [1]

[1]INDUSTRIAL ENGINNERING DEPARTMENT, UNIVERSITY OF ROME "TOR VERGATA" - Rome (Italy),
[2]ISMN – CNR, P.O. Box 10, 00015 Monterotondo Stazione - Rome (Italy)

The term of layered double hydroxides (LDHs) is used to entitle synthetic or natural lamellar hydroxides with two or more kinds of metallic cations in the main layers and hydrated interlayer domains containing anionic species. LDHs, also known as hydrotalcite materials, have attracted considerable interest from both industry and academia. LDHs are very interesting for their intercalation properties, because they are able to host even complex organic molecules. Namely for this reason they can be applied in many different fields, such as separation technology, catalysis biomedical science and nanocomposite material engineering. Four types of (Zn, Al) LDHs, representative of the two hosted anions (Cl- and NO3-) and two times of growth (6 and 24 hour) were prepared by a simple one-step hydrothermal process at room temperature using Zn salt precursors sputtered on Al foils, which act as a reactant and substrate [1]. Moreover, the (Zn, Al) LDHs intercalated with amino acid cysteine and functionalized with ionic liquid were studied.

The properties of LDH nanoplatelets were analysed by surface-sensitive techniques. X-ray Photoelectron (XPS) and Ultraviolet Photoelectron (UPS) spectroscopies have been used to investigate the composition of samples. The structure of LDHs was studied by X-ray diffraction (XRD), whereas the morphology was investigated by scanning electron microscopy (SEM). The thermal stability was investigated by thermal desorption spectroscopy (TDS) in ultra-high vacuum.

References

M. Richetta, L. Digiamberardino, A. Matoccia, et al, Surf. Interface Anal. 48 (2016) 514-518

NAMA1.2-4O208

THE PENTAMER CHAIN STRUCTURE OF SI NANORIBBONS ON AG(110)

L. Masson [1], T. Leoni [1], E. Moyen [1], G. Prévot [2], R. Bernard [2], C. Hogan [3]
[1]CINaM AMU CNRS - Marseille (France), [2]INSP UPMC CNRS - Paris (France), [3]ISM CNR - Rome (Italy)

Since the discovery in 2005 of the synthesis of Si nanoribbons (NRs) on Ag(110) upon Si deposition at room temperature (RT), a long debate concerning the atomic structure of these NRs began after the reported graphene-like electronic signature measured by ARPES [1] and attributed to the silicene character of the Si NRs. Si NRs with a width of 0.8 nm are randomly distributed on silver terraces or self-assembled in a (5x2) unit cell to form a 2D single-atom-thick Si layer composed of regularly spaced NRs with a width of 1.6 nm, for Si deposition at RT and 460 K, respectively. Our first contribution to solve the atomic structure of the Si NRs was to provide compelling evidence, by a STM-GIXD study, of an unexpected Ag(110) missing row reconstruction associated with the release of Ag atoms induced by the Si NR growth [2]. Recently, we published a combined theoretical (DFT calculations) and experimental (STM, GIXD) study [3] which definitively elucidates the atomic structure of the Si NRs, among the numerous models proposed in the literature [4]. The Si NRs correspond to an original Si phase composed of pentamer chains lying in the missing rows of the reconstructed surface (see Fig. below).

Figure : a) STM image (77 K) of Si nanoribbons (NRs) below completion of the Si monolayer. I = 480 pA, V_{sample}= 40 mV. The atomic rows of Ag(110) are visible. b) Schematic model of a Si NR on the missing row reconstructed Ag(110) surface and the corresponding simulated STM image.

References

[1] P. De Padova et al., Appl. Phys. Lett. 96, 261905 (2010)
[2] R. Bernard et al., Phys. Rev. B 88, 121411(R) (2013)
[3] G. Prévot et al., Phys. Rev. Lett. 17, 276102 (2016)
[4] J. I. Cerdá et al., Nat. Commun. 7, 13076 (2016)

NAMA2.2-5O222

HE AND NE IRRADIATION INDUCED DEFECTS IN MULTIWALLED CARBON NANOTUBES

P. Philipp, S. Eswara, J.N. Audinot, T. Wirtz

Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, Luxembourg Institute of Science and Technology (LIST), 41 rue du Brill, L-4422 Belvaux, Luxembourg

The mechanical, structural, electronic and magnetic properties of carbon nanotubes can be modified by electron or ion irradiation. In this work we used a correlative approach combining Raman spectroscopy with TEM and numerical simulations using SDTRIMSP to study defect formation in suspended multiwalled carbon nanotubes (MWCNTs) for 25 keV He^+ and Ne^+ ion irradiation at normal incidence for fluences ranging in between 10^{14} to 10^{18} ions/cm^2. A new methodology based on Au TEM grids was developed and validated in order to ensure compatibility across the different experimental techniques. The influence of sample thickness on damage accumulation and amorphisation of the MWCNTs will be discussed in detail. For He^+ irradiation, Raman spectra show that amorphisation starts at a fluence of 10^{16} ions/cm^2. Nevertheless, the structure of the single carbon nanotubes (CNTs) is still visible for higher fluences on the TEM images. In one case unzipping of the CNT to a nanoribbon has been observed, which shows that damage accumulation does not necessarily lead to the loss of the graphitic structure of the CNTs. For Ne^+ irradiation, no net start for amorphisation could be found in the Raman data. In TEM images, areas with thicker layers contain some spots where the initial CNT structure is no longer visible, but in most areas the tubular structure is maintained. This can be attributed to the sputter yields which are much higher for Ne^+ irradiation than for He^+ irradiation. Specifically, for the heavier species the sputter rates are high on the top and bottom side of the MWCNT layer, leading to the removal of matter on both sides of the sample. Possibly it is equal to or only slightly smaller than the damage accumulation rate in the MWCNTs for areas of the sample with small thickness.

NAMA1.2-1O225

DEVELOPMENT OF PHOTOSENSITIZER@NANOPARTICLES AS NOVEL CATALYST FOR WATER SPLITTING: EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF THE SURFACE COMPOSITION

R. Gonzalez Gomez [1], L. Cusinato [2], D. Ciuculescu-Pradines [1], C. Amiens [1], I. Del Rosal [2], R. Poteau [2], K. Philippot [1]
[1]CNRS, LCC (Laboratoire de Chimie de Coordination) - Toulouse (France), *[2]INSA, LPCNO (Laboratoire de Physique et Chimie de Nano-Objects) - Toulouse* (France)

The prediction for energy demand by the year 2050 is in the 30-50 TW range, which is more than a 100% increase regarding the consumption in 2010.[1] An attractive and clean energy vector to solve this problem could be hydrogen (H_2).

Hydrogen can be obtained through the splitting of water but this reaction is thermodynamically unfavorable by 474.4 $kJ.mol^{-1}$. In principle, this energy could be supplied by sunlight using a proper catalyst. Homogeneous molecular catalysts have been reported for water splitting process,[2] and more recently, metal nanoparticles (MNPs) have been identified from the decomposition of molecular complexes in working conditions and demonstrated to be the active species.[3] The proper design of such nanocatalysts and the understanding of their photophysical and catalytic properties are real challenges to be overcome.

In this context, we are interested in the development of novel nanocatalysts for water splitting, namely controlled photosensitizer@nanoparticles systems, by connecting photosensitizing centers (like modified $[Ru(bpy)_3]^{2+}$ complexes) to the surface of MNPs using carboxylic and phosphonic acids as anchoring groups. For this purpose, we started studying the surface properties of RuNPs stabilized by carboxylic acids as a model in order to bring an understanding of structure/property relationships at the nanoscale. The RuNPs nanoparticles were synthesized following the organometallic approach[4] using octanoic acid (OcAc) as a stabilizer and TEM analysis revealed small NPs of 1.6 nm mean size with a good morphology and dispersion. The surface state of these RuNPs has been probed by NMR and thermogravimetric techniques leading to a mapping of their surface. In parallel, DFT calculations have been performed according to a thermodynamic model fed with DFT energies,[5] with a systematic analysis of the bond properties and of the electronic states. As it will be presented, the experimental and theoretical results are in good agreement giving thus a first step to design a proper catalyst that can provide an efficient way to generate H_2.

References

1- International Energy Outlook July 2013; Energy Information Administration, U.S. Department of Energy.

2- (a) L. Duan, et al. *Nat. Chem*. 2012, 4, 418. (b) Y. Sun, et al. *Chem. Sci*. 2013, 4, 118.G

3- (a) J. J. Stracke, et al. *J. Am. Chem. Soc.* 2011, 133, 14872. (b) K. S. Joya, et al. *Angew. Chem. Int. Ed.* 2013, 52, 10426.

4- C. Amiens, et al. *New J. Chem*., 2013, 37, 3374.

5- L. Cusinato, et al. *Nanoscale*, 2016, 8, 10974.

NAMA2.4-5O242

STRUCTURAL AND OPTICAL CHARACTERIZATION OF ZNO/BI2SE3 HETEROSTRUCTURES

D. Erts [1], M. Baitimirova [1], R. Viter [2], J. Andzane [1], M. Bechelany [3], G. Petersons [1]
[1]Institute of Chemical Physics of University of Latvia - Riga (Latvia), [2]Institute of Atomic Physics and Spectroscopy of University of Latvia - Riga (Latvia), [3]European Institute of Membranes of University of Montpellier - Montpellier (France)

Bismuth selenide (Bi_2Se_3) is known as 3D topological insulator (TI) of considerable interest since it has a narrow bulk energy gap (~ 0.3 eV) and a simple stable surface state protected by time reversal symmetry. The presence of the surface states on Bi_2Se_3 have been experimentally identified by reducing the bulk conductance using different approaches as tuning the gate voltage, introducing dopants and nanostructuring. Recent theoretical investigations predict the existence of spin-plasmon (SP) mode on the surface of TI, arising from the coupling between spin and charge excitations resulting from the locking of the spin and momentum [1]. It is well-known that SP resonances can enhance photoluminescence (PL) from semiconductor emitters and has been observed from various ZnO hybrid structures, such as ZnO/metals, ZnO/carbon nanotube and ZnO/graphene. Experimentally, the enhancement of PL was reported for ZnO/Bi_2Te_3 hybrid structures, where mechanically exfoliated Bi_2Te_3 flakes with thicknesses below 200 nm were placed on the surface of ZnO [2]. In turn, creation of graphene/Bi_2Se_3 heterostructures resulted in efficient hot carrier separation and strong photogating across the graphene/Bi_2Se_3 interface, significantly improving photoelectrical properties of graphene [3].

Studied in this work ZnO/Bi_2Se_3 heterostructures were fabricated by consequent deposition of ZnO and Bi_2Se_3 nanolayers using atomic layer deposition (ALD) [4] and catalyst-free physical vapour deposition methods [5] respectively. Quartz, silicon and monolayer graphene were used as deposition substrates. Structure and morphology of prepared ZnO/Bi_2Se_3 heterostructures were studied by electron and atomic force microscopy as well as by energy-dispersive X-ray diffraction technique. Optical properties of pure ZnO, ZnO/Bi_2Se_3 and graphene/Bi_2Se_3/ZnO heterostructures were determined and discussed.

References

1. S. Raghu et al., S. B. Chung, X.-L. Qi, and S.-C. Zhang, Phys. Rev. Lett. 104, 116401 (2010)
2. Z.-M. Liao, B.-H. Han, H.-C. Wu et al., AIP Advances 2, 022105 (2012)
3. J. Kim, S. Park, H. Jang, N. Koirala et al., ACS Photonics, 4, 482 (2017)
4. M. Baitimirova, R. Viter, J. Andzane et al., J. Phys. Chem. C 120, 23716 (2016)
5. J. Andzane, G. Kunakova, S. Charpentier, V. Hrkac, L. Kienle, M. Baitimirova, T. Bauch, F. Lombardi and D. Erts, Nanoscale 7, 15935 (2015)

NAMA1.2-2O253

SURFACE ANALYSIS OF IRON AND STEEL NANO-POWDER AND ITS INFLUENCE ON SINTERING

S. Manchili, R. Shvab, A. Zehri, E. Hryha, J. Liu, L. Nyborg
Chalmers University of Technology - Gothenburg (Sweden)

Traditional powder metallurgy (PM) involves compaction and sintering of metal powder to produce components. High sinter density is desired in PM components as the requirement for performance is increasing day-by-day. One of the promising ways to achieve improved densification during sintering is through the addition of nano-powder to the conventional micrometer sized metal powder. It is well known that the surface chemistry of the powder has a decisive effect on sintering and consequently the properties of the components produced. Extensive research has hence been conducted to elucidate the surface chemistry and its influence on sintering for powder used in conventional PM. Nano-powder, owing to high surface to volume ratio can contribute to the activation of sintering at lower temperatures and enhance the sinter density. In this context, the surface chemistry of the nano-powder is also expected to exhibit substantial influence on the sintering. The present investigation is aimed at studying the surface chemistry of iron nano-powders of three different size fractions: 35-45, 40-60 and 60-80 nm and low alloyed steel nano-powder in the size range of 20-90 nm, intended to be mixed with the traditional iron powder as sintering enhancing agents. X-ray photoelectron spectroscopy (XPS) and high-resolution scanning electron microscopy (HR SEM) equipped with energy dispersive X-ray spectroscopy (EDX) were used for this purpose. Results showed that the surfaces of both types of nano-powder were covered by thin Fe-Cr-Mn oxide enriched in Mn and Si. The absence of Fe-metal peak in the XPS spectra obtained from the original surface indicated that the oxide film was at least 3-4 nm. The results obtained from thermogravimetry (TG) analysis to investigate the sintering of nano-powder showed good correlation with their surface chemistry as obtained from XPS.

Thanks/Acknowledgement

The authors would like to thank Höganäs AB for their scientific cooperation. Swedish Foundation for Strategic Research is gratefully aprreciated for funding this research.

NAMA1.1-2O256

EXTRACTING INFORMATION ON THE STRUCTURE OF CORE-SHELL NANOPARTICLES FROM THE INELASTIC BACKGROUND IN XPS SPECTRA

H. Kalbe [1], M. Hronek [1], C.J. Powell [2], W.S.M. Werner [1]
[1]*Vienna University of Technology - Vienna* (Austria), [2]*National Institute of Standards and Technology - Gaithersburg* (United States of America)

Several methods are established for the estimation of shell thicknesses of core-shell nanoparticles from XPS peak intensities [1,2,3]. However, these methods completely discard the information that can be extracted from the shape of the inelastic background. A set of novel evaluation methods is presented and discussed that extend the capabilities of quantitative XPS for the investigation of CSNP samples.

It has already been established that the inelastic background signals can be utilised to estimate planar layer thicknesses [4]. Here, an accurate method is presented to retrieve the shell thickness as well as the core radius of CSNP from fitting simulated XPS spectra to experimental data by modelling the inelastic background with shell thickness and core radius as fit parameters. With the existing methods, accessible shell thicknesses are limited by the information depth of XPS experiments of typically 5-10 nm, but since the peak intensities of core signals are far surpassed by the background signal intensity for large shell thicknesses the background shape analysis shows promise to considerably extend the accessible shell thicknesses past the previous limit. Furthermore, the simultaneous calculation of the core radius was previously only possible for extremely small particles, less than 1 nm [2], which can possibly be extended to the calculation of core radii up to 10-20 nm.

In the presented method, the XPS spectra are calculated in Monte-Carlo simulations of the photoelectron trajectories [1]. To do this accurately, one has to account for the fact that the inelastic mean free path (IMFP) of the electrons changes over the wide range of energy losses that has to be simulated. The corresponding mathematical approach will be discussed.

Another extension to the existing XPS quantification models for CSNP that will be presented is the simulation of dispersed powders instead of single particles. Furthermore, the inclusion of eccentric cores and distributed shell thicknesses and core radii and their influence on the XPS spectrum will be discussed.

Thanks/Acknowledgement

The funding from the 14IND12 Innanopart project by the EU through the EMPIR initiative is gratefully acknowledged.

References

[1] W.S.M. Werner et al., Nist Database for the Simulation of Electron Spectra for Surface Analysis, SRD 100, Version 2.0, National Institute for Standards and Technology (NIST), Gaithersburg, MD, USA, 2014

[2] H. Kalbe et al., J. Electron Spectrosc. Relat. Phenom. 212, 2016, 34-43

[3] A. Shard, J. Phys. Chem. C, 116(31), 2012, 16806-16813

[4] S. Tougaard, J. Vac. Sci. Technol. A 14, 1996, 1415-1423

NAMA2.2-4O270

TUNING THE TWO DIMENSIONAL STRUCTURE OF NANOSCALED BITS AT FLUID INTERFACES

O. Konovalov [1], **G. Li Destri** [1], **D. Pontoni** [1], **J. Geuchies** [2]

[1]*European Synchrotron Radiation Facility - Grenoble (France),* [2]*Utrecht University – Debye Institute for Nanomaterials Science - Utrecht (Netherlands)*

The recently upgraded ID10 beamline at the ESRF has obtained significant improvement in the instrumentation for surface studies on bare and buried soft surfaces and interfaces. In the presentation the instrumental capabilities will be demonstrated with structural studies of two dimensional self assembly of several types of nano objects.

Bottom up self-assembly of functional materials at liquid surfaces and interfaces has recently emerged as method to design and produce novel 2D nanostructured membranes and devices with tailored properties. The optimization of the nanostructure and the follow-up of the assembly require nanometrically-resolved structural characterizations techniques. We apply grazing incidence x-ray scattering and X-ray reflectivity to investigate in-sity and in-real time the growth and structure of nano-particles films at oil-water and ethylene glycol interface. Example of the silica inter-particle distance tuning with the surfactants and ions concentration will be presented as well as an in situ study of the formation mechanism of two-dimensional superlattices from PbSe nanocrystals [1].

References

[1] Geuchies J.J., et al., Nature Materials 15, 1248-1254(2016)

NAMA2.1-1O282

XPS STUDY OF MIXED-PHASE 1T-2H FEW-LAYER MOS2 OBTAINED BY ONE-POT HYDROTHERMAL SYNTHESIS

M. Fontana [1], P. Rivolo [1], M. Castellino [2], M. Serrapede [1], A. Gigot [1], E. Tresso [1], C.F. Pirri [1]
[1]Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT), Corso Duca Degli Abruzzi, 24 - Torino (Italy), [2]Istituto Italiano di Tecnologia, CSFT@PoliTO, C.so Trento 21 10129 - Torino (Italy)

Molybdenum disulfide (MoS2) is a layered transition-metal dichalcogenide (TMD) with significant potential for energy conversion and storage (ECS) applications [1], due to its interesting physical-chemical properties coupled with the possibility of obtaining 2D nanostructures. MoS2 exists in three different polytypes (stable 2H, meta-stable 1T and 3R). Recently, incorporation of the metallic 1T phase into the stable semiconducting 2H matrix has attracted great interest due to the increased performance of the hybrid MoS2 as hydrogen evolution reaction (HER) electrocatalyst [2] and supercapacitor electrode material [3]. Due to the possibility to provide surface-sensitive chemical information, X-ray Photoelectron Spectroscopy has been used for the identification of mixed phase few-layer 1T-2H MoS2 and for the quantification of relative amount of 1T and 2H phase [4]. In this work, we report a XPS study of few-layer 1T-2H MoS2 nano-flakes obtained with a simple hydrothermal synthesis using phosphomolybdic acid and L-cysteine as precursors. Detailed analysis of the polytype-sensitive features of the photoelectron spectrum is presented, alongside comparison with commercial 2H MoS2 powder (Fig. a). Complete characterization of the morphology and structure of the material is achieved through Raman spectroscopy, X-Ray Diffraction, Field-Emission Scanning Electron Microscopy and Transmission Electron Microscopy (Fig. b). Finally, the electrochemical properties of the few-layer 1T-2H MoS2 nano-flakes are investigated in the three-electrode configuration, in view of their application as supercapacitor active material.

References

[1] G. Zhang, H. Liu, J. Qu, J. Li, Energy Environ. Sci. 9 (2016) 1190–1209.

[2] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla, Nano Lett. 13 (2013) 6222–7.

[3] M. Acerce, D. Voiry, M. Chhowalla, Nat. Nanotechnol. 10 (2015) 313–318.

[4] A. Gigot, M. Fontana, M. Serrapede, M. Castellino, S. Bianco, M. Armandi, B. Bonelli, C.F. Pirri, E. Tresso, P. Rivolo, ACS Appl. Mater. Interfaces. (2016), 8 (48), 32842-32852

NAMA2.2-2O283

EFFECT OF SILANE COUPLING AGENTS ON THE ADHESION STRENGTH OF PRINTED CU CIRCUIT ON POLYIMIDE

C-J. Lee [1], J.J. Moon [1], K.H. Jung [1], B.G. Park [2], S.B. Jung [1]

[1]School of Advanced Materials Science & Engineering, Sungkyunkwan University - Suwon (Korea, republic of), [2]SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University - Suwon (Korea, republic of)

Printed electronics is now attracting attention in flexible electronics applications such as flexible displays, printed circuit boards and radio frequency identification (RFID) tags. However, it is difficult to maintain high adhesion strength between printed metal circuit and polymer substrate because of the weak chemical bonding of metal and organic materials. Therefore, the additional process is necessary for improve adhesion strength between polymer substrate and metal circuit. One of the solutions can be proposed is the silane coupling agent. The Silane coupling agents are silicon-based chemicals containing two types of reactivity that can form bond with metals and organic materials.

We coated with silane coupling agents with various functional groups such as epoxy, amine and mercapto on polyimide substrates to compare the effects of silane coupling agents on the adhesion strength between the screen-printed Cu circuit and PI substrate. The Cu nanopaste was printed on on a coated PI substrates using a screen printer and sintered in air and reduced in H2. The chemical bonding between the coated silane coupling agent and the PI substrate interface was investigated by X-ray photoelectron spectroscopy (XPS). The adhesion strength of the screen-printed Cu circuit and Polyimide substrate interface was measured by a roll-type 90° peel test. The flexibility of the screen-printed Cu circuit was evaluated by sliding test. The failure mode was analyzed with a field emission scanning electron microscopy (FE-SEM). As a result, the adhesion strength between printed Cu pattern and polyimide increased with silane coupling agents. The silane coupling agent containing amine functional group significantly improved the adhesion strength, because it has superior bond between organic substrates and metals by chemical reactions such as copolymerization and graft copolymerization.

Thanks/Acknowledgement

This work was supported by “Human Resources Program in Energy Technology” of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 20154030200870)

References

1. K.H. Jung, K.S. Kim, B.G Park, and S.B. Jung, J. Nanosci. Nanotechnol.14, 9493 (2014)
2. N. Inagaki, and S. Tasaka & T. Baba, Journal of Adhesion Science and Technology, 15:7, 749-762 (2001)
3. J. Jang, and T. Earmme, Polymer, 42, 2871-2876 (2001)

NAMA2.3-2O303

SURFACE FUNCTIONALISATION AND SOLVENTS PHASE TRANSFER OF REDUCED GRAPHENE OXIDE

S. Pérez García [1], U. Méndez Romero [1], E. Wang [2], L. Licea Jiménez [1]
[1]*Centro de Investigación en Materiales Avanzados, S.C. Unidad Monterrey - Monterrey* (Mexico),
[2]*Chalmers University of Technology - Gothenburg* (Sweden)

Since its synthesis in 2004, graphene was considered to improve almost all fields in technology due its ground-breaking properties.[1] However, most applications in electronics or organic photovoltaics, is related to transparent electrodes.[2] Because graphene is a zero-band gap material, i.e., its molecular orbitals have a characteristic cone shape, is crucial to make some chemical modifications to use it as semiconductor material.[3] For instance, the oxidation process by Hummers method, generates graphene oxide (GO) forming a band gap (Eg) and therefore HOMO-LUMO levels, which is expected from organic semiconductors, unfortunately, is quite high. However, its Eg is related to the C/O ratio, which means, that by chemical reduction can be lowered.[4] Also, because it's a hydrophilic molecule, is necessary to make a surface functionalisation to make it soluble in common organic solvents, for cenrtain applications i.e. for printed electronics.[5] Herein, we report the synthesis of reduced graphene oxide (rGO) functionalised by phase transfer and then chemically reduced in situ by an eco-friendly reductant agent. Analises of Eg, C/O ratio and HOMO- LUMO levels were analysed by UV-Vis-NIR spectroscopy, XPS and CV respectively. Also surface analysis of the surface modification and functionalisation were carried out by means of XPS.

Thanks/Acknowledgement

The authors are grateful for the financial support from CONACYT México and Red de Nanociencias y Nanotecnología.

References

1. Novoselov, K.S., et al., Electric Field Effect in Atomically Thin Carbon Films. Science, 2004. 306(5696): p. 666-669.
2. Garg, R., et al., Deposition Methods of Graphene as Electrode Material for Organic Solar Cells. Advanced Energy Materials, 2016.
3. Güttinger, J., et al., Transport through graphene quantum dots. Reports on Progress in Physics, 2012. 75(12): p. 126502.
4. Velasco-Soto, M.A., et al., Selective band gap manipulation of graphene oxide by its reduction with mild reagents. Carbon, 2015. 93: p. 967-973.
5. Bai, S., et al., Reversible phase transfer of graphene oxide and its use in the synthesis of graphene-based hybrid materials. Carbon, 2011. 49(13): p. 4563-4570.

NAMA3-3O305

MODIFICATION OF METAL OXIDE NANOPARTICLES AND THEIR APPLICATION ON GLASS SURFACE FOR FUNCTIONAL COATIGS

L. Licea Jiménez, A.R. Vázquez Velázquez, M.A. Velasco Soto, S.A. Pérez García
Centro de Investigación en Materiales Avanzados S.C., Unidad Monterrey - Monterrey (Mexico)

The modification of nanoparticles materials has taken importance recently, mainly in the modification of the material surface, because when modified the surface get different characteristics in comparison to the initial material. Changes are possible through functionalization, this process bring new features and properties to a material by changing the surface chemistry of the material, generating a novel material [1-3]. In the present work, we describe the functionalization of metallic oxides nanoparticles as TiO2 and SiO2 with a coupling agent. After the functionalization, the nanoparticles were dispersed in a medium of ethanol and acrylic acid, which acted as polymer matrix. Later, coatings were deposited onto glass substrates by aerospray technique. The materials were characterized by XPS, water contact angle, SEM and UV-VIS. The results shown the effect of the functionalization on the nanocomposite We found that coatings are superhydrophilic, transparent and potentially useful for self-cleaning coatings.

Thanks/Acknowledgement

Authors are grateful to CONACYT-SENER, Fondo Sectorial de Sustentabilidad Energética (CEMIESOL P21).

References

1. Catalina, C., et al., Nanocomposite acrylic paint with self cleaning action. J. Coat. Technol. Res., 2012. 9: p. 687-693.
2. J.Basu, B., et al., Effect of microstructure and surface roughness on the wettability of superhydrophobic sol-gel nanocomposite coatings. J. Sol-Gel Sci Technol, 2010. 56: p. 278-286.
3. Taurino, R., et al., Preparation of scratch resistant superhydrophobic hybrid coatings by sol-gel process. Progress in Organic Coatings, 2014. 77: p. 1635-1641.

NAMA2.1-2O338

CORE-SHELL AU@PRUSSIAN BLUE ANALOGUE NANO-HETEROSTRUCTURES: TOWARDS MULTIFUNCTIONALITY AT THE NANOSCALE

J. Long, G. Maurin-Pasturel, Y. Guari, J. Larionova
Institut Charles Gerhadt Montpellier - Montpellier (France)

omparatively to metal/metal oxides nanoparticles, the synthesis and study of Prussian Blue Analogues (PBA) nanoparticles is a recent field of study in coordination chemistry. These systems are the ideal candidates to study the evolution of magnetism upon size reduction. On the other hand, gold nanoparticules present remarkable properties arising from the surface Plasmon resonance phenomena. Combining the properties of both systems paves the way towards multifunctional systems. We present here a new synthetic strategy to design core-shell Au@PBA nanoheterostructures based on a coordination chemistry approach. The obtained core-shell nanoparticles show optical properties resulting from the surface Plasmon band and magnetic properties relative to the PBA shell. Additionally, these nanoparticles can be used to either i) remove the gold core to obtain hollow PBA nanoparticles or ii) subsequently grow a second PBA shell of different composition with tunable thickness in order to modulate the magnetic properties. We show here that the peculiar architecture of these nanoparticles modify greatly influence the magnetic behavior, leading to a spin-glass behavior for small magnetic shell thickness.

Thanks/Acknowledgement

The authors thank the Université de Montpellier and CNRS for financial support.

References

- G. Maurin-Pasturel, J. Long, Y. Guari, F. Godiard, M.-G. Willinger, C. Guérin, J. Larionova, Angew. Chem. Int. Ed. 2014, 53, 3872.
- J. Larionova, G. Maurin-Pasturel, J. Long, M. A. Palacios, C. Guérin, C. Charnay, M.-G. Willinger, A. A. Trifonov and Y. Guari, Chem. Eur. J., 2017, DOI: 10.1002/chem.201605903

NAMA2.4-4O347

COMPARISON OF SURFACE ANALYTICAL TECHNIQUES ON ATOMIC LAYER DEPOSITION SAMPLES

K. Lamann [1], L. Veith [2], D. Breitenstein [2], R. Ter Veen [2], B. Bock [2], M. Fartmann [2], B. Hagenhoff [2]

[1]Münster University - Münster (Germany), [2]Tascon GmbH - Münster (Germany)

The analytical techniques Low Energy Ion Scattering (LEIS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-Ray Photoelectron Spectroscopy (XPS) differ in information depth and quantification options. Aim of this study was to compare these quality criteria with respect to the analysis of samples generated by Atomic Layer Deposition (ALD).

For this purpose, a series of ALD layers providing different degrees of coverage and/or layer thickness of the coated material were analysed by different modes of the respective techniques. In the LEIS analysis, the excitation was performed with $^{4}He^{+}$ as well as $^{20}Ne^{+}$ primary ions. In ToF-SIMS, primary ion species as well as energies were varied, whereas in XPS analyses under 45° as well as under 10° were performed.

The application of these different techniques enables a cross-validation of the results. Moreover, options and limitations of the individual techniques are compared.

NAMA2.2-3O366

REAL-SPACE VISUALIZATION OF THE PAIR CORRELATION FUNCTION IN A 2D MOLECULAR GAS

P. Matvija, F. Rozboril, I. Ostadal, P. Sobotik, P. Kocan
Charles University, Faculty of Mathematics and Physics - Prague (Czech republic)

We use the STM to study adsorption of fluorinated copper phthalocyanine ($F_{16}CuPc$) molecules on the metal-passivated Si(111) surface. At room temperature, the $F_{16}CuPc$ forms a 2D surface gas of mobile and quickly diffusing molecules. Although diffusion of individual isolated molecules on the defect-free surface is random, molecules in the 2D gas correlate their motion to positions of the closest neighbors. The correlation is usually described by the pair correlation function.

Here, we utilize the STM to directly visualize the distribution of the molecules on the surface (see the figure below). We show that in the proximity of fixed molecules the STM images correspond directly to the pair correlation function of the 2D gas. We support the data interpretation by lattice-gas kinetic Monte Carlo simulations and we use the method to analyze interactions between the molecules and surface defects.

Thanks/Acknowledgement

This work was supported by Czech Science Foundation (contract no. 16-15802S) and by the Charles University in Prague (project GAUK No. 326515).

NAMA3-4O388

STUDY OF THE MECHANISM OF THE FUNCTIONALIZATION OF THE C/CU NANOSTRUCTURE SURFACE WITH SP-ELEMENTS

G. Sapozhnikov [1], I. Shabanova [2], N. Terebova [2]

[1]1Udmurt State University - Izhevsk (Russian federation), *[2]2Physicotechnical Institute of the Ural Branch of the Russian Academy of Sciences - Izhevsk* (Russian federation)

In the present work, the X-ray photoelectron spectroscopy method is used for studying the change of the atomic magnetic moment of copper in C/Cu nanostructures functionalized with sp-lements (P, N). The procedure has been developed for determining of the copper atomic magnetic moment in C/Cu nanostructures by the parameters of the multiplet splitting of the Cu3s X-ray photoelectron spectra correlating with the number of uncompensated d-electrons, atomic magnetic moment and variation in the chemical bond and the nearest surrounding of the atoms of d-metals.

The above-mentioned procedure is used for determining the copper atomic magnetic moment in the C/Cu nanostructures with grafted atoms of phosphorus, and for studying the mechanism of the nanostructure surface functionalization and the influence of the functional groups on the change of the atomic magnetic moment due to the participation of the d-electrons of copper atoms in the hybridized chemical bond with sp-electrons of phosphorus atoms.

It is shown that in the functionalized ammonium polyphosphate C/Cu nanostructures, the copper atomic magnetic moment increases in 1.5 times in comparison with that in the non-functionalized C/Cu nanostructures. Consequently, the nearest surrounding of copper atoms and their chemical bond are changed. With an increase in the content of the functional groups in the C/Cu nanostructures, the atomic magnetic moment of copper increases insignificantly, i.e. additional phosphorus atoms do not form bonds with copper atoms, and phosphorus is in the oxidized state. Phosphorus atoms form bonds only with copper atoms in C/Cu nanostructures. This is indicated by the variation of the number of uncompensated 3d-electrons of copper due to the change in the nearest surrounding of copper atoms, since the degree of the covalence of the Cu-P bond is higher than that of Cu-C. For better understanding of the functionalization mechanism, ammonium polyphosphate has been replaced by phosphoric acid which is more active in the functionalization processes, and as a result, a twofold increase in the copper atomic magnetic moment in the functionalized C/Cu nanostructures has been observed.

Thanks/Acknowledgement

The work is supported by the fundamental research program of the Ural Branch of the Russian Academy of Sciences of the years 2015-2017, project № 15-9-2-50

NAMA2.1-3O404

NETWORKS OF NOBLE METAL NANOPARTICLES STABILISED BY ROD-LIKE Π-CONJUGATED DITHIOLS: A STRUCTURAL AND MORPHOLOGICAL INVESTIGATION CARRIED OUT BY SYNCHROTRON RADIATION INDUCED XPS AND TEM.

C. Battocchio [1], C. Laura [1], N. Chiara [1], F. Laura [2], F. Ilaria [2], I. Giovanna [1]
[1]University Roma Tre, Dept. of Science, Via della Vasca Navale 79, 00146 - Rome (Italy), [2]University Sapienza, Dept. of Chemistry, P.le A. Moro 5, 00185 - Rome (Italy)

Rod-like bifunctional organometallic thiols containing square-planar Pt(II) centres, i.e. trans,trans-[(HS)Pt$(PBu_3)_2$(C≡C-C_6H_4-C_6H_4-C≡C)$(PBu_3)_2$Pt(SH)] (PtDEBP-$(SH)_2$), have been used as stabilizing and interconnecting ligands for palladium, gold and silver nanoparticles (NPs). The here proposed nanostructured systems, namely AuNPs, AgNPs and PtNPs have been characterized by means of transmission electron microscopy (TEM), Infra Red Spectroscopy in total reflection mode (IRRAS) and synchrotron radiation induced X-ray photoelectron spectroscopy (SR-XPS), with the aim to probe the morphology and the molecular and electronic structure of the nanomaterials. The formation of a direct linkage between Pt(II) and the atoms at NP surface through a single S bridge was observed for all systems [1]. All noble metal NPs show diameters of about 5 nm, which can be controlled by carefully modulating the synthesis parameters [2]. For all three metals, the nanoparticles inter-linkage, leading to a network of regularly spaced NPs, can be envisaged with the formation of dyads, as supported by SR-XPS data and by TEM imaging analysis [3]. Furthermore, the comparison between SR-XPS data collected on metal NPs and Self Assembling Monolayers and multilayers of the pristine rod-like dithiols deposited onto "flat" polycrystalline gold surfaces (Au/Si(111) wafers) lead to ascertain that an electronic interaction occurs between the Pt(II) centres and the biphenyl moieties of adjacent ligands.

The here demonstrated ability to obtain networks of regularly spaced noble metal nanoparticles opens outstanding perspectives in the field of optoelectronics.

References

1. C. Battocchio, I. Fratoddi, L. Fontana, E. Bodo, F. Porcaro, C. Meneghini, E. Magnano, S. Nappini, S. Mobilio, M.V. Russo, G. Polzonetti, Physical Chemistry Chemical Physics 16, 2014, 11719-11728;
2. C. Battocchio, C. Meneghini, I. Fratoddi, I. Venditti, M. V. Russo, G. Aquilanti, C. Maurizio, F. Bondino, R. Matassa, M. Rossi, S. Mobilio, G. Polzonetti, The Journal of Physical Chemistry C, 2012, 116 (36), 19571–19578;
3. R. Matassa, I. Fratoddi, M. Rossi, C. Battocchio, R. Caminiti, M. V. Russo, The Journal of Physical Chemistry C, 2012, 116 (29), 15795–15800.

NAMA2.2-1O424

PULSED LASER DEPOSITION OF SRTIO3 TEMPLATES ON SI (100): COVERAGE, ANNEALING AND BUFFER LAYER THICKNESS EFFECTS

D. Diaz-Fernandez [1], M. Spreitzer [1], T. Parkelj [1], J. Kovac [2], D. Suvorov [1]
[1]Advanced Materials department, Jožef Stefan Institute - Ljubljana (Slovenia), [2]Department of Surface Engineering and Optoelectronics, Jožef Stefan Institute - Ljubljana (Slovenia)

SrTiO3 (STO) is the most successfully epitaxially grown complex oxide on silicon, which makes it a perfect candidate for the creation of templates for the integration of other complex oxides on silicon. The Pulsed Laser Deposition (PLD) technique offers considerable advantages compared to Molecular Beam Epitaxy, but the lack of research on the growth of ultra-thin layers of this family of materials by this technique in comparison to MBE cast doubts about the impact of the growth parameters on the sample properties and quality. In this work, we will present our latest results on the characterization and optimization of the growth of epitaxial ultra-thin (10 ML, 3-4 nm) STO layers on Si (001) by Pulsed Laser Deposition (PLD) using in-situ RHEED, AFM, XPS and XRD. A 1/2 monolayer (ML) of Sr buffer layer is firstly grown on the clean Si (001) surface by PLD, and the growth of STO is carried out in separate deposition, oxidation and crystallization stages, with other parameters having previously optimized in previous efforts[1,2]. The effect of the thickness before each stage, crystallization temperature and Sr buffer layer thickness has been tested. We have found that a combination of a ½ ML Sr buffer layer, STO deposition and oxidation in batches of 2 ML, and a crystallization at 515 °C during 15 min, offers the best balance between crystallographic properties, stoichiometry, and STO density. These results are explained in terms of thermal budget minimization, STO coverage of the buffer layer, and smoothness of the buffer layer. The usefulness of these ultra-thin layers as templates has also been tested with the overgrowth of 30-50 nm STO layers: the impact of the template quality on their crystallographic properties will also be examined. [MS1] These results improve the general knowledge about this growth and interface, and serve as an example of the usefulness of PLD for the integration of complex oxides on silicon

References

[1] D. Klement, PhD thesis, Mednarona Podiplomska Šola Jožefa Stefana, 2015

[2] D. Klement, M. Spreitzer and D. Suvorov, Applied Physics Letters, 2015, 106, 071602.

NRG - Energy production and storage

NRG1-3O043

COMBINING SURFACE ANALYSIS METHODS TOWARDS A BETTER UNDERSTANDING OF DEGRADATION MECHANISMS IN LI-ION NEGATIVE ELECTRODES

E. De Vito [1], B. Pilipili Matadi [2], S. Genies [1], A. Delaille [2], Y. Bultel [3]
[1]CEA Tech - Grenoble (France), [2]CEA Tech - Chambéry (France), [3]INPG - Grenoble (France)

Li-ion technology is among the most commercially reliable solutions for electrochemical storage, particularly for the electric vehicle (VE) market. The fading of such systems is often related to electrode degradation in various ageing or cycling conditions; it is thus mandatory to better understand the causes for such failures. It is well known that the nature and amount of the solid electrolyte interphase (SEI), which forms at the surface of the active material during cycling, can be one of the main issues preventing durability of the cells. For that purpose, our lab is actively working on the characterization of these degradation mechanisms, trying to understand some fundamental aspects of lithiation or lithiation loss mechanisms, nature and dynamics of the SEI etc.

Recent works allowed us to figure out the degradation of silicon electrodes in various configurations by using XPS, AES, ToF-SIMS or FIB cross analysis [1-3]. This has also recently been applied to the study of commercial graphite electrodes. The first example reports high temperature (60°C) calendar ageing of cells composed of graphite negative electrodes and nickel-manganese-cobalt (NMC) positive electrodes. The presence of metallic lithium was evidenced by NMR analyses on the negative electrode; however the combination of FIB-SIMS and AES brought another clear confirmation of lithium plating and allowed to describe even more precisely the nature and morphology of the lithium-rich deposits. In the second example, commercial cells have been cycled at 5°C by following 2 end-of-voltage windows strategies: 2.70 V-4.20 V (0% SOC-100% SOC) and 3.42V-4.08V (10% SOC-90% SOC). It was observed that the former is fading a lot faster than the latter (cycled in the limited 3.42-4.08 V potential range). A complete characterization study, also involving XRD and NMR, showed that the generation of SEI is much more important between 90 and 100% SOC and may induce lithium trapping inside the graphite particles. These results show the high impact of storage and cycling policy on the integrity of these Li-ion cells.

Thanks/Acknowledgement

The research leading to these results was performed within the MAT4BAT project (http://mat4bat.eu/) and received funding from the European Community's Seventh Framework Program (FP7/2007-2013) under grant agreement n°608931.

References

[1] E. Radvanyi *et al*, **Phys. Chem. Chem. Phys.**, 2014,16, pp 17142-17153

[2] A. Bordes *et al*, **Chem. Mater.**, 2016, 28 (5), pp 1566–1573

[3] N. Dupré *et al*, **Chem. Mater.**, 2016, 28 (8), pp 2557–2572

NRG1-1O049

SURFACE ANALYTICAL APPROACHES TO CHARACTERIZE HIGH VOLTAGE CATHODE MATERIALS FOR LI-ION BATTERIES

R. Azmi [1], C. Draeger [1], S. Indris [1], H. Ehrenberg [1], M. Bruns [2]

[1]Karlsruhe Institute of Technology, IAM-ESS - Eggenstein-Leopoldshafen (Germany), *[2]Karlsruhe Institute of Technology, KNMF - Eggenstein-Leopoldshafen* (Germany)

Recent environmental concerns have motivated the extensive amount of research on the improvement of lithium-ion batteries (LIBs), since due to their relatively high energy density, LIBs are still the major candidates for the application in electric vehicles. In the frame of developing novel electrode materials or to improve today's state-of-the-art electrodes, surface analytical methods are indispensable to characterize the respective surfaces and interfaces. In particular, combined X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can provide quantitative information on chemical binding states in a non-destructive manner (XPS) together with molecular information at high sensitivity and high spatial resolution (ToF-SIMS).

In consequence, XPS routinely is used for chemical state elucidation in battery's research and development activities. However, in the case of the first row transition metals, which are commonly used in LIBs, the XPS analytical potential is not widely utilized in its entirety. This is mainly due to the complex multiplet-splitting and the additional shake-up features in the respective 2p XP spectra, although fundamental studies are available mainly by the work of Biesinger et al. [1] using pure reference materials.

Simplified peak fitting, however, causes difficulties in data interpretation, which often leads to a controversy about the oxidation states of the battery's cations. In the present study, therefore, XPS characterization of powder electrode surfaces of newly improved promising active materials like $LiCoMnO_4$ and doped $LiNi_{0.5}Mn_{1.5}O_4$ was performed considering the complex multiplet-splitting. As reference systems we used r.f. magnetron sputtered Li-Ni-Co-Mn-O thin films to evaluate the data processing procedure separated from topography effects and e.g. the electrode's binder and conductive carbon contribution. The resulting peak templates were then applied to the real electrodes based on the new powder materials in the pristine as well as in different battery cell cycling states.

Additionally, high spatial resolution ToF-SIMS images of the powder electrodes provide detailed information about the elemental distribution. The homogeneous dopant distribution throughout the particles was checked by ToF-SIMS sputter depth profiling.

Thanks/Acknowledgement

Financial support from the Federal Ministry of Education and Research (BMBF) within the DESIREE project, grant no. 03SF0477B, is acknowledged.

This work was partially carried out with the support of the Karlsruhe Nano Micro Facility (KNMF), a Helmholtz research infrastructure at Karlsruhe Institute of Technology.

References

[1] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, Appl. Surf. Sci., 257 (2001) 2717–2730.

NRG3-2O082

CRYSTALLOGRAPHIC STUDY OF PHOTOCATALYTIC BANBO2N CRYSTALLINE PARTICLES PREPARED BY FLUX METHOD

T. Yamada [1], Y. Murata [2], S. Suzuki [3], K. Teshima [4]

[1]Center for Energy and Environmental Science, Shinshu University - Nagano (Japan), [2]Graduate School of Science and Technology, Shinshu University - Nagano (Japan), [3]Faculty of Engineering, Shinshu University - Nagano (Japan), [4]Center for Energy and Environmental Science & Faculty of Engineering, Shinshu University - Nagano (Japan)

Photocatalytic water splitting from solar energy is one of desirable H_2 production procedures because of its environmental friendly, ubiquitous, and exhaustless characteristics. For effective use of sun light, it is necessary to utilize visible light, since the solar provides over 50 % of visible light, but only 5 % of UV light in its whole energy. Oxynitrides are known as one of promising candidates of visible-light responsive photocatalyst available to split water. Barium niobium oxynitride, $BaNbO_2N$ belongs to cubic-type perovskite. Exhibiting the highest visible-light absorbance ability in oxynitrides up to *ca*. 740 nm, it is expected that $BaNbO_2N$ exhibits good solar-energy conversion property. So far, a few studies about photocatalytic properties of $BaNbO_2N$ have been reported but the performance of $BaNbO_2N$ as photocatalyts is still poor. For improvement of photocatalytic performance of $BaNbO_2N$, the contributions of primary factors to the performance should be separately evaluated. In this study, we demonstrated the preparation of various $BnNbO_2N$ to evaluate the crystallographic characteristics of them to discuss with their photocatalytic performances.

For growths of $BaNbO_2N$, we adopted 2-step process. Firstly, different sizes of $Ba_5Nb_4O_{15}$ crystals were grown in molten $BaCl_2$ flux with a solute concentration of 5 mol% at 600 to 1000 ºC for 10 h. In all temperature conditions, single phases of $Ba_5Nb_4O_{15}$ were obtained from X-ray diffraction (XRD) analyses. From scanning electric microscopic (SEM) observations, the average particle sizes of them increases from 0.3 to 1.2 µm, as holding temperature increased. At the second step, they were heated in NH_3 atmosphere at 950 ºC for 10 h. Each crystal was identified to single-phase $BaNbO_2N$. From their SEM images, segregations to porous secondary particles were found with keeping the initial shapes of the precursors. We denoted them as BNON-X (X = 600 - 900). X indicates the growth temperature of $Ba_5Nb_4O_{15}$ crystals. The photocatalytic properties of BNON-Xs were evaluated as oxygen gas evolution under Xe lamp irradiation (λ > 420 nm). The BNON-X exhibits gradual increase of oxygen evolution as X increased and reaches to *ca*. 7 times as large as that of X = 600. To clarify the origin of different photocatalytic activities, the crystallographic natures of BNON-Xs were investigated in terms of crystal phases, crystallinities, morphologies, and surface chemical conditions, which will be precisely introduced in the presentation.

Thanks/Acknowledgement

This work was supported by JSPS Grant-in-Aid for Scientific Research (A) 25249089.

NRG2-3O123

X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE CHEMICAL SURFACE REACTIVITY OF CU(IN,GA)SE2 ABSORBER DURING AIR AGEING: INFLUENCE OF THE INITIAL SURFACE STATE

A. Loubat [1], M. Bouttemy [2], S. Gaiaschi [3], M. Frégnaux [2], D. Aureau [2], J. Vigneron [2], P. Chapon [3], D. Lincot [4], J.F. Guillemoles [4], A. Etcheberry [2]
[1]*IPVF - Versailles* (France), [2]*CNRS-ILV - Versailles* (France), [3]*HORIBA - Longjumeau* (France), [4]*IRDEP - Chatou* (France)

Photovoltaic cells based on CIGS ($Cu(In,Ga)Se_2$) thin film absorbers are among the most efficient in photo-conversion. It is well known that the photovoltaic cells' performance mainly rely on the absorber properties, within the bulk but above all at the front and back interfaces. Nowadays, the interfaces optimization is a crucial issue to consider for ultimate efficiencies achievement. XPS analyses of as-deposited CIGS layers evidence specific signatures of the deposition process and further storage conditions. The surface composition strongly differs from the bulk one and requires being prepared prior to the following absorber deposition step. In this context, the present work examines chemical engineering capability to adjust the CIGS surface composition as well as to control the contamination and doping levels. Results obtained using HCl [1], KCN and mixed HCl-KCN treatments are presented. By crossing the high resolution XPS and X-ray induced Auger electrons data, we are able to affirm that we reach different level of remarkable oxide elimination depending on the chemical treatment used. In addition, for CIGS absorbers, the key parameters governing the bandgap and the front side band alignment, the GGI=Ga/[Ga+In], CGI=Cu/[Ga+In] and CIG/Se=[Cu+In+Ga]/Se ratio, are measured and their comparative evolution discussed.

Secondly, the evolution in time of the three treated surfaces is monitored. The reactivity of CIGS surface is an important parameter as it conditions the storage procedure and the acceptable delay for post processing in manufacturing procedure. Whatever the treatment, the XPS and X-AES spectra envelopes of the CIGS "air aged" surface highlight a slow phenomenon of re-oxidation involving In, Ga and Se elements while the Cu signal seems less-affected. However, a constant GGI value, concomitant with significant variations of CGI and CIG/Se ratio, is pointed out. As a consequence, the surface initial balance is mainly modified by Cu and Se elements contents. The question of the Se stability (oxidation, Se^0 formation) and of the atomic network arrangement explaining the superficial Cu loss will be discussed.

Thanks/Acknowledgement

This work was carried out in the framework of the project I of IPVF (Institut Photovoltaïque d'Ile-de-France). This project has been supported by the French Government in the frame of the program of investment for the future (Programme d'Investissement d'Avenir – ANR-IEED-002-01).

References

[1] A. Loubat & al., Thin solid film, Accepted-In Press, 2016.

[2] D. Regesch & al., Appl. Phys. Lett., 101 (11), 112108, 2012.

[3] D. Hauschild & al., J. Appl. Phys., 115 (18), 183707, 2014.

NRG2-4O150

INVESTIGATION OF WORK FUNCTION AND CHEMICAL COMPOSITION OF THIN FILMS OF BORIDES AND NITRIDES

A. Mezzi [1], P. Soltani [1], S. Kaciulis [1], A. Bellucci [2], M. Girolami [2], M. Mastellone [2], D.M. Trucchi [2]
[1]ISMN-CNR - Rome (Italy), [2]ISM-CNR - Rome (Italy)

In the last decades, an increasing interest of the scientific community has been addressed to the renewable energy field [1]. In particular, the solar radiation is considered as an abundant, cheap, clean and sustainable energy source. In this context, promising solid state devices for the conversion of primary energy into electricity like thermionic-photovoltaic (TIPV) converters have been developed. They consist of three elements: electron emitter, collector and photovoltaic (PV) cell [2]. The main characteristics of the emitter are the enhanced capability to emit electrons and the selective thermal emittance, which should be able to satisfy the specific requirements of the PV cell in terms of radiation absorption. Basically, an ideal cathode must be characterized by a low work function, but, for a thermionic energy converter, it has to be higher than that of the anode. In the present work, thin films of different borides and nitrides deposited by pulsed laser deposition (PLD) are proposed in order to improve the performance of TIPV devices. The emitting layers of lanthanum hexaboride (LaB_6) and cerium hexaboride (CeB_6) have been well established, therefore they are considered good candidates in terms of low work function and high melting point. As it regards nitrides, amorphous carbon nitride (CN_x) and hydrogenated aluminium nitride (AlN:H) have been individuated as valid alternatives to borides, because they are characterized by an even lower work function. The films of these materials with a thickness up to 200 nm have been grown on different substrates by PLD. Because the properties of borides and nitrides are strongly dependent on the content of boron or nitrogen, their chemical composition and work function were investigated by XPS and UPS techniques. These analyses were carried out by using an Escalab 250 Xi, equipped with a monochromatized Al Kα and ultra-violet He sources. The work function was determined from the cut-off in the He I spectra. Finally, the homogeneity of the chemical composition along the thickness of the samples has been investigated by XPS depth profiling carried out by means of Ar^+ ion sputtering.

Thanks/Acknowledgement

This work is supported by the AMADEUS project that has received funds from the European Union's Horizon2020 research and innovation programme under grant agreement 737054.

References

[1] Fatih Bayrak, Nidal Abu-Hamdeh, Khaled A. Alnefaie, Hakan F. Öztop, Renewable and Sustainable Energy Reviews, 74 (2017) 755.

[2] A. Datas, Appl. Phys. Letters, 108 (2016) 143503.

NRG2-5O194

PHOTOVOLTAIC PEROVSKITE SURFACE CHEMICAL ANALYSIS: THE CHALLENGE OF A QUANTITATIVE XPS APPROACH

A. Etcheberry [1], E. Pellereau [1], M. Frégnaux [1], B. Geffroy [2], D. Tondelier [2], C. Dindault [2], Y. Bonnassieux [2], M. Arthur [2]

[1]*ILV - UMR8180 - Versailles (France)*, [2]*PICM - UMR 7647 - Palaiseau (France)*

Hybrid organic-inorganic perovskite material $CH_3NH_3PbI_3$ (MAPI) used as a light harvester in photovoltaic cells has shown very interesting features in terms of efficiency and manufacturing costs, and could compete with other photovoltaic (PV) absorbers [1]. However an important difficulty concerns the instability problem of the absorber which must be understood and solved for large applications in PV devices. Nowadays, lot of groups work to address this issue. Using X-ray diffraction (XRD) and/or UV-Vis optical spectroscopy [2,3], it is possible to access the chemical evolution of the perovskite, generally associated with opto-electrical measurements (J-V and power conversion efficiency etc …) [4]. The characterization of the material evolution combining the chemical and physical aspect is therefore a very challenging purpose, which makes X-ray photoelectron spectroscopy (XPS) the most adapted method to complement other studies.

Our work focuses on the degradation process that should occured at the surface of a perovskite during the XPS. Analysis of MAPI with this technique is particularly interesting as it exhibits composition and chemical environment for each elements in the first 10 nm. However, the relative high photon energy as well as the ultra-high vacuum (UVH) inherent to XPS analysis raises the issue of how the analysis can affect the perovskite material (composition, chemical shift), and is the purpose of the presented work.

We therefore performed experiments sequences, exploring specific and narrow binding energy regions, which were designed to check the influence of X-ray and/or UVH. For this purpose, a spin-coated MAPI sample without capping was analyzed. Sequences of XPS measurement were imposed at different points of the samples, combining effect of X-ray permanent exposure, long time UHV exposition, etc. For each specific zone, evolution of the I/Pb and N/Pb ratio were followed.

The main results are, that no changes are observed under UHV within short time X-ray exposure, typically 30 minutes, while long time-exposure, about 5 hours, nitrogen and iodine slightly decrease. These results are important as they demonstrate that perovskite can be pertubated under X-ray exposure associated with XPS measurement. Fortunately, the time needed to record the XPS spectra is short compared to the perovskite degradation kinetics observed under combined UVH and X-ray exposure. This work then comforted the XPS analysis method as an efficient tool to evaluate the ageing mechanisms of PV perovskite.

Thanks/Acknowledgement

This work is supported by Charmmmat LabEx Paris Saclay

References

[1] 10.1039/C4TA04994B

[2] 10.1002/anie.201503153

[3] 10.1002/anie.201603694

[4] 10.1021/ja511132a

NRG1-5O227

GAS CLUSTER DEPTH PROFILING OF THIN-FILM LI ION BATTERIES

J. Counsell, S. Hutton, C. Blomfield
Kratos Analytical

In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed to also increase the energy storage density. There has been an explosion of interest in solid-state lithium ion batteries, which are a promising technology to replace conventional liquid electrolyte lithium ion cells because of their much greater intrinsic safety.1 As in all batteries, however, the chemistry and stability of the electrode-electrolyte interface is critical to the performance of the device. In solid state systems, reaction layers (from either chemical or electrochemical reaction of the battery components) have been observed2,3 by techniques such as TEM, but are not comprehensively chemically characterized.

Here we will apply XPS depth profiling techniques to probe the distribution of elements below the surface of LiPON thin-films prepared via ALD methods4. Depth profiling has been used extensively across a broad range of applications however damage caused by impinging ions on the structure of the analysis material has always been a concern for the analyst. More recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials. We extend the application of cluster ions beyond organics to inorganic materials. With the use of high energy $Ar_{250-3000}^{+}$ ions, it is possible to obtain accurate information regarding the true chemical nature of LIPON thin-films. A comparison is made with conventional monatomic Ar^{+} in particular the differences in stoichiometry obtained. Ion implantation and migration is also discussed as are the unfortunate chemical effects from organic sources.

References

(1) Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R.; Armand, M.; et al. High-Power All-Solid-State Batteries Using Sulfide Superionic Conductors. Nat. Energy 2016, 1, 16030.

(2) Santhanagopalan, D.; Qian, D.; McGilveray, T.; Wang, Z.; Wang, F.; Camino, F.; Greatz, J.; Dudney, N.; Meng, Y. Interface Limited Lithium Transport in Solid-State Batteries. J. Phys. Chem. Lett. 2013.

(3) Zhu, Y.; He, X.; Mo, Y. Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations. ACS Appl. Mater. Interfaces 2015, 7, 23685–23693.

(4) Kozen, A.; Pearse, A.; Lin, C-F.; Schroeder, M.; Noked, M.; Lee, S.; Rubloff, G. Atomic Layer Deposition and in Situ Characterization of Ultraclean Lithium Oxide and Lithium Hydroxide. J. Phys. Chem. C 2014, 27749–27753

NRG1-2O229

X-RAY PHOTOELECTRON SPECTROSCOPY TO HIGHLIGHT COMBINED CATIONIC AND ANIONIC REDOX PROCESSES DURING BATTERIES CYCLING

D. Foix [1], M. Sathiya [2], E. Mccalla [2], J.M. Tarascon [2], D. Gonbeau [1]
[1]IPREM/ECP (UMR5254), Université de Pau - Pau (France), [2]Chimie du Solide-Energie, FRE 3677, Collège de France - Paris (France)

Electrode materials based on Li-rich layered oxides are of growing interest for high-energy Li-ion batteries because of staggering capacities associated with a reversible anionic process.

The redox chemistry associated with the lithium insertion/deinsertion process of these Li-rich phases has been analyzed by our group using X-ray photoemission spectroscopy (XPS) on different model compounds $Li_2Ru_{1-x}M_xO_3$ (M=Mn, Ti, Sn) [1-3]. The results in association with different analysis techniques and supported by Density Functional Theory (DFT) calculations have revealed the existence of cumulative cationic and anionic reversible redox processes (Ru^{4+}/Ru^{5+} and O^{2-}/O_2^{n-}).The involvement of O^{2-} anion in the redox process was explained, as the result of M(d)−O(sp) hybridization associated with a reductive coupling mechanism. However, the extent to which cationic and anionic electronic transfers take place upon Li delithiation/relithiation has not been thoroughly explored, particularly in relation to the changes in the M−O interactions.

Here we report XPS studies (combining core peaks and valence intensity analyses) at different stages of charge/discharge on high-capacity Li-rich materials $Li_2Ru_{1-x}Sn_xO_3$ and $Li_2Ir_{1-x}Sn_xO_3$ [4]. We reveal that, depending on the nature of the metal (Ru or Ir), there is a delicate balance between metal and oxygen contributions. For instance, we show a greater implication of oxide ions for Ir based electrodes, consistent with the higher covalent character of Ir-O bonds compared to Ru−O bonds. Indeed, for Ru-based electrodes, the metal is the main site involved at the first plateau in charge, whereas oxidation of oxide ions is dominant on the high-voltage plateau. For Ir-based electrodes, a concomitant oxidation of iridium and oxide ions is already observed before the high-voltage plateau, consistent with an important mixing of Ir 5d and O 2p states and resulting in a more important contribution of peroxo-like species for Ir based materials. Overall, this work highlights that photoemission electron spectroscopy is a powerful tool for understanding cationic/anionic redox mechanisms in high-capacity electrode materials.

References

[1] Sathiya M., et al., Chem.Mater., 2013, 25, 1121−1131.
[2] Sathiya M., et al., Nature Mater., 2013, 12, 827-835.
[3] Sathiya M., et al., Nature Mater., 2015, 14, 230-238.
[4] Foix D., et al., J. Phys. Chem. C, 2016, 120, 862-874.

NRG3-4O238

IMPROVED ELECTROCHEMICAL PERFORMANCE OF AN ALL SOLID-STATE MICROBATTERY BY ELECTRODEPOSITION OF POLYMER ELECTROLYTE INTO THE

G. Salian [1], C. Lebouin [1], T. Djenizian [2]
[1]Aix-Marseille University - Marseille (France), [2]Ecole Nationale Supe´rieure des Mines de Saint-Etienne, Flexible Electronics Department, Centre Microelectronics Provence - Gardanne (France)

3D microbatteries have been considered to satisfy the requirements of portable devices such as medical implants, sensors or smart cards. All solid-state microbatteries involving self-supported titania nanotubes (TiO_2 nts) have been considered, due to their high surface area and short diffusion lengths for Li^+ ion transport [1]. It has been previously reported by our team that the electropolymerization of the polymer electrolyte through cyclic voltammetry (CV) leads to the conformal deposition of the electrolyte into the 3D TiO_2 nts, which influences positively the capacity of this material [2,3]

In this work, we study the influence of this conformal deposition and the filling of porosity of both electrodes as an interface layer on the electrochemical performances of a full microbattery. So far, a microbattery (Fig. 1a) based on TiO_2 nts as anode and $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) composite cathode, separated by a drop cast layer of polymer (PMMA-PEG+LiTFSI), was studied [4]. This microbattery delivers a reversible capacity of 155 $mAh.g^{-1}$ (73 $\mu Ah\ cm^{-2}\ \mu m^{-1}$) at 0.1C rate that is almost twice higher to the capacity without electropolymer layers (Fig. 1b). The electropolymerization on both the electrodes improves the electrode-electrolyte interface which leads to an enhancement of the performances of the whole microbattery. Characterizations of the layers and the influence on the electrochemical performances of currently studied full microbatteries based on different electrodes materials, in terms of chemistry and synthesis method, will be presented.

Fig.1 a) Cross section of the microbattery b) Comparison of the galvanostatic cycling at 0.1C rate of 3 microbatteries : without electropolymer, with electropolymer(EP) on TiO_2nts and with electropolymer(EP) on both TiO_2 nts and LNMO.

References

1) B.L. Ellis, P. Knauth, T. Djenizian, Adv. Mater. 26 (2014) 3368-3397.

2) N. Plylahan, N.A. Kyeremateng, M. Eyraud, F. Dumur, H. Martinez, L. Santinacci, P. Knauth, T. Djenizian, , Nanoscale Res. Lett. 7 (2012) 349-353.

3) N. Plylahan, M. Letiche, M.K.S. Barr, B. Ellis, S. Maria, T.N.T. Phan, E. Bloch, P. Knauth, T. Djenizian, , J. Power Sources 273 (2015) 1182-1188.

4) G.D.Salian, C.Lebouin, A.Demoulin, M.S. Lepihin, S. Maria, A.K. Galeyeva, A.P. Kurbatov, T.Djenizian, J. Power Sources 340 (2017) 242-246.

NRG1-4O269

NEW INSIGHTS IN THE CHARACTERIZATION OF ELECTRODE/ELECTROLYTE INTERFACES WITHIN LIMN2O4/LI4TI5O12 CELLS, BY X-RAY PHOTOELECTRON SPECTROSCOPY, SCANNING AUGER MICROSCOPY AND TIME-OF-FLIGHT SECONDARY IONS MASS SPECTROMETRY

N. Gauthier [1], J.B. Gieu [1], C. Courrèges [1], L. El Ouatani [2], C. Tessier [2], H. Martinez [1]
[1]IPREM, UMR 5254 CNRS/UPPA, Technopôle Hélioparc, 2 av. du Président Pierre Angot, 64000 Pau, France - Pau (France), [2]SAFT, 111-113 Boulevard Alfred Daney, 33000 Bordeaux, France - Bordeaux (France)

Lithium-ion batteries have revolutionized the portable electronic market due to their high electrochemical performances and they are now widely developed for transportation or stationary storage of renewable energies. Thus, various electrode materials are optimized related to the targeted application [1]. For electrical vehicles, cells composed of high-voltage spinel oxide LiMn2O4 (LMO) facing Li4Ti5O12 (LTO) are very promising due to their low cost, liability and high rate capabilities. However, their electrochemical performances can be limited by the formation of passivation layers (5-10nm) at the electrode/electrolyte interfaces [2]. This work aims to study the evolution of both LTO and LMO electrode/electrolyte interfaces and the interactions between the two electrodes during cycling by X-ray Photoelectron Spectroscopy (XPS), Scanning Auger Microscopy (SAM) and Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS). These three complementary surface analysis techniques provide a complete study of interfaces: XPS results quantitatively show that both electrodes are covered by surface layers of similar composition during the first charge. However, the layer formed on the LTO electrode is thicker than the one formed on the LMO electrode and contains small amounts of MnF2 compound, homogeneously spread over the surface, as revealed by SAM elemental mapping. Moreover, depth-profile ToF-SIMS analysis indicate that manganese compounds are located on top of the LTO surface layer (figure 1) [3]. Analysis after long cycling as well as cycling with electrodes separated by compartments are currently in progress to study the evolution of interfacial layers composition and thickness with cycling and to better understand the interactions between the two electrode materials.

Figure 1 : O 1s XPS spectra of LTO pristine electrode and LTO electrode cycled until the end of the first charge a), SEM image (up) and SAM elemental mappings of oxygen (down) b), ToF-SIMS 3D elemental distribution of Mn+, Li3F2+ and Ti+ c) of LTO electrode cycled until the end of the first charge.

References

[1] Tarascon et al. Nature 2001, 414, 359–367.

[2] El Ouatani et al. Journal of The Electrochemical Society, 156(6): A468, 2009.

[3] Gieu et al. Submitted in February 2017 in the Journal of Material Chemistry.

NRG2-2O353

INVESTIGATION ON THE SURFACE REACTIVITY OF LAYERED MANGANESE OXIDES: AN EXPERIMENTAL AND THEORETICAL COMBINED APPROACH

A. Quesne-Turin, D. Flahaut, G. Vallverdu, L. Croguennec, M. Ménétrier, I. Baraille
CNRS/ UNIV PAU & PAYS ADOUR, INSTITUT DES SCIENCES ANALYTIQUES ET DE PHYSICO-CHIMIE POUR L'ENVIRONNEMENT ET LES MATERIAUX - Pau (France)

$LiCoO_2$ is the most widely used positive electrode material of today's Li-ion batteries. In the last years, much research has been performed to explore alternative materials as mixed transition metal oxides $LiNi_xMn_xCo_{1-2x}O_2$ (NMC). We previously pointed out that the role of the transition metal nature in $LiMO_2$ material on the surface reactivity and the adsorption type reaction[1].

Within this framework, we decided to study the surface reactivity of Li_2MnO_3 which can be view as a model compound for MnIV-rich layered oxides such as NMC or even Li-rich materials. The strategy consists in coupling adsorption of gaseous probe molecule (SO_2), X-ray photoelectron spectroscopy (XPS) and DFT calculation to identify the influence of the oxidation state of the transition metal on the adsorption reaction type (basic/acidic or redox).

We focus our study on strengthening the experimental/calculation coupling by studying the reactivity on a single crystal surface of Li_2MnO_3. The XPS and calculation conclude both to a redox adsorption mode with the formation of sulphate species. Chemical maps of the crystal surface after adsorption (Figure 1) obtained by Auger spectroscopy provide information on the adsorption sites location.

Stacking faults and spinel type default are usually encountered in the Li_2MnO_3 materials. Thus, we will present the impact of the stacking faults rate on the surface reactivity of Li_2MnO_3 polycrystals. Moreover, reactivity of $Li_{1+x}Mn_{2-x}O_4$ spinel materials will be checked to follow the influence of the spinel type default on the surface reactivity.

Figure 1: Auger chemical map of a Li_2MnO_3 crystal after SO_2 adsorption. On the top left, a secondary electron mapping. On the top right, bottom left and right, the auger chemical map, respectively, of manganese, sulphur and carbon elements.

References

[1] Andreu, N. et al., ACS Appl. Mater. Interfaces 2015, 7, 6629.

NRG3-1O369

DEPTH PROFILE INTERFACE ANALYSIS ON PEROVSKITE BASED PHOTONIC DEVICES

Y. Busby
University of Namur - Namur (Belgium)

Yan Busby1, Antonio Agresti2, Sara Pescetelli2, Aldo Di Carlo2, Jean-Jacques Pireaux1 and Laurent Houssiau1.

1 Research Center in Physics of Matter and Radiation (PMR), Laboratoire Interdisciplinaire de Spectroscopie Electronique (LISE), University of Namur, rue de Bruxelles 61, B-5000 Namur, Belgium

2 C.H.O.S.E. (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

To develop advanced spectroscopies allowing three-dimensional analysis of hybrid interfaced materials stacks is both highly desirable and challenging. This contribution will show recent results from depth profile interface analysis on photonic devices such as solar cells or light-emitting devices based on organo-lead halide perovskite absorbers. Through this approach, we could successfully correlate the device functionality (performance and stability) to the in depth elemental composition and chemistry at the interfaces. We combined quantitative chemical analysis from High-resolution X-ray photoelectron spectroscopy (XPS), and 3D molecular imaging with time-of-flight secondary ion mass spectrometry (ToF-SIMS). Materials erosion was performed with low-energy (< 1 keV) ion beams (Ar+ or Cs+) to preserve the chemical information and the quality of interfaces.

In mixed halide perovskite absorbers, Cl segregation have been successfully resolved.[1] In organo lead halide perovskite solar cells, the interface quality was correlated to the perovskite deposition procedure and to the environment where perovskite precursors were converted.[2] In mesoscopic perovskite based LEDs the device lifetime has been correlated to the degradation of the hole-transporting material (HTM) and to the perovskite−HTM interface.[4]

Recent results on graphene-based perovskite solar cells will be also discussed showing that the design of interlayers based on 2D materials could very efficiently enhance the device stability by blocking the diffusion of elements such as gold and iodine during operation.[4]

References

[1] M Ralaiarisoa; Y Busby; J Frisch; I Salzmann; J-J Pireaux; N Koch, Correlation of Annealing Time with Crystal Structure, Composition, and Electronic Properties of CH3NH3PbI3-xClx Mixed-Halide Perovskite Films Physical Chemistry Chemical Physics, 2016, DOI: 10.1039/C6CP06347K

[2] F Matteocci; Y Busby, J-J Pireaux; G. Divitini; S Cacovich; C. Ducati; A Di Carlo, Interface and Composition Analysis on Perovskite Solar Cells ACS Appl. Mater. Interfaces 2015, DOI: acsami.5b08038.

[3] A L Palma, L Cinà, Y Busby, A Marsella, A Agresti, S Pescetelli, J-J Pireaux, A Di Carlo, Mesoscopic perovskite light emitting diodes ACS Appl. Mater. Interfaces, 8, 2016

[4] A. Agresti, Y Busby et al, (in preparation)

NRG2-1O386

MECHANISMS OF LITHIUM INTERCALATION INTO ALD-PROCESSED THIN FILM POSITIVE ELECTRODE OF V2O5 IN IONIC LIQUIDS INVESTIGATED BY XPS AND TOF-SIMS

J. Swiatowska [1], L. Santos [1], V. Lair [1], S. Zanna [1], A. Seyeux [1], A. Melendez-Ceballos [1], P. Tran-Van [2], M. Cassir [1], P. Marcus [1]

[1]CNRS-Chimie ParisTech - Paris (France), [2]Renault, Electric Storage System Division - Guyancourt (France)

Room temperature ionic liquids (RTILs) attract much attention as a new type of environmentally benign electrolytes for Li-ion batteries (LiB) due to their high electrochemical stability, wide liquid phase temperature range, non-volatility, non-flammability and non-toxicity [1-4]. Here, Li intercalation/deintercalation in presence of the ionic liquids: N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($PYR_{14}TFSI$) and N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide ($PYR_{13}FSI$) containing 0.3 M LiTFSI, was evaluated in a thin 100 nm layer of V_2O_5 deposited on Al substrate by Atomic Layer Deposition (ALD). Potentiodynamic tests performed in LiTFSI/$Pyr_{14}TFSI$ show a quasi-reversible Li intercalation during 10 cycles (between 2.4 and 5V) with an average coulombic efficiency of 99%. The capacity, calculated from the 1st cycle, is found to be 182 mAh g^{-1}, about 19% higher than the theoretical capacity reported for V_2O_5 (147 mAh g^{-1}). XPS analysis confirms that the intercalation of more than 1 mol of Li^+ per V_2O_5 is achieved (Fig. 1b) as also the possible presence of a solid permeable interface (SPI) on the V_2O_5 surface. Likewise, the Li^+ in-depth distribution on the V_2O_5 layer after intercalation in RTILs measured by ToF-SIMS ion depth profiles, show small irreversible electrode modifications with the presence of lithium through the entire V_2O_5 layer with significant lithium trapping at the V_2O_5 layer/Al substrate interface. The irreversible modifications of the V_2O_5 thin film electrode induced by cycling was also confirmed by the XPS results showing the decrease of V^{5+} ions with concomitant increase of V^{4+} ions (Fig. 1c) comparing to the pristine sample (Fig. 1 a).

Thanks/Acknowledgement

The authors would like to acknowledge Renault and Institut de la MobilitéDurable (IMD) forfinancial support of this work, as well as Ré gion Ile-de-France for partial funding of the XPS and ToF-SIMS equipment.

References

[1] H. Ohno, Chapter 1: Importance and Possibility of Ionic Liquids, in H. Ohno (Eds): Electrochemical Aspects of Ionic Liquids: John Wiler & Sons, Inc., Publication, 2005

[2] J. F. Brennecke, E. J. Maginn, AIChE J. 47 (2001) 2384.

[3] H. Sakaebe, H. Matsumoto, Electrochem. Comm. 5 (2003) 594.

[4] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosatti, Nat. Mater. 8 (2009) 621.

NRG3-3O399

NANOSCALE CHEMICAL CHARACTERIZATION OF SOLID STATE MICROBATTERY STACKS BY MEANS OF AUGER SPECTROSCOPY AND ION MILLING CROSS SECTION PREPARATION

J-B. Ledeuil [1], A. Uhart [1], B. Pecquenard [2], F. Le Cras [3], M. Proust [4], H. Martinez [1]
[1]IPREM UMR 5254 CNRS UPPA - Pau (France), [2]ICMCB–UPR 9048 and Bordeaux INP - Bordeaux (France), [3]CEA LETI/ Université Grenoble Alpes - Grenoble (France), [4]ST Microelectronics - Tours (France)

The current sustained demand for ‘smart’ and connected devices has induced a need for more miniaturized power sources, hence for microbatteries. Lithium-ion or ‘lithium-free’ all-solid-state thin-film batteries are adapted solutions to this issue. The capability to carry out spatially resolved chemical analysis is fundamental for the understanding of the operation in an all-solid-state micro battery. Classically cumbersome and not straightforward techniques as TEM / STEM / EELS and FIB preparation method are used. The challenge in this work is to make the characterization of Li based material possible by coupling ion milling cross section preparation method and AES techniques to characterize the behavior of a $LiCoO_2$ positive electrode in an all solid state microbattery. The surface chemistry of the $LiCoO_2$ has been studied before and after LiPON deposition. Modifications of the chemical environments characteristic of the positive electrode have been reported at different steps of the electrochemical process. An original qualitative and a semi quantitative analysis has been used in this work with the peak deconvolution method based on real, certified reference spectra to better understand the lithiation / delithiation process. This original coupling has demonstrated that a full study of the pristine, cycled and post mortem positive electrode in a microbattery is also possible. The ion milling preparation method allows having access to a large and representative sample area (cross cut) and the resolution of Auger analysis is sufficiently resolved in energy to separate the Lithium and the Cobalt signal in an accurate way.

OXI - Oxides

OXI2-2O151

SOFT X-RAY CHARACTERIZATION OF ION BEAM SPUTTERED MAGNESIUM OXIDE (MGO) THIN FILM

M. Sinha [1], M. Gupta [2], M.H. Modi [2], P. Jonnard [3]

[1]Soft X-ray Applications Lab,Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology - Indore (India), *[2]UGC-DAE Consortium for Scientific Research, University Campus Khandwa Road Indore 452017, India - Indore* (India), *[3]LCPMR / UPMC/ CNRS - Paris* (France)

Oxide thin films have wide technological application owing to their unique properties. Of the several oxides, Magnesium oxide (MgO) is an interesting material owing to its dielectric property as well as good chemical and thermal stability. It is well known for its use as substrate in depositing high quality oxide films. Thin films of MgO are widely used as barrier layers in magnetic tunnel junctions. There are several instances in literature where MgO is regarded as a suitable material for its use as protective layer on multilayer mirrors. However, the presence of defects or interface formation in reaction with other layer/substrate under certain condition can affect its structural and optical properties leading to a change in its performance.

In the present study characterization of magnesium oxide (MgO) thin film is carried out using soft x-ray reflectivity (SXR) technique. The MgO thin film was deposited using ion beam sputtering technique at a base pressure of 4.2e-7 mbar with Ar flow at 5 sccm. The SXR measurements are carried out using reflectivity beamline at Indus synchrotron source. The analysis of the angle dependent reflectivity data indicates the presence of a silicide layer between the principal layer (MgO) and Si substrate interface. To get a further insight about the interface and surface total electron yield measurements are performed near oxygen K edge region. Details of SXR and TEY analyses will be presented.

OXI1-5O159

DIELECTRIC RESPONSE OF ANODIC ALUMINIUM OXIDE LAYERS BY IMPENDANCE SPECTROSCOPY AND XPS CHEMICAL STATE ANALYSIS

L. Jeurgens [1], F. Evangelisti [1], O. Guseva [1], R. Hauert [1], F. Ambrosio [2], A. Pasquarello [2], P. Schmutz [1], C. Cancellieri [1]

[1]*Empa, Swiss Federal Laboratories for Materials Science and Technology - Dübendorf* (Switzerland), [2]*Ecole Polytechnique Fédérale de Lausanne (EPFL), Chaire de Simulation à l'Echelle Atomique (CSEA) - Lausanne* (Switzerland)

The individual electronic and lattice contributions to the dielectric response of amorphous Al oxide layers with uniform thicknesses in the range of 50 – 500 nm, as grown by anodization up to 350 V, were resolved by combining electrochemical impedance spectroscopy (EIS) and XPS chemical state analysis. The EIS analysis, which probes the bulk dielectric response (ε_{tot}) of the oxide layers, shows that anodization in the low (< 100 V) and high (100–250 V) voltage domain results in the formation of barrier-type Al_2O_3 layers with an average dielectric constant of $\varepsilon_{tot} = 10.3$ and $\varepsilon_{tot} = 12.6$, respectively. The value of ε_{tot} originates from the sum of the contributions of the electronic polarization (ε_e) and of the crystal structure lattice vibrations (ε_{lat}). The Auger parameter, α, as measured by XPS, is known to be sensitive to the electronic polarizability only and hence the value of α can be related to the electronic (high frequency) contribution of the bulk dielectric constant. The measured value of α was found to decrease with increasing anodizing potential (V) due to an overall increase of the oxide density (see Fig. 1a). A corresponding estimate of the electronic contribution ε_e was deduced from the averaged value of the O Auger parameter (α) of each anodized oxide layer, as measured by XPS sputter depth profiling. Next the lattice contribution ε_{lat} was deduced from the difference between ε_{tot} and ε_e [1]. It follows that the value of ε_{lat} increases with increasing anodizing potential approaching values close to those of bulk crystalline Al_2O_3 polymorphs (see Fig. 1b). The electronic contribution ε_e, on the other hand, only marginally depends on the anodizing voltage. The results have been compared to dielectric constants calculated for atomistic amorphous models within the framework of density functional theory (DFT), which confirmed that the amorphous Al_2O_3 polymorphs of higher density (4.1 g/cm^3) indeed exhibit a higher dielectric constant [1].

References

[1] F. Evangelisti, M. Stiefel, O. Guseva, R. Partovi-Nia, R. Hauert, E. Hack, L.P.H. Jeurgens, F. Ambrosio, A. Pasquarello, P. Schmutz, C. Cancellieri, Electronic and structural characterization of barrier-type amorphous aluminium oxide, Electrochimica Acta 224 (2017) 503–516.

OXI2-3O178

HARD X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF THE RESISTIVE SWITCHING IN TITE/AL2O3 CONDUCTIVE BRIDGE RANDOM ACCESS MEMORIES

M. Kazar Mendes [1], E. Martinez [1], O. Renault [1], R. Gassilloud [1], M. Bernard [1], J. M. Ablett [2], N. Barrett [3]

[1]Univ. Grenoble Alpes, F-38000 Grenoble, France / CEA, LETI, MINATEC Campus, F-38054 - Grenoble (France), [2]Synchrotron SOLEIL, L'Orme des Merisiers, BP 48 Saint-Aubin, 91192 - Gif-Sur-Yvette (France), [3]SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 - Gif-Sur-Yvette (France)

We investigate the electrochemical reactions involved in the switching mechanism of Al_2O_3-based CBRAMs with a top TiTe active electrode [1] (see inset in Figure 1). The conducting bridge random access memory (CBRAMs) mechanism is related to the formation and dissolution of a conductive filament [2]. Data storage relies on switching the resistivity between two high and low resistance states by applying voltage or current pulses. We have used hard X-ray photoelectron spectroscopy to learn about electrochemical reactions involved in the switching mechanism with sufficient depth sensitivity. Photon energies of 6.9, 8.0 and 10.0 keV were chosen to obtain a non-destructive in-depth chemical characterization with varying sampling depths. The HAXPES experiments were performed at the Galaxies beamline (Soleil) on As-grown samples, after ex-situ forming (Formed) and after Reset operations. The comparison between the different resistance states shows the role and evolution of the electrode/electrolyte interfaces during electrical biasing. Results highlight the reduction of Ti (Figure 1) together with alumina oxidation after forming. The sample polarization causes oxygen migration, probably in the O^{2-} form, pushed by the upper negative bias towards the interface between the active electrode and the solid electrolyte (Al_2O_3). When reversing the polarity of the applied voltage (Reset operation), we observe Ti reoxidation and alumina reduction, characterizing oxygen migration towards the active TiTe electrode.

References

1. J.R. Jameson, D. Kamalanathan, Subquantum conductive-bridge memory, Appl. Phys. Lett. 108 (2016) 053505.
2. R. Waser, R. Dittmann, G. Staikov, K. Szot, Redox-Based Resistive Switching Memories - Nanoionic Mechanisms, Prospects, and Challenges, Adv. Mater. 21 (2009) 2632–2663.

OXI2-5O215

ASSESSMENT OF MEDIUM-TERM RADIOACTIVE RELEASES IN CASE OF A SEVERE NUCLEAR ACCIDENT ON A PRESSURIZED WATER REACTOR: EXPERIMENTAL STUDY OF FISSION PRODUCTS RE-VAPORISATION FROM (CS,I) DEPOSITS

A-S. Mamede [1], D. Obada [2], A.C. Grégoire [3], L. Gasnot [4]
[1]Unité de Catalyse et Chimie du Solide UCCS UMR CNRS 8181, Université de Lille - Villeneuve D'ascq (France), *[2]IRSN, CEN Cadarache / PC2A UMR 8522, Université de Lille - Saint-Paul-Lès-Durance* (France), *[3]IRSN, CEN Cadarache - Saint-Paul-Lès-Durance* (France), *[4]PC2A UMR 8522, Université de Lille - Villeneuve D'ascq* (France)

INTRODUCTION

During a pressurised water reactor severe accident leading to core meltdown, volatile radioactive fission products (FP), such as caesium and iodine are released from the nuclear fuel. They can be transported through the reactor coolant system (RCS) and eventually can be released in the environment, with heavy consequences for the population. In order to better understand the phenomenology of a severe accident, the French Institute for Radioprotection and Nuclear Safety(IRSN) has developed dedicated theoretical tools which are capable of simulating the development of a said accident. However, some phenomena cannot be modelled yet, due to the lack of experimental data. The goal of this work is to study the re-vaporisation of fission products deposits from RCS surface. This phenomenon has been highlighted during the Phébus-FP tests[1], which was followed by some studies meant to characterize the nature of re-vaporized species[2], without a particular focus on surface analysis.

RESULTS

The present study is focused on the re-vaporisation of CsI from stainless steel surfaces present in the RCS (304L, 316L and Inconel 600) in the 750-970°C temperature range. The influence of the initial surface state has been particularly studied, as well as the influence of the re-vaporisation parameters: atmosphere, heating gradient and final temperature, in order to determine the quantity and the nature of residual matter. Thus, surface analysis techniques such as XPS and ToF-SIMS have been applied to establish the chemical composition of the surface before and after re-vaporisation. Thus, it has been highlighted that during re-vaporisation in steam atmosphere Cs and I are released integrally, whereas in air atmosphere, a non-negligible quantity of Cs interacts with the surface of the steel, composed mainly of chromium oxides [3](Figure1b), and forms mixed Cs-Cr compounds(Figure1a), as Cs_2CrO_4. These results have been confirmed by ToF-SIMS analysis, whose higher surface sensitivity allows the detection of fragments that are representative of the mixed Cs-Cr oxide phase. Finally, ToF-SIMS depth profiling has been performed revealing the influence of the different re-vaporisation parameters on the diffusion of Cs in the oxide layer.

References

[1] Haste et al., Ann.Nucl.Energy(2013),61,102-121

[2] Bottomley et al., Ann.Nucl.Energy(2014),74,208-223

[3] Biesinger et al., Surf.InterfaceAnal.(2004),36,1550-1563

OXI1-4O260

CHARGE ATTACHMENT INDUCED TRANSPORT – BULK AND GRAIN BOUNDARY DIFFUSION OF POTASSIUM IN PRMNO3

K-M. Weitzel [1], **J. Martin** [1], **C. Jooss** [2], **T. Kramer** [2], **M.J. Choe** [3], **K. Thornton** [3]

[1]*Philipps-Universität Marburg - Marburg* (Germany), [2]*Universität Göttingen - Göttingen* (Germany), [3]*University of Michigan - Ann Arbor* (United States of America)

In this work we describe a generalization of the previously developed bombardment induced ion transport technique [1,2]. Here, the transport of potassium through praseodymium-manganese oxide ($PrMnO_3$; PMO) has been investigated by means of the charge attachment induced transport (CAIT) technique [3]. To this end, potassium ions have been attached to the front side of a 250 nm thick sample of PMO. The majority of the potassium ions become neutralized at the surface of the PMO, while some of the potassium ions diffuse through. Ex situ analysis of the sample by time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveals pronounced concentration profiles of the potassium, which is indicative of diffusion. Two diffusion coefficients have been obtained, namely, the bulk diffusion coefficient and the diffusion coefficient associated with the grain boundaries. The latter conclusion is supported by transmission electron microscopy of thin lamella cut out from the sample, which reveals twin grain boundaries reaching throughout the entire sample as well as model calculations.

Thanks/Acknowledgement

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG We 1330/17-1 and DFG Jo 348-10/1) and by the U.S. Department of Energy, Award Number DE-SC0012583 is gratefully acknowledged.

References

[1] M. Schäfer, K.-M. Weitzel, PCCP, 13 (2011) 20112-20122.

[2] K.-M. Weitzel, in “Diffusion Foundations: Progress in Ion Transport and Structure of Ion Conducting Compounds and Glasses“, Volume 6, H. Mehrer (ed.), Trans Tech Publ. Ltd., p. 107-143, (2016)

[3] J. Martin et al., PCCP, in press, (2017)

OXI2-1O299

TIN DIOXIDE WIRE-LIKE CRYSTALS SURFACE MODIFICATION BY SYNCHROTRON XANES AND XPS STUDIES

S. Turishchev [1], O. Chuvenkova [1], S. Ryabtsev [1], Y. Yurakov [1], B. Agapov [1], R. Ovsyannikov [2], M. Manyakin [1], S. Kurganskii [1], O. Dubrovskii [1], E. Domashevskaya [1]

[1]Voronezh State University - Voronezh (Russian federation), [2]Helmholtz Zentrum Berlin - Berlin (Germany)

Wire-like crystals based on functional tin oxides are prospective structures for modern electronic applications due to possible bulk zero defective and highest surface perfection that are stipulating the mechanical strength, charge carrier mobility and other parameters comparable to theoretically predicted. High surface/volume ratio, i.e. very developed surface, makes these materials highly sensitive to different surface exposures. Controlled modifications of wire-like crystals make non-destructive and sensitive to the local atomic environment techniques really demanded for the characterization of such materials.

Nanosized wire-like tin oxide crystals were formed using gas-transport synthesis. Variations of growing conditions, followed by temperature treatments in ambient, hydrogen and UHV, treatments in nitric acid and other modifications have been performed under control of XRD, SEM and TEM. All modification stages were accompanied by detailed atomic and electronic structure investigations with the use of synchrotron X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS) studies. Additional HAXPES experiments allowed to refine reference SnO information. XANES data ab-initio calculations of main tin-oxygen compounds were performed for deep understanding of the wire-like crystals transformations.

Nontreated wire-like SnO_2 crystals surface is covered by 1 nm of SnOx (equal to the reference metal foil natural oxide). UHV treatment did not lead to noticeable changes in SnO_2 wires surface while after the following in-situ H treatment the metallic tin appearance is observed. The following restoration ex-situ anneal recovers wires surface to SnO_2 indicating at the treatments reversibility. The "defect" states are observed in a gap near the main absorption edge of SnO2 that is mostly like caused by oxygen vacancies [1]. Nitric acid treatment leads to a noticeable surface amorphization with reconstruction of SnO_2 wire-like crystals electronic structure. The possible interaction of the modified surface structure of SnO2 nanowires with falling synchrotron X-rays resulting in effective XANES Sn $M_{4,5}$ spectrum shape reversing was observed.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh and RFBR according to research projects № 16-42-360612 p_a (with government of Voronezh region), 16-32-00860 mol_a.

References

[1] Chuvenkova O.A., et. al. Physics of the Solid State., 2015, vol. 57, p. 153

OXI1-3O300

X-RAY PHOTOELECTRON SPECTROSCOPY INVESTIGATIONS OF ULTRATHIN SIO2 LAYERS GROWN BY PEALD ON SIGE

M. Mahjoub [1], B. Pelissier [1], L. Sébastien [1], S. David [1], F. Bassani [1], H. Grampeix [2], F. Martin [2], A. Veselov [3], T. Suni [3], B. Thierry [1]
[1]CNRS, LTM, MINATEC Campus, F-38054 - Grenoble (France), *[2]CEA, LETI, MINATEC Campus, F-38054 - Grenoble* (France), *[3]Picosun, Tietotie 3, 02150 - Espoo* (Finland)

SiGe has become an alternative material for CMOS technology due the ease of its integration into a Si process. Moreover, the Ge percentage variation allows to control the band gap and the carrier mobility [1]. However, this integration is limited by the ability of performing a thinner high-k dielectric, which insures a high interface quality.

Thermal grown SiO2 is the most used method to perform high-k dielectric. Nerveless, this method consumes substantially the SiGe channel, lead to Ge pile up and is not suitable for 3D structures as FinFets due to the shadowing effect of the O2 plasma. Thus, Plasma-enhanced atomic layer deposition (PEALD) is considered as an alternative method. Indeed, PEALD allows to work at low temperature and to control the SiO2 thickness layer. However, to enable the successful application of PEALD, the characterization of the deposited layers is crucial.

In this work, we present a thin PEALD SiO2 layer (<3 nm) deposited at low temperature (80°) on SiGe wafers. parallel Angle-Resolved X-ray photoelectron spectroscopy (pAR-XPS) [2] were used to investigate the chemical composition of this layer and the SiO2/SiGe interface. Using the maximum entropy algorithm, the depth profiles of the performed stacks were done. These profiles show a GeO2 layer at the interface and the absence of Ge pile up. Moreover, the diffusion of a minor Ge oxide to the surface was evidenced. HR-STEM and ELLS images (Fig.1) confirm the presence of the GeO2 layer but don't give any information about the Ge oxide diffusion. Thus, we show that the pAR-XPS can be used as a powerful tool to investigate thin ALD oxide layers due to its hypersensitivity to the surface[3].

Thanks/Acknowledgement

This work has been supported by the Waytogofast project and the French ANR program «Investissements d'Avenir", contract ANR-10-EQPX-33

References

[1] L. Gomez, C. Ni Chléirigh et all, IEEE Electron Device Lett., vol. 31, no. 8, pp. 782–784, Aug. 2010.

[2] L. Fauquier, B. Pelissier et all, Mater. Sci. Semicond. Process., 2016.

[3] B. Pelissier, A. Beaurain et all Microelectron. Eng., vol. 86, no. 4–6, pp. 1013–1016, 2009.

OXI1-2O317

HOW TO ACHIEVE LONG-RANGE ORDERED NANOPARTICLES

N. Alyabyeva [1], A. Ouvrard [1], A. Zakaria [1], F. Charra [2], B. Bourguignon [1]
[1]ISMO, CNRS, Univ. Paris-Sud, Université Paris-Saclay - Orsay (France), *[2]CEA Saclay, IRAMIS Institut Rayonnement Matière de Saclay, SPCSI - Gif/yvette* (France)

Long-range ordered nanoparticles (NPs) have gained interest for heterogeneous catalysis and molecular electronics [1]. The past decade, have appeared promising surfaces like Al_2O_3/Ni_3Al(111) on which high density narrow size distributed NPs can be grown [2]. Finding the proper growth parameters to obtain long-range ordered NPs is still an open question that we try to answer by investigating (i) alumina and (ii) nanoparticle ordering using Low Energy Electron Diffraction (LEED) and Scanning Tunnel Microscopy (STM). Alumina film was prepared by oxidizing Ni_3Al(111) at different temperatures from standard values reported in literature to higher ones (720→920°C). Pd NPs are grown on Al_2O_3 and long-range quality is investigated using STM.

(i) LEED and STM show the periodical strain induced in Al_2O_3 layer by the substrate, composed of two commensurate unit cells of 4.2 and 2.2 nm periodicity. Nanoparticles grow with the 4.2 nm periodicity [2]. As growth temperature increases, spot sharpness and intensity in LEED patterns are improved, while at micron scale, STM reveals larger Al_2O_3 terraces with less defects. STM and LEED results, both in a good agreement, indicate a long-range order improvement with increasing Al_2O_3 growth temperature. STM shows that long-range order along the 4.2 nm structure is increasing with temperature, while the 2.2 nm structure is not temperature dependent.

(ii) Growth of Pd NPs on Al_2O_3 allowed us establishing the oxidation temperature impact on NP density and ordering along the 4.2 nm regular array. We observe a packing density increase by a factor 5, from standard temperature to the highest (larger than in the literature by 200°C). Temperature effect on NP ordering is directly related to the 4.2 nm network observed in the Al_2O_3 layer.

In conclusion, oxide quality and subsequent long-range ordering of NPs with growth temperature have been investigated by LEED and STM. We observe that the oxide growth temperature is critical. Temperature effect may be related to the actual stoichiometry of the Ni_3Al(111) sample, which would explain the large difference in recipe compared to literature. We suggest that this temperature investigation could be used to find the best recipe for any Ni_3Al sample.

Thanks/Acknowledgement

We gratefully acknowledge the French National Agency for Research (Agence Nationale pour la Recherche, ANR) for financial support through the JCJC program (Project LEMON - DS0305).

References

[1] J. Cai et al., Nature, vol. 466, pp. 470-473, 2010.

[2] L. Gavioli et al., Prog. in Surf. Sci., vol. 86, pp. 59-81, 2011.

OXI1-1O323

THE EARLY STAGES OF GROWTH OF ZNO ON HOPG AND GRAPHENE/CU: A COMPARATIVE STUDY

C. Morales [1], A. Black [2], F. Jiménez [2], J. Méndez [3], F. Yubero [4], L. Soriano [1]
[1]*Universidad Autónoma de Madrid (UAM) - Madrid (Spain),* [2]*IMDEA Nanociencia - Madrid (Spain),* [3]*ICMM-CSIC - Madrid (Spain),* [4]*ICMSE-USE - Madrid (Spain)*

ZnO has been grown on different carbon-based substrates, namely HOPG and Graphene grown on polycrystalline Cu by reactive evaporation of metallic zinc in an oxygen atmosphere of 1.5 x 10-3 mbar at room temperature. In situ characterization of the growth has been done by successive evaporation steps followed by X-ray Photoemission Spectroscopy (XPS) measurements. Chemical analysis has been performed by means of factor analysis using the Zn LMM Auger spectra [1] to characterize the chemical changes of Zn during the growth. Quantitative Analysis was done by means of inelastic peak shape analysis (QUASES [2]) from the XPS survey spectra in order to get morphological information from the surface. The characterization was completed ex situ for a series of samples with representative growth stages by means of Atomic Force Microscope (AFM). Both, AFM and QUASES results have been compared to get a more complete view of the morphology of the surface.

Chemical analysis reveals that in the early stages of growth on the HOPG substrates, Zn is completely oxidized forming ZnO clusters whereas on the graphene/Cu substrates, metallic Zn is observed at the very early stages of growth. Further growth gives rise to the formation of ZnO oxide, being predominant at intermediate and final stages of growth. Although in both substrates the way of growth is the same, i.e. formation of islands until coalescence (Wolmer-Weber growth mode), the size of the initial islands is very different, being of the order of 1 µm on HOPG and around 10 nm on the graphene/Cu substrate. For the HOPG substrate, the growth can be described as a slow nucleation of ZnO clusters, mainly produced at the graphite steps, followed by a rapid growth of these structures. On the other hand, the growth on the graphene/Cu substrate seems to be produced in two different steps: initial intercalation of metallic Zn between graphene and Cu along with the formation of 2 nm ZnO islands covering about the half of the sample, and posterior growth of ZnO islands leading to coalescence.

Thanks/Acknowledgement

This investigation has been funded by the MINECO of Spain through the FIS2015-67367-C2-1-P project. One of the authors (C. Morales) thanks the MEDC for a FPU grant. Authors also thank Segainvex for technical support.

References

[1] G. Deroubaix, P. Marcus, Surf. Interface Anal, 18, 39, (1992)

[2] S. Tougaard, QUASES, software package for quantitative XPS/AES of surface nanostructures by inelastic peak shape analysis; see www.QUASES.com.

OXI2-4O405

XPS CHARACTERIZATION OF BLACK TIO2 AND BLACK ZRO2.

M. Fantauzzi [1], A. Aronne [2], D. Atzei [1], B. Elsener [1], C. Imparato [2], A. Rossi [1]
[1]Università di Cagliari - Dipartimento di Scienze Chimiche e Geologiche - Cagliari (Italy), [2]Università di Napoli Federico II - Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Napoli (Italy)

The synthesis of light-responsive TiO_2 for photocatalytic applications requires the modification of the electronic band structure of TiO_2: doping with metal or non-metal ions, sensitization by organic molecules, formation of heterojunctions either with other semiconductors or with graphene oxide are the methods that usually have been exploited. Together with these methods, an alternative way to modify the electronic structure of TiO_2 was proposed: this method involves the synthesis of self-doped Ti^{3+}/oxygen vacancy, or incorporation of H-doping, induced by a reduction treatment generally obtained under severe conditions.

In this work the surface composition of hybrid yellow-coloured TiO_2–acetylacetonate material (HSGT) obtained by hydrolytic sol–gel route was investigated by XPS [1].

Results allowed us to confirm the formation of a surface Ti–acac complex and to ascertain the presence of small amounts of Ti^{3+}. The HSGT sample was then heat treated at 400°C in air (HSGT-400), providing a black titania sample. XPS results showed that no more Ti-acac complex was present at the surface of the materials. Acetylacetone acts as a reducing agent leading to the formation of about 26% of Ti atoms having an oxidation state lower than IV (Figure 1).

Similarly to TiO_2, a yellow hybrid ZrO-acetylacetonate material (HSGZ) was synthetized and the XPS results confirmed the formation of a Zr-acac complex. No reduced Zr was detected on the surface of the pure tetragonal light-responsive zirconia obtained by heating HSGZ at 400°C in air (HSGZ-400) (Figure 2).

The difference in the surface chemistry between the two oxides and their different electronic properties will be discussed.

References

[1] A Aronne, M Fantauzzi, C Imparato, D Atzei, L De Stefano, G D'Errico, F Sannino, I Rea, D Pirozzi, B Elsener, P Pernice, A Rossi, RSC Adv., 2017, 7, 2373-2381

POL - Polymers

POL1-1O108

DECOMPOSITION MECHANISM OF LIGNIN MODELS ON PT(111) : COMBINING SINGLE CRYSTAL EXPERIMENTS AND FIRST PRINCIPLE CALCULATIONS

C. Ould Hamou [1], R. Réocreux [2], C. Michel [2], P. Sautet [3], B.J. Giorgi [4]
[1]Centre for Catalysis Research and Innovation, Deparment of Physics, University of Ottawa - Ottawa (Canada), [2]Univ Lyon, Ens de Lyon, CNRS UMR 5182, Université Claude Bernard Lyon 1 - Lyon (France), [3]Department of Chemical and Biomolecular engineering, University of California, - Lyon (France), [4]Centre for Catalysis Research and Innovation, Department of Chemistry and Biomolecular Sciences, University of Ottawa - Ottawa (Canada)

Lignin is indeed nature's most abundant aromatic polymer (10–30% of biomass) and therefore represents an extraordinary sustainable source of highly valuable aromatic compounds. The removal of oxygen to produce higher value compounds is a necessity but it still remains one of the challenging tasks for lignin exploitation [1]. In this study, some fundamental questions regarding the reactivity of lignin models such as anisole and 2-phenoxyethanol are addressed in order to compare the facility of the C-H vs. C-O vs. C-C bond cleavage (Figure 1).

The adsorption and decomposition of Anisole and 2-Phenoxyethanol on clean Pt(111) was studied as a function of temperature and exposure by means of X-ray photoelectron spectroscopy (XPS),Temperature programmed desorption (TPD) and DFT calculations (optPBE functional).

Under UHV conditions, anisole gives benzene, CO and H_2 as the main desorbing products of the decomposition. Phenoxy is the key intermediate of the decomposition of anisole. Interestingly enough, phenol has not been observed, while it is one of the main products under catalytic conditions (1-100 bars H_2).It seems that UHV condition do not allow the hydrogenation of phenoxy into phenol and the presence of carbonaceous species actually performs the deoxygenation of phenoxy into benzene (Figure2)[2].

The reactivity of 2-Phenoxyethanol on Pt(111) eventually falls back to the reaction network of the anisole decomposition, the phenoxy intermediate is obtained and yields benzene due to the presence of numerous carbonaceous species. At higher coverages the presence of phenol and traces of anisole are observed.

Thanks/Acknowledgement

The authors are thankful to the LIA FunCat and the Natural Sciences and Engineering Research Council of Canada for its financial support

References

[1] Pandey,M. P.; Kim,C. S. Lignin Depolymerization and Conversion:A Review of Thermochemical Methods.Chem.Eng.Technol.2011,34,29–41.

[2] Réocreux,R.; Ould Hamou,C.A.; Michel,C.; Giorgi, J. B.; Sautet, P.Decomposition Mechanism of Anisole on Pt(111):Combining Single-Crystal Experiments and First-Principles Calculations. ACS Catal.2016,6,8166–8178 .

POL2-3O131

MICRO OR NANOSTRUCTURED CONDUCTIVE POLYMERS ELECTROGENERATED USING A TEMPLATE-FREE METHOD.

C. Debiemme-Chouvy, A. Fakhry, H. Cachet
Laboratoire Interfaces et Systèmes Electrochimiques -UMR 8235 - Paris (France)

Due to their potential applications, micro or nanostructured conductive polymers have attracted growing attention. Up to now, conductive polymer structures were primarily obtained using 'hard' or 'soft' templates. In this presentation, it will be shown that the direct electrosynthesis of either oriented nanowire array or interconnected nanofiber networks of polypyrrole (PPy) or microstructures of poly(3,4-ethylenedioxythiophene) (PEPOT) can be achieved without using any template (see below SEM images, left: PPy, scale bar: 200 nm ; right: PEDOT, scale bar: 1 µm), these structures being electrogenerated onto a flat electrode (Au, Pt, GC, ...).[1,2] Actually, in order to obtain such micro or nanostructures, the electro-oxidation of the monomers should be performed in the presence of both a high concentration of weak-acid anions such as HPO_4^{2-} which confer to the solution a basic pH and a low concentration of non-acid anions such as ClO_4^-. The growth mechanism of the polymer nanostructures will be discussed. Notably, it will be highlighted why the presence of weak-acid anions at the electrode-solution interface is essential. At the very beginning of the process water oxidation should take place. This reaction which occurs at a pH-dependent potential leads to the formation of hydroxyl radicals and to evolution of O_2. It will be shown that the interfacial pH which varies during the monomer oxidation due to proton release is the key point of the process.[3]

References

[1] C. Debiemme-Chouvy, *Electrochem. Commun.* **11** (2009) 298-301.

[2] A. Fakhry, F. Pillier, C. Debiemme-Chouvy, *J. Mater. Chem. A* **2** (2014) 9859-9865.

[3] A. Fakhry, H. Cachet, C. Debiemme-Chouvy, *Electrochim. Acta* **165** (2015) 297-303.

POL2-1O175

SURFACE ANALYSIS OF WOOD: CORRELATION OF XPS AND TOF-SIMS DATE WITH GROWTH RINGS, ORIENTATION, AGE AND SPECIES

J. Watts, **J. Banuls-Ciscar**
University of Surrey - Guildford (United kingdom)

Wood is a complex structure of cellulose, hemicellulose, lignin, and extractives arranged in a cellular fashion. At the macroscopic level the most obvious features of wood in its unprocessed state are early and late growth rings present in the sapwood and heartwood. Once processed into timber products such as planks and so forth the orientation of cut present very different structures, the two extremes of sectioning being a radial cut and a tangential cut. In this work the use of XPS and ToF-SIMS has been explored in an attempt to differentiate between macroscopic features of pine (*pinnus sylvestris*), the age and different species of hardwood.

The characteristic XPS spectra of cellulose and lignin are well documented (e.g. 1), and XPS (background analysis and argon cluster profiling) indicates sapwood is dominated by a thin layer of lignin and extractives at the surface. A simple plot of the intensity of the unfunctionalised (C-C) carbon component in the C1s peak fit versus O/C atomic ratio is able to differentiate between sapwood and heartwood. Such a graphical approach, provides a linear relationship between the main components of the wood (cellulose, lignin and extractives). This has also been employed for the analysis of wood fibres Soxhlet extracted using a variety of solvent schemes (2). Time related acquisition of XPS spectra has enabled the migration of the extractives present to be studied as a function of sap wood and heartwood and radial and tangential cuts.

In previous work the manner in which processing of ToF-SIMS data using NMF can be used to provide a quantitative analysis of wood in terms of cellulose/lignin ratios has been established (3). This work has now been extended to study age related *pinnus sylvestris* specimens (up to 100 years old) and different hardwood species. The different specimen types are readily separated with the application of PCA routines to the ToF-SIMS data.

Thanks/Acknowledgement

Thanks go to Clive Ezeh and Jake Hollins for ToF-SIMS/PCA work on the aging and speciation studies respectively, and particularly to Gustavo Ferraz Trindade for the development of the magnificent MVA suite of programmes used in this work.

References

1. J Bañuls-Ciscar, M-L Abel, J F Watts, *Surf Sci Spectra,* **23,** 1-8, (2016).
2. J Bañuls-Ciscar, D Pratelli, M-L Abel, J F Watts, *Surf Interf Anal,* **48,** 589-592, (2016).
3. G F Trindade, J Bañuls-Ciscar, C K Ezeh, M-L Abel, J F Watts, *Surf Interf Anal,* **48,** 584-588, (2016).

POL2-2O198

AN EXAMINATION OF THE EFFECT OF SILICONE CONTAMINATION ON IONIC LIQUID SPECTRAL QUANTIFICATION.

E. Smith [1], E. Dick [2], A. Santos [2], P. Licence [2]
[1]nmRC and School of Chemistry, University of Nottingham, - Nottingham (United kingdom), [2]Carbon Neutral Laboratory, School of Chemistry, University of Nottingham, - Nottingham (United kingdom)

Recent interest in low vapour pressure room temperature ionic liquids (ILs) has led to a number of researchers publishing analyses using ultra high vacuum techniques such as XPS. It is often difficult to obtain very pure ionic liquids and one of the most common surface contaminants is silicone which appears to segregate to the IL surface. In XPS this is detected directly via the Si 2p and 2s peaks (and Si 1s peak is the excitation is energetic enough) with additional increased O 1s and C 1s.[1,2] Because they have relatively low sensitivity the Si 2p and 2s peaks can be small and of the same order as the noise in a standard wide scan spectrum. Unfortunately, the presence of a very thin over-layer of material on top of the IL surface can perturb the quantification of the elemental peaks because they are different KEs and therefore experience different attenuation in the over-layer. This can be demonstrated very clearly with fluorine containing ILs such as C8MIm NTf2 with peaks in the KE range ~ 800 eV to 1300 eV (F 1s and S 2p) with the low KE peaks underestimated in quantification. Herein we analyse example XP spectra of ILs with CASAXPS and QUASES software to demonstrate the difference between a clean IL surface and a heavily contaminated one and one with silicone below normal detection levels. An example spectrum of a below detection level silicone contamination on an IL is shown in figure 1.

Figure 1 A wide scan spectrum of C6im2 2NTf2 showing a 'slightly contaminated' ionic liquid surface, which might be mistaken for a 'clean' one.

Thanks/Acknowledgement

EPSRC grant EP/K005138/1. University of Nottingham - Equipment Account

References

1. .Smith, E. F., Garcia, I. J. V., Briggs, D. & Licence, P. Ionic liquids in vacuo; solution-phase X-ray photoelectron spectroscopy. Chem. Commun. 5633–5635 (2005). doi:10.1039/b512311a
2. Santos, A. R., Blundell, R. K. & Licence, P. XPS of guanidinium ionic liquids: a comparison of charge distribution in nitrogenous cations. Phys. Chem. Chem. Phys. (2015). doi:10.1039/C5CP01069A

POL2-4O217

NANO-FITR NEAR-FIELD SPECTROSCOPY OF POLYMERS AT SUB-200MS PER SPECTRUM SPEED

A. Huber
neaspec GmbH - Munich (Germany)

We demonstrate acquisition of nanoscale resolved material-specific nano-FTIR absorption spectra of polymers at unmatched measurement speeds. Spectroscopic signatures of weak absorption lines of PS and LDPE in the mid-IR spectral range can still be analysed in the obtained spectra.

nano-FTIR [1] employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample. Detection of the elastically tip-scattered light simultaneous to AFM imaging yields nanoscale resolved near-field images [2,3]. Utilizing broadband laser sources like a mid-IR supercontinuum laser for tip illumination enables near-field spectroscopic measurements at nanoscale spatial resolution with unprecedented signal quality. The exceptional signal to noise ratio obtained even for polymeric and biological samples provides the basis to reduce measurement times orders of magnitude and to acquire characteristic nearfield spectra in the 100-200ms time scale.

Figure 1 shows the topography and near-field absorption images of the polymer test structure consisting of a 50nm thin film on a Si substrate with (sub)micron-sized islands of Low-Density Poly-Ethylene (LDPE) in a Poly-Styrene (PS) matrix. nano-FTIR spectra obtained on different sample regions reveal the characteristic IR absorption lines for LDPE at ca. 1470cm-1 or around 1450/1500cm-1 for PS, respectively. The nano-FTIR near-field absorption spectra of a ca. 50nm thin polymer PS/LDPE test structure clearly reveal the material-specific IR spectroscopic signatures of the polymers.

Besides non-invasive nanoscale resolved material identification or analysis of the secondary structure of biolocial specimens[4], nano-FITR enables quantitative measurements of dielectric values for polymers [5] or the determination of free carrier concentration and mobility in low-dimensional structures [6,7].

References

[1] F. Keilmann, R. Hillenbrand, Phil. Trans. R. Soc. Lond. A 362, 787 (2004)
[2] F. Huth, et al., Nano Lett. 12, 3973 (2012)
[3] C. Westermeier, et al., Nature Comm. 5, 4102 (2014)
[4] R. Wiens, et al., Faraday Discuss. 187, 555 (2016)
[5] A. A. Govyadinov, et al., J. Phys. Chem. Lett. 4, 1526 (2013)
[6] J. M. Stiegler, et al., Nature Comm. 3, 1131 (2012)
[7] Z. Fei, et al., Nature Nanotech. 8, 821 (2013)

POL1-2O279

DIRECT MEASUREMENT OF SODIUM CONCENTRATION IN DIFFERENT POLY-IMIDES WITH LA-ICP-MS, LIBS, AR-CLUSTER TOF-SIMS AND O2-CLUSTER TOF-SIMS: A METHOD COMPARISON

S. Schwab [1], M. Bonta [2], T. Anderl [2], A. Limbeck [2], S. Kayser [3], Z. Julia [3], S. Miethaner [4], M. Bauer [4], M. Nelhiebel [1], H. Hutter [5]

[1]Kompetenzzentrum Automobil und industrieelektronik - Villach (Austria), [2]Technische Universität Wien - Wien (Austria), [3]ION-TOF - Münster (Germany), [4]Infineon AG - Regensburg (Germany), [5]Technische Universität Wien - Villach (Austria)

Ion migration is a highly relevant risk for modern high voltage transistors. Already small contamination within the gate oxide of these devices can cause a shift in the threshold or breakdown voltage, thus leading to chip failure. Materials used for chip encapsulation (e.g. polymers and mold compounds) are believed to be the main contamination source for mobile ions. Due to the high natural abundance and the small ionic radius, sodium is the most critical species. In general, the concentration of possible contaminants, is regularly analysed in the semiconductor industry to ensure high quality standards (usually done by initial quality control). However, analysis of the final encapsulation materials after the production process usually requires considerable effort (advanced sample preparation techniques). Therefore, the use of techniques for direct solid analysis, which do not require sample preparation, would be beneficial.

Within this work, four different methods for direct measurement of the sodium concentration in three different poly-imide layers using the method of standard addition are presented. The four different methods are laser ablation inductive coupled plasma mass spectrometry (LA-ICP-MS), laser induced breakdown spectroscopy (LIBS), time of flight secondary ion mass spectrometry (TOF-SIMS) using an argon cluster gun for sputtering and TOF-SIMS using an oxygen cluster gun. The results of the four methods will be discussed. The limits of detection as well as the measurement precision of the un-spiked samples will be investigated for all methods. In addition, the pros and cons of all four methods will be discussed in detail. Furthermore it will be outlined if it is possible to use the same external standards for signal quantification and determination of the sodium concentration in the three different imides.

Thanks/Acknowledgement

This work was support by ionTOF (Münster, Germany). This work was jointly funded by the Austrian Research Promotion Agency (FFG, Project No. 854247) and the Carinthian Economic Promotion Fund (KWF, contract KWF-1521/ 28101/40388).

POL2-5O280

ENVIRONMENTAL CHARGE COMPENSATION - NEAR AMBIENT PRESSURE XPS AS A TOOL FOR SURFACE CHEMICAL ANALYSIS OF INSULATORS WITHOUT CHARGING EFFECTS

A. Thissen, P. Dietrich, M. Meyer, S. Bahr
SPECS Surface Nano Analysis GmbH - Berlin (Germany)

Since many decades XPS (or ESCA) is the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools combine reliable quantitative chemical analysis with comfortable sample handling concepts, integrated into fully automated compact designs.

Generically insulators will positively charge in XPS due to the irradiation with X-rays and the emission of photoelectrons. Without compensation this effect leads to strong continuous shifts and asymmetric line shapes of the emission lines in the spectra. To perform an exact characterization and quantification of strongly insulating materials different concepts of charge compensation or neutralization have been developed over the last decades. A short overview is given starting from low energy electrons offered from so-called "flood guns" or other sources, via compensation by a combination of electrons and ions to rare methods like illumination with visible light during the analysis and compensation by the produced electron-hole pairs. The opportunities and challenges of the different methods are compared.

The development of XPS method towards environmental or (near) ambient pressure working conditions has revolutionized this method regarding applications. In-situ and in-operando measurements in pressure of up to and above 25mbar are easily possible, even with laboratory based systems and using EnviroESCA even in a standard analytical tool.

During the last months, measurements on insulators have shown, that they can be measured with exception in surrounding pressures of a couple of mbar without any charging. This new technique of charge neutralization is neamed Environmental Charge Compensation (ECC).

This presentation summarizes results of measurements on insulating polymer samples, showing the resulting spectroscopic resolution for C1s and O1s emission lines. A comparison for PET and PTFE to other neutralization techniques is given. In addition measurements on bulk insulators from polymeric materials, ceramics, food samples, aqueous solutions, stones, soil and even zeolites are shown, that cannot easily be obtained in UHV based XPS systems.

Furthermore the effect is described in detail, including the influence of pressure and gas composition on the charge neutralization. An outlook is presented towards completely new resulting fields of application of XPS, when combined with ECC.

POL1-3O398

POLYMER BRUSHES FOR THIN FILM METAL OXIDE FORMATION AND AREA SELECTIVE DEPOSITION APPLICATION

C. Cummins, M. Morris
Trinity College Dublin - Dublin (Ireland)

Polymer brushes are discussed with a view to their potential nanoelectronic use. Polymer brushes chemically attached to site specific areas are introduced for area selective deposition (ASD) application. ASD is a process that allows the placement of materials or molecules at specific substrate locations without the need for additional lithography layers.1 The process has emerged as a promising candidate for advancing nanoelectronic devices with advantages including reduced cost and waste, and minimizing starting materials/precursors. Here, we introduce a novel process to extend ASD through the use of tailored polymer brushes. ASD studies to date have focused on the use of vapor processes to functionalize site specific locations, e.g. self-assembled monolayers and atomic layer deposition. Issues with vapor processing include poor surface coverage and prolonged exposure times.2 Our method centres on the use of spin coated polymer brushes to functionalize specific areas of patterned copper/silicon substrate surfaces, allowing good surface coverage through attention to substrate chemistry and judicious polymer brush choice (see figure for example). Furthermore, the functionalization processes developed can be carried out in a short period (<1hr). XPS, SEM, and TEM data of functionalized surfaces will be described. We will describe processes employed to create excellent uniformity on desired locations with high selectivity, i.e. brushes deposited to block or activate site specific regions at substrate surfaces. Polymer brushes with different end functional groups (e.g. –OH, -SH, -NH2) and their potential as area selective materials will be discussed. The processes and results to be overviewed will provide a new and innovative way to achieve ASD that are pertinent to nanoelectronics and polymer science. Moreover, results will be described on the functionalized brush surfaces ability to fabricate inorganic (metal oxide, perovskite) thin film and features in a facile manner.

Thanks/Acknowledgement

The authors gratefully acknowledge financial support for this work from Science Foundation Ireland and AMBER CRANN.

The authors gratefully acknowledge the assistance of staff of the Advanced Microscopy Laboratory, AMBER CRANN.

References

1. Fang, M.; Ho, J. C., ACS Nano 2015, 9 (9), 8651-8654.
2. Minaye Hashemi, F. S.; Prasittichai, C.; Bent, S. F., ACS Nano 2015, 9 (9), 8710-8717.

POL1-4O400

UV PHOTOEMISSION SPECTROSCOPY COMBINED WITH ARGON GAS CLUSTER ION BEAM SPUTTERING FOR CHARACTERIZATION OF INTERFACE ENERGETICS IN THIN MULTILAYER ORGANIC STRUCTURES

M. Marzec [1], J. Rysz [2], P. Dabczynski [2], A. Budkowski [2], A. Bernasik [3]
[1]AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology - Kraków (Poland), [2]Smoluchowski Institute of Physics, Jagiellonian University - Kraków (Poland), [3]AGH University of Science and Technology, Faculty of Physics and Applied Computer Science - Kraków (Poland)

A detailed understanding of the interface dipole formation between metal electrode and thin organic film and at organic/organic heterojunctions plays a key role for the fabrication of organic electronic devices. Energy level alignment across organic interfaces related to e.g. charge carrier injection, is of utmost importance for organic light-emitting diodes (OLEDs), photovoltaics (OPVs), transistors (OFETs) or chemical sensors. The interface energetics determines device performance such as driving voltage and stability of electron and hole injection in OLED, or open circuit voltages in OPV devices. Since the organic electronic devices are typically composed of a few nanometer-thick large area layers, the interfaces become regions where overall device properties, integrity and stability are determined.

The evaluation of electronic density of states (DOS) enables to better understand observed physical properties of materials and interfaces. In order to unravel electronic structure the UPS- (Ultraviolet Photoelectron Spectroscopy) and XPS- (X-ray Photoelectron Spectroscopy) based valance band measurements can be applied. The UPS is better suited to probe energy level alignment at the interfaces whereas XPS represents the total DOS of the sample. Combining above methods with gas cluster ion beam (GCIB) sputtering allows to investigate chemical composition and/or electronic properties of the materials from the surface to hundreds of nanometers or more into the bulk. However, each material requires a separate approach to define the advantages and limitations of the GCIB assisted depth profiling and to reveal its suitability for quasi damage-free in-depth analysis.

Here we describe XPS and UPS depth profiling using GCIB (Ar_{2500}^{+}) on multilayer polymer thin film structures. First, to study SAM influence on the electrode surface, we used model systems which were thin films of poly(3,4-ethylenedioxythiophene) / polystyrene sulfonate (PEDOT:PSS) modified with various organosilane SAMs. In the next step, PEDOT:PSS layer functionalized with SAMs was covered with thin film of poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM) blend. These can be recognized as a part of organic solar cell devices. Obtained results showed that combination of XPS or UPS together with GCIB depth profiling can be used to verify the presence and chemical structure of SAM placed at buried organic/organic interfaces and gave information about e.g. work function changes through the considered multilayer system.

Thanks/Acknowledgement

This work was partially supported by the Polish National Science Centre project no. 2013/09/N/ST5/00874

SLI - Solid-liquid interface

SLI2-3O026

CRYO-XPS: PROBING INTACT INTERFACES IN NATURE AND LIFE

A. Shchukarev, M. Ramstedt
Department of Chemistry, Umeå University - Umeå (Sweden)

During the last two decades, we have developed a new approach for investigating intact solid-aqueous solution interfaces, cryogenic XPS [1], based on fast freezing of centrifuged wet pastes followed by traditional XPS measurements at liquid nitrogen temperatures. For mineral suspensions, cryogenic XPS is an important complement to traditional analyses of supernatant solutions and surfaces of dry solids, as it reveals novel insights of the electrical double layer in terms of its structure and composition. Furthermore, cryo-XPS can be used to study changes in the biochemistry of bacterial cell walls followed by external stimuli or genetic modification. Interfacial features related to biocompatibility of implant materials have also successfully been studied using cryogenic XPS.

In the presentation, we review how the technique has been applied to: minerals in electrolyte solutions, intact bacterial surfaces, biomaterial interfaces in biologically relevant media, and we present a recent application area – environmental air-sensitive wet specimens formed under anoxic conditions (soils and sediments). Sample preparation and handling protocols, applicable to any suspension or gel, are discussed in detail. We also outline future requirements and perspectives for development of methodologies in solid-aqueous solution interface analysis.

References

[1] Shchukarev A, Ramstedt M. *Surf. Interface Anal*. **2017**, *49*, 349-356

SLI1-5O132

X-RAY PHOTOELECTRON SPECTROSCOPY OF IONIC LIQUIDS – FROM HALF CELL MEASUREMENTS TO IN SITU ELECTROCHEMICAL XPS STUDIES

A. Foelske-Schmitz [1], M. Sauer [1], D. Weingarth [2], R. Koetz [3]
[1]TU Wien - Vienna (Austria), [2]Heraeus Holding GmbH - Hanau (Germany), [3]Paul Scherrer Institut - Villigen (Switzerland)

X-ray Photoelectron Spectroscopy (XPS) investigations of the liquid/ultra-high vacuum (UHV) interface have been of fundamental interest for several decades [1]. In these and subsequent studies, charging was observed and XP spectra were commonly referenced to the C 1s line [2]. Ionic liquids (IL) are particularly interesting to study as their negligible vapor pressure allows for XPS measurements without need of complex experimental setups. Again charging was reported to occur and the C 1s line of aliphatic chains was suggested to be used as internal reference [3].

Weingarth et al. developed an in situ electrochemical (EC) XPS cell and followed charging phenomena by recording the open circuit potential (OCP) under X-ray illumination using a twin anode [4]. It is well established that the OCP reflects the potential difference between an electrode and an electrolyte. In electrochemical equilibrium the OCP is constant, however, expected to change if physical or chemical properties of the two phases are changed.

Conversely, BE measurements may allow for determination of the OCP in one half-cell if significant charging of the IL caused by the X-ray induced photoemission can be excluded in course of the measurement. Since significant charging could not be observed by means of in situ EC XPS using a small spot monochromatic X-ray source directed to the bulk of the IL [5], we have further investigated double layer phenomena by means of XPS using a mono source. Recorded core level data of [EMIM][TFSI] on different substrates before and after 4h of irradiation indicates that significant charging does not occur in course of the measurement. Binding energies, however, were found to vary by 0.4 eV among the used substrates, thus confirming that the potential drop at the substrate/IL interface determines the OCP and therewith the BE values measured at the IL/UHV interface.

In the course of the presentation, recent XPS data of IL/UHV interfaces will be presented and elucidated by means of existing literature.

References

[1] H. Siegbahn, K. Siegbahn, J. Electron Spectrosc. Relat. Phenom., 1973, 2 319

[2] R. Moberg, F. Bökman, O. Bohman, H.O.G. Siegbahn, J. Am. Chem. Soc., 1991, 113, 3663-3667

[3] I.J. Villar-Garcia, E.F. Smith, A.W. Taylor, F. Qiu, K.R.J. Lovelock, R.G. Jones, P. Licence, Phys. Chem. Chem. Phys., 2011, 13, 2797-2808

[4] A. Foelske-Schmitz, D. Weingarth, A. Wokaun, R. Kötz, ECS Electrochem. Lett., 2013, 2, H13-H15

[5] D. Weingarth, PhD thesis, 2013, ETH NO. 21213

SLI1-4O167

TO THE DETERMINATION OF IONS AND WATER MOLECULES DISTRIBUTION AT THE INTERFACE OF SILICA NANOCONFINEMENT SYSTEM: AN EXPERIMENTAL AND MODELLING APPROACH

D. Rebiscoul [1], M. Baum [1], S. Hocine-Metahri [1], S. Tardif [2], B. Siboulet [1], J.F. Dufrêche [1], F. Rieutord [2]
[1]*ICSM - Bagnols-Sur-Cèze* (France), [2]*CEA - Grenoble* (France)

Chemical reactions such as materials hydrolysis in aqueous solution are controlled by an interfacial layer which can be strongly modified in nanoconfined. The determination of these modifications in nanoporous materials is essential to explain or to predict their behaviour. While the water and ions distributions at the material surface in nanopore are studied by atomistic modelling[1], the characterization of this interfacial layer is still a scientific challenge.

Generally, the water and ions distribution at the interface of dense materials are obtained experimentally using grazing incidence characterization techniques[2] such as X-ray reflectivity (XRR), XRF, XPS and AFM sometimes coupled with modelling[3]. XRR is an interesting technique since it probes the electron density profiles as a function of the depth perpendicular to the surface. Bellucci et al, have used XRR and density functional theory to characterize the vertical structure of quartz−liquid interface, with quartz in contact with RbCl solutions[4]. Coupled with modelling, it allows the obtention of the interfacial water structuring and the distribution of Rb at the interface.

With the same approach presented Figure 1, we determined experimentally the electron density profiles inside a silica nanoconfinement system. We used a silica-based model system consisting of two parallel and plane surfaces spaced of 5 nm (nanochannels) filled with electrolyte solution XCl_2 (X = Ba, Ca, Mg) at 1 M and 0.1 M. From, hard X-ray reflectivity curves obtained on BM32 beamline, electron density profiles were extracted directly by an inverse Fourier transform assuming the symmetry of the profiles[5]. In order to obtain some information about the surface charge, the nanochannels filled with electrolyte were modelled by atomistic modelling and the X-ray reflectivity curves were fitted using the electron density profiles obtained from modelling. These preliminary results are, as far as we know, the first ones using an experimental and modelling approach to described ions and water molecules distribution at the interface of a silica nanoconfinement system.

Thanks/Acknowledgement

L. Mercury and N. Tas for nanochannels supply.

References

1. Argyris, D. 2010
2. Wogelius, R. et al., 1999
3. Skelton, A. et al, 2011
4. Bellucci, F. et al, 2015
5. Rieutord, F. et al, 2001

SLI1-1O174

ASPARTIC ACID AND ARGININE ON CU(110): FROM THE LIQUID SOLUTION TO THE MOLECULAR FILM

V. Humblot [1], R. Totani [1], C. Méthivier [1], H. Cruguel [2], C.M. Pradier [1]
[1]Laboratoire de Réactivité de Surface - UMR CNRS 7197, Université Pierre et Marie Curie, UPMC Paris 6, 4 place Jussieu, 75252 Paris Cedex 05 - Paris (France), [2]Institut des NanoScience de Paris, Université Pierre et Marie Curie, UPMC Paris 6, 4 place Jussieu, 75252 Paris Cedex 05 - Paris (France)

Peptides are versatile molecules, whose properties can be conveniently tailored through genetic engineering and chemical functionalization. For this reason they are employed as building blocks for functional materials with applications in nanotechnology, medicine and biotechnology[i].

The knowledge of amino acids (peptides subunits) adsorption processes on metallic surfaces is mandatory to implement peptides and proteins in these applications, but also to collect information on the obtained functional materials and to control the biointerfaces behavior[ii].

In this work, we examined the interaction mechanisms of aspartic acid and arginine, the main components of the polypeptide RGD (arginine-glycine-aspartic acid), with a Cu(110) single crystal surface. The molecular films have been obtained by means of an electrospray ionization source (ESI)[iii]: with respect to the traditional Knudsen cells, ESI allows an adsorption from an aqueous solution at room temperature, avoiding the high sublimation temperatures and all molecular damages related to them[iv].

The chemical state and the anchoring points of the molecules on the surface have been investigated with X-ray Photoelectron Spectroscopy (XPS) and Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-RAIRS). Scanning Tunneling Microscopy (STM) furnished complementary information about the structures of the adlayers.

We show that the adsorption occurs differently for the two molecules: via the amine reactive groups for arginine and via both the carboxylate and the amine reactive groups for aspartic acid. In accordance, they self-assemble in a very different way:

Aspartic acid creates islands of dimers showing a 2D pattern whose unit cell is disorientated from the crystallographic axes,
While arginine assembles in line along the Cu [001] direction.

Thus, for arginine the molecule-substrate interactions dominate on long-range distances, influencing the molecular arrangement along one of the crystallographic axis. Conversely, for aspartic acid, intermolecular interactions are predominant and are responsible for the dimerization process and the creation of extended 2D arrays.

References

[i] Costa et al., Surf. Sci. Reports, 2015, 70, 449-553

[ii] Barlow et al, Surf. Sci. Reports, 2003, 50, 201-341

[iii] C. Méthivier, V. Humblot, C.-M. Pradier, J. Phys. Chem. C, 2016, 120 (48), 27364-27368.

[iv] C. Méthivier, H. Cruguel, D. Costa, C.-M. Pradier, V.Humblot, Langmuir, 2016, 32 (51), 13759–13763.

SLI2-2O190

STABILITY OF IONIC LIQUID BASED ELECTROLYTES IN LITHIUM METAL BATTERIES INVESTIGATED BY OPERANDO X-RAY PHOTOEMISSION SPECTROSCOPY AND ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

J. Morales [1], C. Santini [2], R. Bouchet [3], A. Benayad [1]
[1]Université Grenoble Alpes & CEA, LITEN, Department of Nanomaterials, 17 rue des Martyrs, 38054 Cedex 09 - Grenoble (France), [2]CNRS-UMR 5265, 43 Bd du 11 Novembre 1918, 69616 - Villeurbanne (France), [3]LEPMI-INP Grenoble UMR 5279, 1130 rue de la Piscine, 38402 - St. Martin D'hères (France)

Lithium metal is the ultimate negative electrode due to its very high specific capacity (3860 $Ah.kg^{-1}$) and its very low oxidation-reduction potential ($E°_{Li^+/Li}$ = -3.03V / ESH). Nevertheless, heterogeneous electrodeposition during the charging process leads to the growth of dendrites causing short-circuit problems with the risk of premature battery failure and in the worst case thermal runaway and battery fire [1]. In this context, ionic liquids (IL) based electrolytes have been regarded as an alternative solution to overcome some of these problems due to their improved thermal and electrochemical stability, flame retardant and low vapor pressure [2, 3].

In this work, we propose an ex-situ study coupling X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) in order to get inside into the reaction mechanisms between two ILs based electrolytes, (1-Hexyl-3-methylimidazolium bis(fluorosulfonyl)imide) C_1C_6ImFSI and (1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) $C_1C_6ImTFSI$, and lithium metal during electrochemical tests. Figure 1 shows the chemical and morphological evolution through the XPS sulfur S 2p core level, SEM-Auger electron spectroscopy (AES) and the interface resistance change probed by EIS of lithium electrode in contact with C_1C_6ImFSI based electrolyte, aged in a coin cell configuration for 20 days. The lithium surface evolution upon cycling in IL based electrolytes will be discussed as well. In this work, the chemical surface evolution probed by ex-situ XPS will be compared to that acquired by the mean of operando XPS developed in the laboratory.

Figure 1. Chemical, morphological and electrochemical surface evolution studied by XPS, SEM-AES and EIS of lithium metal aged in C_1C_6ImFSI based electrolyte during 20 days in a coin cell configuration.

References

[1] W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang & J. Zhang, “Lithium metal anodes for rechargeable batteries”, Energy Environ. Sci., 2014, 7, 513-537

[2] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno & B. Scrosati, “Ionic-liquid materials for the electrochemical challenges of the future”, Nature Materials, 2009, 8, 621-629

[3] A. Basile, A.I. Bhat & A.P. O'Mullane, “Stabilizing lithium metal using ionic liquids for long-lived batteries”, Nature Communications, 2016, 7:11794

SLI1-3O250

QUANTITATIVE DETERMINATION OF ADSORBATES AND CHARGE ACCUMULATION AT METAL ELECTRODES WITH SPECTROSCOPIC ELLIPSOMETRY

C. Cobet, S. Vázquez Miranda, M. Chien, R. Sharif, K. Hingerl
Johannes Kepler University - Linz (Austria)

Currently, considerable effort is put on improving the microscopic understanding of electro-chemical reactions. This is triggered by economic and ecologic demands on energy harvesting solutions, where the development of efficient electro-catalytic reactions and the improvements of batteries play an important role. The key functionality is usually determined by atomic scale structural, chemical and physical properties of the solid-liquid interfaces. Unfortunately, most of the surface sensitive techniques, which are successfully used in UHV surface science, cannot be applied in liquid environments. Nevertheless, the progress in the development of scientific analytic tools for solid-liquid interfaces is significant. The electro-chemical scanning tunneling microscopy (EC-STM) and almost ambient pressure XPS are prominent examples. Another obvious approach is using optical methods in the transparency spectral range of either the electrode or the electrolyte. In the presented work we will demonstrate that the extremely high surface sensitivity of spectroscopic ellipsometery can be used to gain also quantitative information on the amount of surface adsorbates and the charge accumulation at metal electrodes. In our studies, we combine NIR-NUV ellipsometry with results of conventional CV, impedance spectroscopy, and EC-STM in order to study the surface of crystalline metal electrodes in-situ and quasi in-operando. In prove of principle examples we use single crystal copper and silver surfaces in various electrolytes. As an example the ellipsometric angle Delta is plotted in the figure in comparison to cyclic voltammetry (CV) for the copper (110) surface in HCl solution. A particular attention is drawn to catalytic electrochemical process like the hydrogen evolution reaction, where the overall transferred charge, as determined by CV, cannot be used to achieve information about respective surface changes. The latter reaction is actually studied intensively since decades but the fundamentals of the catalytic process are still controversially discussed.

SLI1-2O286

STRUCTURE/REACTIVITY RELATION DURING ELECTROCATALYTIC OXIDATION OF ETHANOL ON PALLADIUM

F. Carla [1], G. Fantappie [1], A. Lavacchi [2]
[1]*ESRF - Grenoble* (France), [2]*ICCOM - CNR - Firenze* (France)

Palladium based materials show an high catalytic activity towards ethanol oxidation reaction in alkaline environment. For this reason the possibility of using Pd as replacement for Pt in direct ethanol fuel cells has been investigated by a large number of research groups. It's known that the ethanol oxidation reaction is strongly affected by the formation and dissolution of surface Pd hydroxides and oxides, nevertheless the details behind the mechanism of action of oxidized species of Pd on its electrocatalytic activity is not yet completely understood. The lack of information regarding the role of surface Pd oxides during the ethanol oxidation reaction is mainly due to the fact that in-situ investigation of electrochemical processes is strongly limited by the presence of solvent and electrolyte. The possibility of using hard X-rays to detect structural changes and investigate surface modifications during electrochemical reactions offers a unique opportunity in real-time characterization of solid-liquid interfaces.

In this contribution we'll present the results of a recent in-situ Surface X-ray Diffraction experiment conducted at ID03 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble. X-ray Reflectivity, Grazing incidence small angle x-ray scattering and crystal truncation rods analysis have been used to characterize the structure of Pd(111) and Pd(100) single crystals during reaction conditions. The data show that the influence of ethanol on the potential of formation of a passivating oxide layer and the relation between surface roughness and catalytic activity.

SLI2-1O382

IONIC LIQUID BOUNDARY LAYERS AT A CHARGED GOLD SURFACE AS REVEALED BY NEUTRON REFLECTIVITY

S. Glavatskih [1], G. Pilkington [1], K. Harris [1], E. Bergendal [1], G. Palsson [2], A. Vorobiev [3], M. Rutland [1]

[1]*KTH Royal Institute of Technology - Stockholm* (Sweden), [2]*Uppsala University - Uppsala* (Sweden), [3]*ILL - Grenoble* (France)

Ionic liquids (ILs) have been identified as promising replacements for conventional lubricants due to their high chemical and thermal stability, low melting points and negligible volatility. Furthermore, their excellent conductivity and wide electrochemical windows present a new horizon for tribotronic lubrication solutions, whereby the friction coefficient is controllable though use of an electric field.1-4 However, high production costs and environmental concerns regarding fluorinated ions have largely limited commercialisation of IL lubricants.

To address these issues, a number of novel, non-halogen containing ILs have been developed5,6 that exhibit excellent tribotronic lubrication properties, both as neat lubricants and when added as lubricant additives.3,4 But to fully understand and harness these phenomena, an intimate understanding of the effect of an electrical potential on the interfacial structuring of ions in IL/solvent blends is required.

To this end, we have performed neutron reflectivity measurements to study the interfacial structuring of the non-fluorinated ionic liquid trihexyltetradecyl-phosphonium-bis(mandelato)borate ([P6,6,6,14][BMB]) at an electrified gold surface when dispersed in a polar solvent. Due to the wide variation in the scattering lengths densities of the different ions, our results provide a powerful structural probe of the interface region and reveal clear changes in the ionic composition of the interfacial region with applied potential. Such results provide valuable insight into the tribotronic properties of ILs and will hopefully help pave the way towards cost effective ionic liquid lubricant solutions.

Thanks/Acknowledgement

The Knut and Alice Wallenberg Foundation (Project number KAW2012.0078) and the Swedish Research Council (Project number 2014-4694) are gratefully acknowledged for their financial support.

References

1. S. Glavatskih. Tribotronics – Monitoring-based active friction control, Encyclopedia of Tribology, Springer (2013), 3906-3910. ISBN: 978-0-387-92896-8
2. H. Li, R. J. Wood, M. W. Rutland and R. Atkin, Chemical Communications, 2014, 50, 4368-4370.
3. P. Cooper, H. Li, M. W. Rutland, G. Webber and R. Atkin, Physical Chemistry Chemical Physics, 2016, 18, 23657-23662.
4. H. Li, A. E. Somers, P. C. Howlett, M. W. Rutland, M. Forsyth and R. Atkin, Physical Chemistry Chemical Physics, 2016, 18, 6541-6547.
5. F. U. Shah, S. Glavatskih, D. R. MacFarlane, A. Somers, M. Forsyth, O. N. Antzutkin, Physical Chemistry Chemical Physics, 2011, 13, 12865-12873.

6. O. N. Antzutkin, F. U. Shah and S. Glavatskih, US Patent 9518243, 2016.

SPEC - In situ spectroscopy

SPEC2-1O015

SPECTROSCOPIC OBSERVATION OF INTERFACE STATES AT SIO2/4H-SIC INTERFACE

Y. Yamashita [1], R. Hasunuma [2], T. Nagata [1], T. Chikyow [1]
[1]*National Institute for Materials Science - Tsukuba* (Japan), [2]*Tsukuba University - Tsukuba* (Japan)

Silicon carbide (SiC) has recently attracted a great deal of attention as a promising material for the next generation of power devices. For the SiO_2/SiC interface, the energy distribution of the interface states in the SiC whole-gap have not been observed even though the observation of the energy distribution of interface states is indispensable for further improvement of the electrical properties. We have recently developed a spectroscopic method to observe the energy distribution of interface states based on photoelectron spectroscopic measurements under bias voltage (PES-BA), that is, spectroscopic measurements under a bias voltage application between a metal layer and semiconductor substrate [1]. This method can be applied to observe the energy distribution of interface states in the SiC whole-gap region. In this study, we have investigated the energy distribution of interface states at the SiO_2/4H-SiC(0001) interface using PES-BA.

We used a Pt(10nm)/SiO_2(8nm)/4H-SiC(0001) structure. The PES-BA measurements were performed at BL15XU in SPring-8, one of the largest 3rd generation synchrotron facilities. For PES-BA measurements, the incident photon energy was 5.95 keV, while the total energy resolution was 240 meV.

For the interface states, two components were observed as shown the figure. One component was exhibited nearly uniform density in the entire SiC band-gap while another component was sharp interface states formed near the conduction band minimum. The interface states formed in the whole gap were attributed to large graphic carbon clusters. The interface state density observed near the conduction band minimum was proposed to Si_2-C-O state at SiO_2/SiC interface.

Thanks/Acknowledgement

This work is supported in part by a Grant-in-Aid for Scientific Research on Priority Areas, (Grant No. 17069006 and 23560033), from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] Y. Yamashita et al., J. Appl. Phys. 113, 163707 (2013)

SPEC2-2O143

IN SITU ATR-FTIR INVESTIGATIONS OF EARLY STAGES OF GAAS (001) AND (111)B SURFACE NITRIDATION

G. Monier [1], P.E. Hoggan [1], C. Robert Goumet [1], L. Bideux [1], D. Paget [2], P. Dumas [3], S. Kubsky [3]

[1]Université Clermont Auvergne, CNRS, Institut Pascal, F-63000 CLERMONT-FERRAND, FRANCE - Clermont Ferrand (France), [2]Physique de la matière condensée, Ecole Polytechnique, CNRS, Université Paris Saclay, 91128 Palaiseau, France - Palaiseau (France), [3]SOLEIL Synchrotron, BP48, L'Orme des Merisiers, 91192 Gif sur Yvette Cedex, France - Gif Sur Yvette (France)

Preparation of well-cleaned, stabilized and passivated surfaces is of relevant importance for the semiconductor processing and device performance. Indeed the passivation of III-V semiconductor surfaces and, in particular, GaAs is critical in enhancing the performance of devices since the defect states detrimentally affect the electronic and optical properties of the materials. In this way, the use of in situ real-time diagnostics is important to control the surface chemistry.

The aim of the present work was to perform Attenuated Total Reflectance-Fourier Transform Infra-Red spectroscopy (ATR-FTIR) investigations during N2 plasma treatment of GaAs surfaces at 500°C inside an UHV chamber using the high intensity light of SOLEIL synchrotron at SMIS beamline (Fig.1). Moreover this work uses the complementarities of DFT normal-mode frequency calculations with ATR-FTIR measurements to assist in the assignment of vibrations involving bonds to nitrogen atoms, especially by rendering partially amorphous the GaN layer (by removing the crystal symmetry constraint (a C4 axis here) and carrying out a couple of Car Parrinello steps in geometry optimization) as it was previously demonstrated [1].

s and p polarizations were used to study the evolution of the different GaN vibrations during the nitridation of GaAs for two surface orientations (001) and (111)B. Results show that normal stretch vibrations are always detected at the same frequency matching very well with the DFT calculations whereas other vibration modes (bridge and hollow stretch for GaAs(001) and tripod stretch and bend for GaAs(111)B) induced by the non-crystallinity of the GaN layer exhibit variable frequencies. Furthermore evolutions of these frequencies with the nitridation time give us much information on bond creations, especially at the very beginning of the process.

Thanks/Acknowledgement

The authors want to thank the CRRI of Clermont Auvergne University and IDRIS (CNRS calculation hours on ADA: 500 000h DARI N° i2016087351) for allowing machine time for the DFT calculations.

The authors want also to thank the synchrotron SOLEIL (run n° 20130721), especially the SMIS beamline for the FTIR measurements.

References

[1]G. Monier, L. Bideux, C. Robert-Goumet, B. Gruzza, M. Petit, J.L. Lábár, and M. Menyhárd, Surf. Sci. 606, 1093 (2012).

SPEC1-4O232

INTERFACE SEGREGATION IN PD/AU CORE/SHELL NANOPARTICLES PROBED BY SFG

A. Zakaria, A. Ouvrard, N. Alyabyeva, B. Bourguignon
ISMO, CNRS, Univ. Paris-Sud, Université Paris-Saclay - Orsay (France)

Binding molecules to nanostructures has become a hot topic for many applications where reduction of size to nanometer level matters like: sensors, energy, plasmonics, catalysis and molecular electronics. A decade ago very promising new surfaces like Al2O3/Ni3Al(111) have appeared which allow growing high density narrow size distributed NPs [1], particularly well adapted to study small cluster reactivity [2] and that may be used as a template for molecular electronic purposes. Probing adsorbed CO using surface-sensitive vibrational spectroscopy on nanoparticles (NP), provides an original way to understand NP size and composition effects on NP electronic and crystalline structure by addressing molecular-substrate and molecule-molecule couplings [3].

Vibrational Sum Frequency Generation (SFG) experiments have been conducted at 300 K on CO adsorbed on high-density, narrow size distributed core-shell (Pd/Au) NPs grown on ultrathin Al2O3 films on Ni3Al(111) done in UHV conditions. On bare Pd NPs: (i) CO bind on bridge sites and (ii) CO frequency is coverage and NP size-dependent as already observed [3]. For 1 monolayer (ML) thick Au shell, a new site is observed at higher frequency and narrower bandwidth, indicating a lower adsorption energy while bridge Pd sites have disappeared, confirmed by adsorption energy measurements. At mbar pressure, CO adsorbs on gold as expected. On the contrary for 2 and 3 ML thick Au shell, almost no CO are observed unless CO pressure is raised in the mbar range. New adsorption phase and non-reversible adsorption are observed.

New sites are attributed to CO bonded on isolated Pd which migrated from the Pd core towards Au shell surface upon CO adsorption [4]. Pd:Au alloy formation at the core/shell interface is significantly reduced for Au shell thicker than 2 ML. CO-NP interaction varies sensitively with Au shell thickness on Pd core. Adsorption energies is reduced and activation barriers are probably impacted and may affect the catalytic reactivity. SFG spectroscopy of CO on core/shell NPs allows measuring shell thickness with high precision and following structural changes.

Thanks/Acknowledgement

We gratefully acknowledge the French National Agency for Research (Agence Nationale pour la Recherche, ANR) for financial support through the JCJC program (Project LEMON - DS0305).

References

[1] G. Hamm et al., Nanotechnology 17 (2006) 1943-1947
[2] G. Sitja et al., Nano Lett. 13 (2013) 1977
[3] A. Ouvrard et al., J. Phys. Chem. C, 2017, 121 (10), pp 5551–5564
[4] L. Delannoy et al., ChemCatChem 2013, 5, 2707- 2716

SPEC1-1O239

AN IN-SITU NEAR AMBIENT PRESSURE PHOTOEMISSION ANALYSIS OF THE ELECTROCHEMICAL ACTIVATION OF A CATALYST SURFACE

J. Espinos [1], V. Rico Gavira [1], J.R. Sánchez Valencia [1], A. González-Elipe [1], A. Lucas Consuegra [2], J. González Cobos [3], V. Pérez Dieste [4], C. Escudero [4]

[1]Instituto de Ciencia de Materiales de Sevilla. - Sevilla (Spain), [2]Universidad Castilla-La Mancha - Ciudad Real (Spain), [3]Instituto de Ciencia de Materiales de Madrid. - Madrid (Spain), [4]ALBA Synchrotron light source - Barcelona (Spain)

Electrochemical promotion of catalysis entails the enhancement of the catalytic activity of metal catalysts through their surface decoration by promoting atoms injected from a solid electrolyte(1-2). In this work, we have used Near Ambient Pressure Photoemission to study in operando the surface composition of a K-doped Ni/ β-Al2O3 electrocatalyst, at 280ºC and under different atmospheres (UHV, up to 1mbar H2O, up to 1mbar HOCH3) and electrochemical states (injected current, polarization voltage, open circuit, etc.).

To this aim, Ni2p, Ni3p, O1s, K2p, C1s, K3p and Ni3d (VB) photoemission signals have been recorded in operando by excitation of the sample with photons of several energies (100 eV, 460 eV and 1170 eV).

We have shown that by galvanostatic and potentiostatic activation, potassium ions are reversibly reduced (oxydized) to metallic potassium at the Ni/Al2O3 interphase, from where they diffuse to the grain boundaries and outer surface of the nickel electrode. The evolution of the intensty of the K2p photoemission signal has been correlated with the current/voltage curves measured simultaneously, as a function of applied voltage, injected current and time.

Experiments carried out in vacuum or in the presence of water and methanol vapours show differences in the amount of potassium atoms at the surface and in their chemical state, that are attributed to electronic modifications induced by chemical interaction with adsorbed OH- and CH3O- groups.

In addition, under methanol atmosphere, a thin film formed by carbon and metallic potassium is deposited on the surface of the nickel eletrode. The kinetic of the growth of this film was study by following the intensity of Ni3p, C1s, K2p, K3p and Ni3d photoemission signals. Eventually, the thickness of this film rose in such an extent that the nickel electrode was fully buried. The binding energy and shape analysis of K2p and C1s signals and the K/C atomic ratio derived from them suggest that a KC6-like compound is formed. The valence band structure and the work function of this film under methanol vapour have also been determined.

Thanks/Acknowledgement

We thank financial support from MAT2016-79866-R project (AEI/FEDER, UE) and ALBA-CELLS Synchrotron Light Source (project 2016021561).

References

] C.G. Vayenas, S. Bebelis, C. Pliangos, S. Brosda, Tsiplakides D. Electrochemical Activation of Catalysis: Promotion, Electrochemical Promotion and Metal-Support Interactions. New York: Kluwer Academic Publishers/Plenum Press; 2001.

Lambert RM, Palermo A, Williams FJ, Tikhov MS. Electrochemical promotion of catalytic reactions using alkali ion conductors. Solid State Ionics. 2000;136-137:677-85

SPEC2-4O257

FIBTOFSIMS, AFM, SEM INTEGRATION INTO A SINGLE INSTRUMENT FOR 3D CHEMICAL IMAGING AT THE NANOSCALE

L. Pillatsch [1], F. Östlund [2], J. Michler [3]

[1]Empa (Swiss Federal Laboratories for Materials Science and Technology), Laborato-ry for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland - Thun (Switzerland), *[2]TOFWERK AG, Uttigenstrasse 22, CH-3600, Thun, Switzerland - Thun* (Switzerland), *[3]Empa (Swiss Federal Laboratories for Materials Science and Technology), Laboratory for Me-chanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland - Thun* (Switzerland)

Chemical and Physical sample properties often can’t be determined by a single analysis method. Therefore, the combination of complementary analysis methods is mandatory. A FIBSEM instrument is used for analysis methods based on electron and ion signals. The surface topography is measured by secondary electrons (SE) and in-situ atomic force microscopy (AFM) (Figure 1). The chemical composition and detection of trace elements is realized by time of flight secondary ion mass spectroscopy TOFSIMS.

The combination of these analysis techniques allows to define the exact location of sputtered particles of a complex sample in lateral direction by the scan position of the focused ion beam (FIB) and in depth by AFM measurement. 3D reconstruction of a sample composition can be realised.

In this presentation, the integration of AFM and SIMS capabilities in a FIBSEM instrument is shown. Parallel mass detection allows to locate the major composition as well as trace elements of the sample. The depth correction of a SIMS profile of a complex multilayer structure is realised by AFM imaging (Figure 2) [1].

Figure 1.: High vacuum AFM setup with the sample installed on the 10x10 mm range scanning table. The adjustment of the tip height is done by a piezo manipulator below the tip. Coarse motion of the tip to position the tip at the area of interest is realized by slip stick nanomanipulators. The inset picture shows an SEM image of the tip close to the surface.

Figure 2: Depth calibration (black line) of SIMS depth profile of a multilayer structure containing Al. The red line represents the depth profile as function of sputter time.

References

[1] J.A. Whitby et al, Advances in Materials Science and Engineering, 2012, article ID 180437

SPEC2-5O276

ENVIROESCA – ROUTINE SURFACE ANALYSIS UNDER ENVIRONMENTAL CONDITIONS

A. Thissen, D. Paul, B. Stephan
SPECS Surface Nano Analysis GmbH - Berlin (Germany)

Since many decades XPS (or ESCA) is the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools combine reliable quantitative chemical analysis with comfortable sample handling concepts, integrated into fully automated compact designs.

Over the last years it has been possible to develop XPS systems, that can work far beyond the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has become a fastly growing field in research inspiring many scientist to transfer the method to completely new fields of application. Thus, by crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP condtions.

Based on this experience SPECS Surface Nano Analysis GmbH has developed a revolutionary tool to realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA allows for different applications, like extremely fast solid surface analysis of degassing (but also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions.

After introduction of the technological realization a comprehensive survey of results will be given starting from standard solid conductive samples under different pressure conditions, bulk insulators with environmental charge compensation applied, high throughput analysis of batches of similar objects, geological samples, chemical analysis of pharmaceuticals to the comparative analysis of ultrapure liquid water with different aqueous solutions.

The application of Near Ambient Pressure XPS to biological specimen from plants and animals, biofilms and bacteria, as well as food samples is a completely new field for electron spectroscopic studies of the surface chemical composition.

An outlook is presented on the application to electrochemical and other in-operando devices.

Finally the influence of the ambient conditions on quantification in XPS will be demonstrated and discussed.

Thanks/Acknowledgement

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme.

SPEC1-2O284

LITHIUM-ION BATTERY ELECTRODE/ELECTROLYTE INTERFACE EVOLUTION INVESTIGATED BY OPERANDO X-RAY PHOTOEMISSION SPECTROSCOPY

A. Benayad [1], J. Morales [1], C. Santini [2], R. Bouchet [3]

[1]CEA, LITEN, Department of Nanomaterials, 17 rue des Martyrs - Grenoble (France), [2]CNRS-UMR 5265, 43 Bd du 11 Novembre 1918, 69616 - Villeurbanne (France), [3]LEPMI-INP Grenoble UMR 5279, 1130 rue de la Piscine, 38402 St. Martin d'Hères, - Grenoble (France)

Since the first studies regarding the chemical structure of solid electrolyte interface (SEI), origin of capacity fading in lithium ion-battery, surface analyses techniques have been extensively used. In this framework, several studies by ex-situ XPS were reported giving rise the chemical nature of the electrolyte degradation by-product. Hence, the ex-situ XPS analyses were carefully realized based on protocols involving sample protection from air contamination. These protocols, may alter the chemical structure during samples preparation. Hence, new approach based on operando XPS may overcome these problem and pave the way to new phenomena. In order to follow, by operando XPS, the chemical structure change of the SEI during the electrochemical process, several technical aspect must be taken in account, for instance, cell geometry and electrolyte vapor pressure. In this work, we will present an electrochemical cells adapted to the study of the interface electrode/electrolyte by the mean of in-lab operando XPS. Besides developing a compatible electrochemical cell for operando XPS studies, this new approach will be devoted to study the degradation process occurring at the interface between ionic liquid electrolyte (electrolyte with low vapor pressure) and composite electrodes (such us graphite and lithium metal) (Figure 1). Figure 1, shows the operando XPS of F1s and S2p peak registered at the surface of graphite electrode using as electrolyte a mixture of (1-hexyl-3-methylimidazolium (bis(trifluoromethanesulfonyl) imide) C1C6ImNTf2 and (Bis(trifluoromethane)sulfonimide lithium salt) LiNTf2 (1mol.L-1). Our result, registered during the first cycle, shows the formation of LiF, Li2S and reduced sulfur oxides species. To widen our picture of the mechanisms involved during the SEI formation in such system, a parallel ex-situ XPS will be presented.

The chemical structure evolution of the interface electrode/electrolyte in all solid lithium-ion battery will be shown as well.

Figure 1: Operando XPS of F1s and S 2p core peak registered at the interface IL/graphite electrode during the first electrochemical cycling of Li/ C1C6ImNTf2-LiNTf2/Graphite cell.

SPEC2-3O411

BAND ALIGNMENT ENGINEERING AT SEMICONDUCTOR HETEROINTERFACES USING IN-SITU PHOTOELECTRON SPECTROSCOPY

S. Siol [1], J.C. Hellmann [2], S.D. Tilley [3], M. Graetzel [4], J. Morasch [2], J. Deuermeier [2], W. Jaegermann [2], A. Klein [2]

[1]EMPA, Swiss Federal Laboratories for Materials Science and Technology - Dübendorf (Switzerland), *[2]Technische Universität Darmstadt, Institute of Materials Science, Surface Science Division - Darmstadt* (Germany), *[3]University of Zurich, Department of Chemistry - Zurich* (Switzerland), *[4]EPFL, Institut des Sciences et Ingénierie Chimiques, Laboratory of Photonics and Interfaces - Zurich* (Switzerland)

Energy band alignments at heterointerfaces play a crucial role in defining the functionality of semiconductor devices, yet the search for material combinations with suitable band alignments remains a challenge for numerous applications. In this work we demonstrate how changes in bulk defect chemistry can dramatically influence the functional properties of an interface, even within the same material system.

Often changes in deposition conditions influence interfacial properties just as much as the choice of materials itself. One striking example for this is the Cu_2O/ZnO interface, for which many different of values for the band offset have been reported[1]. In a systematic study we investigated the origin of this phenomenon. The energy band alignment at the heterointerface between Cu_2O and ZnO was studied using in-situ photoelectron spectroscopy with stepwise deposition of ZnO onto Cu_2O and vice versa. A total of seven interface experiments were carried out on Cu_2O/ZnO interfaces prepared with different deposition conditions and techniques[2]. A large variation of energy band alignment depending on the deposition conditions of the substrate and the film is observed, with valence band offsets ranging from ΔE_{VB}=1.45–2.7 eV. This variation of band alignment is accompanied by the occurrence or absence of band bending in either material. It can therefore be ascribed to a pinning of the Fermi level in ZnO and Cu_2O, which can be traced back to oxygen vacancies in ZnO and to metallic precipitates in Cu_2O, respectively. The intrinsic valence band offset for the interface, which is not modified by Fermi level pinning, is derived as $\Delta E_{VB}\approx 1.5$ eV, much lower than previously reported values in the literature. The results from this study explain the variation of ΔE_{VB} at the Cu_2O/ZnO interfaces reported here and in literature, but more importantly provide a general strategy to control the energy band alignment at semiconductor heterointerfaces that can be applied to many interesting material systems. With this in mind we discuss other promising material systems for such studies and demonstrate a novel high throughput approach for the screening of interfacial band alignments using combinatorial photoelectron spectroscopy[3], making band alignment engineering much more feasible and potentially paving the way for it to become part of routine semiconductor device development.

References

[1] Ichimura, M. *et al.* Japanese Journal of Applied Physics, 50 (5), 5100, 2011

[2] Siol, S. *et al.* ACS Applied Materials & Interfaces, 8 (33), 21824–21831, 2016

[3] Siol, S. *et al.* Advanced Materials Interfaces, 3 (24), 1600755, 2016

SPEC1-3O416

ELUCIDATING ATOMIC EVENTS IN CUXNI1-X/CEO2 (0 < X < 1) BIMETALLIC NANOPARTICLES

F. Bernardi [1], W. T. De Figueiredo [1], G. B. Della Mea [1], C. Escudero [2], V. Perez-Dieste [2]
[1]*Programa de Pós-Graduação em Física, Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS) - Porto Alegre* (Brazil), [2]*ALBA Synchrotron Light Source - Barcelona* (Spain)

The CO_2 molecule is the main responsible for the greenhouse effect. The increasing numbers associated to the amount of CO_2 emission in the atmosphere have attracted the attention of scientists aiming the discovering of new catalysts to CO_2 dissociation reaction. At the same time, several atomic events may influence the catalytic properties of such systems, like the Strong Metal-Support Interaction (SMSI) effect[1] and atomic rearrangement when the bimetallic nanoparticles are exposed to a gaseous atmosphere.[2] In this work, Cu_xNi_{1-x}/CeO_2 ($0 < x < 1$) nanoparticles were applied to the CO_2 dissociation reaction aiming to investigate the influence of the Cu/Ni ratio on the CO_2 dissociation reaction results. Moreover, the atomic events occurring in the nanoparticles were investigated during the reaction. The nanoparticles were synthesized as described previously.[3] Samples with mean particle diameter of (5+3) nm and different Cu/Ni ratios (as determined by TEM and EDS measurements) were obtained. The nanoparticles were exposed sequentially to a (i) H_2 atmosphere, (ii) $CO_2 + H_2$ atmosphere and (iii) CO_2 atmosphere at 500 ^{o}C. The reactions were followed by mass spectroscopy measurements to identifying the products of the reaction. In order to investigate the atomic events influencing the reaction results, a series of *in situ* measurements were used during the reaction. NAP-XPS measurements were performed by using Synchrotron Radiation at ALBA with 2 different photon energies of 1250 eV and 2000 eV. *In situ* XAS measurements at the Cu and Ni K edge and *in situ* time resolved XAS measurements at Cu K edge and Ce L_3 edge were performed at LNLS. The CO_2 dissociation results show the dependence of the dissociation rate with the Cu atomic population. Also, the formation of a Ni-rich shell is observed for the synthesized nanoparticles. The exposition of the system to a reducing (oxidizing) atmosphere allows an atomic rearrangement with Cu (Ni) migration to the surface of the nanoparticles. The SMSI effect was observed for some of the samples, being dependent on the Cu atomic population at the surface of the nanoparticles. These effects are related to the *in situ* XAS, *in situ* time-resolved XAS and CO_2 dissociation results.

Thanks/Acknowledgement

W.T.F., G.B.D.M., F.B. thank CNPq for the research grant. The authors thank ALBA, LNLS, CMM staff.

References

[1] S. J. Tauster et al, JACS, 100, 170 (1978).
[2] F. Bernardi et al, Cat. Today, 260, 95 (2016).
[3] L. P. Matte et al, J. Phys. Chem. C, 119, 26459 (2015).

SPECIAL SESSIONS

SS2.2-3O241

CHEMICAL STATE ANALYSIS USING AUGER PARAMETERS FOR XPS SPECTRUM CURVE-FITTED WITH STANDARD AUGER SPECTRA

M. Shima [1], K. Tsutsumi [1], A. Tanaka [1], H. Onodera [1], M. Tanemura [2]
[1]JEOL Ltd. - Tokyo (Japan), [2]Nagoya Institute of Technology - Nagoya (Japan)

The Auger parameter analysis is one of the useful methods to analyze chemical state of materials in XPS technique, because charge corrections are not necessary for non-conductive materials and Auger peaks are sometimes more sensitive to chemical states for some materials. [1]For the materials composed of two or more chemical states, however, it is difficult to identify corresponding peak positions precisely. In the previous work, we developed the curve fit calculation technique for Auger spectra analysis. In this technique, curve fitting was performed using standard Auger spectra, and the complicated chemical states were successfully identified [2]. Needless to say, this technique is applicable for X ray excited Auger spectra as well.In the present work, this curve fitting technique was applied for the chemical analysis of copper oxide complex composed of Cu_2O and CuO. 4 samples with different ratio of Cu_2O and CuO were analyzed using XPS system, JPS-9200 (JEOL Ltd.) with X-ray source of achromatic MgKa. The pass energy of the energy analyzer was set to be 10 eV in CAE (Constant Analyzer Energy) mode for Cu2p peak, whereas the retarding ration of 0.02 was employed in CRR (Constant Retarding Ratio) mode for Cu LMM Auger peak.The curve fitting calculation for Cu LMM peak was done using standard spectra of Cu_2O and CuO. Different ratio of Cu_2O and CuO for respective samples was obtained. For a comparison, Auger parameters were then calculated for respective samples with and without curve fitting of Cu LMM Auger peak. Auger parameters thus calculated were shown in fig.1. From the Auger parameters derived without curve fitting, identification of the precise chemical state was very difficult. By contrast, using Auger parameters derived with curve fitting, the component ratio of Cu_2O and Cu was determined. Thus, it is concluded that the Auger parameters derived from the curve fitting were promising for the chemical state analysis for the complicated complex systems.

References

[1] D. Briggs and J. T. Grant, Surface Analysis by Auger and X-ray Photoelectron Spectroscopy.

[2] K.Tsutsumi et al, Journal of the surface science society of Japan Vol. 33(2012), No8, pp.431-436

SS2.2-2O306

ANALYSIS OF ATMOSPHERIC PLASMA TREATED POLYPROPYLENE BY LARGE AREA TOF-SIMS IMAGING AND NMF

G. Ferraz Trindade, D.F. Williams, M. Abel, J.F. Watts
The Surface Analysis Laboratory - University of Surrey - Guildford (United kingdom)

Surface treatment of polymers has been extensively used to improve the performance of adhesion, biocompatibility and other surface-active processes. The most common used treatment methods are flame, plasma, corona discharge and more recently cold-atmospheric plasma. All commercial polymers are influenced by the surface segregation of minor components during or after treatment. Similar phenomena occur during the processing of a range of automotive grade polypropylene (PP) formulations. Such materials have amounts of ethylene propylene-diene monomer (EPDM) or other polymers such as polystyrene or polycarbonate incorporated in their formulation to improve impact resistance. The copolymer formulations are then filled with particles such as carbon black or talc and number of processing aids and other additives are used to improve behaviour and performance. The presence of such molecules at the surface of a polymer can have a deleterious effect on the desired application performance..

In this work we combined large area ToF-SIMS imaging with multivariate analysis methods in order characterise a cold-atmospheric plasma treatment of the surface of an automotive grade polypropylene. The results enabled the investigation of the spatial distribution of the treatment for different flame distances as well as the identification of surface-segregated additives. The ToF-SIMS analysis was carried out using a TOF.SIMS5 system from IONTOF GmbH (Münster, Germany) using 25 keV Bi_3^+ ion beam operated in the high current bunched mode delivering 0.3 pA and images were acquired using the stage raster mode. The total 1 x 1 cm^2 area contains 2000 x 2000 pixels which comprise of 20 x 20 patches of 500 x 500 μm^2 area each. The multivariate analysis followed a methodology previously described [1].

To acquire large area ToF-SIMS maps in an automated and quick manner, it is necessary to abdicate some adjustments such as height and reflector voltage correction at every patch measured. For this reason, the sample must be fairly homogeneous both in terms of charging and topography. The analysed polypropylene pellets are strong insulators and their surface were not perfectly flat within such large area range of analysis. This led ultimately to misaligned spectra at different pixels. The alignment of peaks is essential for accurate fragment identification and multivariate analysis. A few approaches to overcome the misalignment problem will be discussed.

Thanks/Acknowledgement

The authors wish to thank the Coordination for the Improvement of Higher Education Personnel - CAPES (project:11995-13-0)

References

[1] G.F. Trindade, M. Abel, and J. F. Watts, Chemometrics and Intelligent Laboratory Systems 163 (2017): 76-85.

SS2.1-5O061

QUANTITATIVE ANALYSIS OF SATELLITE STRUCTURES IN XPS SPECTRA OF GOLD, SILVER AND YTTERBIUM

N. Pauly [1], F. Yubero [2], S. Tougaard [3]
[1]*Université libre de Bruxelles - Brussels* (Belgium), [2]*Instituto de Ciencia de Materiales de Sevilla - Sevilla* (Spain), [3]*University of Southern Denmark - Odense* (Denmark)

The shape and intensity of the energy distribution of emitted photoelectrons in XPS experiments are strongly affected by both extrinsic excitations due to electron transport and intrinsic excitations induced by the sudden creation of the static core hole. These processes must be taken into account to quantitatively extract the primary excitation spectrum of the considered emission which includes all effects that are part of the initial photo-excitation process, i.e. lifetime broadening, spin-orbit coupling, and multiplet splitting. It was previously shown [1] that both extrinsic and intrinsic excitations could be included in an effective energy-differential inelastic electron scattering cross section for XPS which is then convoluted with the primary excitation spectrum to model the full XPS spectrum. We use this approach to determine the Au *4f*, Ag *3d*, and Yb *4d* primary photoemission spectra from the pure metals. For the Au *4f* and Ag *3d* emissions [2], we observe that the characteristic XPS shake-up features are not only due to photoelectron energy losses. We thus prove the existence of a double shake-up process characterized by a *4d* → *5s*/*5p* transition for Ag and a *5d* → *6s*/*6p* transition for Au. For Yb, we show that primary excitation of each Yb *4d* spin-orbit component is formed by a double peak separated by 8.8 eV and 0.43 branching ratio.

References

[1] N. Pauly, F. Yubero, S. Tougaard, Surf. Sci. 620 (2014) 17
[2] N. Pauly, F. Yubero, S. Tougaard, Appl. Surf. Sci. 383 (2016) 317

SS1.2-2O006

LARGE O-CLUSTER IONS AS SPUTTER BEAM FOR TOF-SIMS DEPTH PROFILING OF ALKALI METALS IN THIN SIO2 FILMS

S. Kayser [1], M. Kleine-Boymann [1], J. Zakel [1], S. Gruber [2], S. Krivec [2], H. Hutter [3]
[1]ION-TOF GmbH - Muenster (Germany), [2]Infineon Technologies Austria AG - Villach (Austria), [3]Vienna University of Technology - Vienna (Austria)

For many years, the acquisition of time of flight - secondary ion mass spectrometry (ToF-SIMS) depth profiles of alkali metals (mainly Li, Na, K) in insulating materials has been a challenge due to the presence of artefacts arising during the measurement procedure. For depth profiling of inorganic materials the sample erosion is commonly carried out using positive ions as O_2^+ or Cs^+, depending on the desired polarity of detected secondary ions. This approach, however, has an inherent drawback, since the impinging ions within the sputter cycles are generating positive charges in the near-surface region of the insulating sample. In combination with a grounded counter electrode, as for instance the sample holder, an electric field arises, in particular prominent in thin insulating films. Fast diffusors as positively charged alkali metals with small ion radii will immediately react on this electric field by migration towards the cathode, causing a distorted depth profile.

In literature several approaches and countermeasures have been proposed as for instance O_2^+ depth profiling at low temperatures or the use of a sputter beam consisting of C_{60} cluster ions.[1,2] However, up to now there is no efficient method which delivers artefact free depth profiles for alkali metal distributions in thin insulating films while preserving a high secondary ion yield by the signal enhancing effect of O_2^+ and having a reasonable erosion rate.

The use of large positively charged O-clusters as sputter beam combines all those advantages, enabling an effective acquisition of depth profiles with artefact free alkali metal distributions. On the one hand, the average energy per incoming sputter particle is reduced heavily due to the high number of O atoms per cluster ion. On the other hand, the net charge introduced in the insulator decreases in comparison to e.g. O_2^+, allowing a more efficient compensation of surface charges.

In this presentation, the use of large O-cluster ions is demonstrated using the example of thin SiO_2 layers (200 nm), deposited on a Si substrate and implanted by alkali metal ions. Such films are frequently in use for semiconductor products or coatings of a variety of materials, indicating the strong need for a fast and effective way to record artefact free alkali metal distributions in insulators.

References

[1] S. Krivec, Th. Detzel, M. Buchmayr, H. Hutter, Appl. Surf. Sci. (2010), 257, 25
[2] D. Kobayashi, Y. Yamamoto, T. Isemura, Surf. Interface Anal. (2013), 45, 113

SS2.1-1O025

DIRECT MEASUREMENT OF GDOES CRATER DEPTH WITH BUILT-IN DIFFERENTIAL INTERFEROMETER

P. Chapon, S. Gaiaschi, S. Richard
HORIBA - Palaiseau (France)

Pulsed RF Glow Dicharge Optical Emission Spectrometry (GDOES) is a well known Ultra Fast Elemental Depth Profiling Technique.

The specificities of the GD plasma (high density, low average energy of the sputtering particles) have also make it in addition an interesting tool to reveal structures for SEM observation and EBSD measurements.In addition the change of plasma gas from the classical Ar to a gas mixing with O addition (patents 50829322 (EP2434275A1) have permitted to sputter thick polymeric layers with excellent depth resolution in order to access to embedded interfaces below organic coatings.

Up to now, GD was relying either on the use of external profilometers to provide the mandatory depth information needed (not an easy task for multilayered coatings as the sputtering rate was continuously changing from layer to layer) or on sputtering rate tables only available for well known simple materials.

The calculations were therefore not offering sufficient flexibility and accuracy for unknown samples or in case of unexpected variations in the layer composition or density.

The use of Differential Interferometry allows for continuous direct crater depth measurement along with the elemental depth profile analysis. This technique developed and patented by HORIBA Scientific can be considered as a major breakthrough for GD-OES as all the information, depth and elemental, is now delivered in a single experiment. The principle and figures of merit of “DIP” (Differential Interferometry Profiling”) will be described.

DIP is also extending the use of GD-OES as a layer thickness measurement technique ideal notably for non transparent layers where Spectroscopic Ellipsometry is more suited for optically transparent ones.

References

S. Gaiaschi, S. Richard, P. Chapon. Accurate depth measurements in GDOES with an on line Interferometer (submitted to JAAS – special issue on GD)

SS1.2-3O044

XPS INVESTIGATION OF MONATOMIC AND CLUSTER ARGON ION SPUTTERING OF TANTALUM PENTOXIDE

M. Baker [1], R. Simpson [1], R. White [2], J. Watts [1]
[1]*University of Surrey - Guildford (United kingdom),* [2]*Thermo Scientific - East Grinstead (United kingdom)*

Inorganic thin films are employed in a vast range of functional devices. Knowledge of their chemical composition as a function of depth is vital in fulfilling the process-structure-properties relationship required to optimise thin film growth conditions and hence functional properties. The use of monatomic Ar for depth profiling through such layers have proved a valuable tool over many years for the surface analyst despite sputtering induced effects leading to preferential sputtering and other ion beam induced effects observed in the XPS spectra for many materials. The introduction of Ar gas cluster ion beams (GCIB) as a new sputtering source on XPS instruments offers new possibilities in depth profiling and its capabilities in depth profiling inorganic materials needs to be explored. This work presents GCIB depth profiles through 30 nm thick Ta2O5 layers grown on Ta foil (European standard BCR-261T). XPS depth profiles using monatomic Ar+and Ar(1000)+ cluster ions have been performed at different incident energies. The preferential sputtering of oxygen induced using 6 keV Ar(1000)+ ions is lower relative to 3 keV and 500 eV Ar+ ions. Ar+ ions exhibit a steady state O/Ta ratio through the bulk oxide but Ar(1000)+ ions show a gradual decrease in the O/Ta ratio as a function of depth. The depth resolution and etch rate is substantially better for the Ar+ beam compared to the Ar(1000)+ cluster beam. Higher O concentrations are observed when the underlying Ta bulk metal is sputtered for the Ar1000 + profiles compared to the Ar+ profiles. These results will be discussed in the light of: (i) known Ar+ ion beam induced effects for Ta2O5 [1]; (ii) the difference in ion-solid interactions between Ar+ and Ar(1000)+ [2]; (iii) known material properties of the Ta2O5/Ta system [3].

Thanks/Acknowledgement

The authors would like to acknowledge the financial support of EPSRC [grant number EP/G037388/1] and Thermo Scientific. The authors would also like to thank Chris Deeks, Dr Tim Nunney and Dr Paul Mack (Thermo Scientific) for technical support and data acquisition and acknowledge the useful discussions with Roger Webb, Professor of Ion Beam Physics (University of Surrey) regarding data interpretation.

References

[1] S.Hofmann, J.M.Sanz, Journal of Trace Microprobe Technology, **1** (1982) 213

[2] I.Yamada *Materials Processing by Cluster Ion Beams, History, Technology and Applications,* CRC Press (2015)

[3] G.P.Klein Journal of the Electrochemical Society, **119** (1972) 1551

SS2.1-3O186

SURFACE AND DEPTH PROFILING OF SOFT ORGANIC THIN FILMS. X-RAY PHOTOELECTRON SPECTROSCOPY STUDY

T. Bendikov [1], S.J. Hutton [2], R. Balgley [1], G. De Ruiter [1], M. Lahav [1], M.E. Van Der Boom [1]
[1]Weizmann Institute of Science - Rehovot (Israel), [2]Kratos Analytical Ltd - Manchester (United kingdom)

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials and thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. In general, XPS is limited to probe the top <15 nm of a sample, and for thicker structures a digging-like etching process is needed.

Recent advances in depth profiling of organic and biological materials are based on sputtering with large Argon ion clusters (Ar^{n+}).[1] Unlike monoatomic ions (Ar^+), large cluster ions do not penetrate deeply into the material, therefore sputter material from the near-surface region only, leaving the subsurface layers undisturbed and undestroyed.

Here we present two examples of successful XPS depth profiling of composite metal-organic architectures self assembled on the pyridine terminated silicon/ ITO substrates. The samples consist of four main components: metal complexes ($[M(mbpy\text{-}py)_3][PF_6]_2$, M = Ru (**1**) or Os (**2**); $Pd(PhCN)_2Cl_2$ (**3**) and (1,4-bis[2-(4-pyridyl)ethenyl]benzene, **BPEB**, (**4**) spacer molecules.

The first system (*Figure 1*) was prepared by sequential immersion of the substrate in solution **1** (alternating with solution **3**) (4 layers) followed by **2** (alternating with **3**) (4 layers). Each layer is ~ 6 nm thick, thus the consequent total thickness of the organic film reaches 40-50 nm.[2]

In the second example (*Figure 2*) molecular assemblies consist of different layers of metal complexes **1** and **2**, separated by repetitive spacers **4** alternated with **3**. Total thickness of the analyzed **[Ru-BPEB$_{12}$-Os]** assembly is ~20 nm.[3]

Figure 1. *Schematic Representation of the System I.*

Figure 2. *Schematic Representation of the System II.*

References

1. P. J. Cumpson et. al., *Surf. Interface Anal.*, **2013**, 45, 1859-1868.
2. G. de Ruiter et. al., *J. Am. Chem. Soc.*, **2013**, 135, 16533-16544.
3. R. Balgley et. al., *J. Am. Chem. Soc.*, **2016**, 138, 16398-16406.

SS2.1-2O218

MONATOMIC AND CLUSTER ARGON ION XPS DEPTH PROFILING OF SRTIO3 AND HFO2

M. Baker [1], P. Mack [2]

[1]University of Surrey - Guildford (United kingdom), [2]Thermo Scientific - East Grinstead (United kingdom)

Metal oxide thin films are employed in a wide variety of functional applications. There is currently strong technological interest in strontium titanate ($SrTiO_3$) and hafnium oxide (HfO_2) due to their specific band gaps and high dielectric constants. $SrTiO_3$ is being studied for use in photocatalysis, energy storage and electronic sensors, whilst HfO_2 is widely employed for optical coatings and optoelectronic device applications. Thin films of $SrTiO_3$ and HfO_2 have been deposited onto silicon substrates using atomic layer deposition. XPS depth profiles have been performed through the thin films using both monatomic and cluster argon ion bombardment. The monatomic Ar^+ profiles were performed using an incident ion energy of 500 eV and the gas cluster ion beam (GCIB) profiles were recorded using 8 keV Ar_{300}^+ and 8 keV Ar_{150}^+ for $SrTiO_3$ and HfO_2 respectively. For HfO_2, the optimum results were found when the GCIB was incident upon the sample at an angle of 70° to the surface normal. These GCIB conditions yielded excellent retention of the original $SrTiO_3$ and HfO_2 stoichiometry during the profile, with evidence of only minor preferential sputtering or ion beam induced reduction (see figures below). However, using 500 eV Ar^+ resulted in the preferential sputtering of oxygen leading to the presence of sub-oxide states in the XPS spectra of Ti in $SrTiO_3$ and Hf and HfO_2. The depth resolution was similar between the monatomic and cluster ion depth profiles for both thin film materials. Using the same incident ion beam angle, the etch rate for 8 keV Ar_{300}^+ was only 2.5 times lower than that for 500 eV Ar^+. The results will be discussed in the light of known ion beam effects when sputtering metal oxide materials.

SS2.1-4O234

SOFT AND PROGRESSIVE SPUTTERING OF A MONOLAYER GROWN ON INDIUM PHOSPHIDE.

D. Aureau, M. Fregnaux, M. Bouttemy, J. Vigneron, A.M. Gonçalves, A. Etcheberry
Institut Lavoisier de Versailles, UMR 8180 UVSQ– CNRS - Versailles (France)

X-Ray photoelectron spectroscopy (XPS) gives information about the nature and the chemical environment of the atoms situated at surfaces. The analyzed depth is between 1 to 10 nm, which raises two issues for ultrathin films. (i) The adventitious carbon at the surface could provide a non-negligible contribution, which may make the result interpretation delicate. (ii) The XPS signal is not only coming from the top surface but also from the layers underneath. Therefore, in order to obtain an analysis not disturbed by the organic contaminations on top of the samples and to have access to the depth-distribution of the detected elements, ion bombardment is used to clean and profile the objects. Nevertheless, the traditional ion etching with mono-atomic argon ions tends to modify some thin layers, as organic or oxide thin films, which makes challenging the analysis. On the other hand, a bombardment with gas cluster ion beam, where the energy per atom is small, is hoped to induce less damages for any surfaces. The capacity to remove only the carbon contamination upon first sputtering steps and then to control progressive atoms by atoms etching is really promising to investigate various ultrathin films such as monolayers on surfaces for example.

The aim of this paper is to investigate the effect of cluster-beam bombardment on a model system, a "polyphosphazene-like" film grown on Indium Phosphide substrate by electrochemical treatment in liquid ammonia. Recently, it has been shown that one monolayer thick phosphazene film can be grown by chronoamperometry.1 In this paper, XPS depth profiling with argon cluster ion source is performed and help to understand the unique XPS ratios obtained for such thin films. Unlike “standard” sputtering technique using monoatomic ions, a gentle progressive digging of the thin layer has been evidenced. Several improvements are obtained by using this soft abrasion process. Moreover, such analysis will undoubtedly indicate essential properties of this ultrathin film. Indeed, as it will be shown, the really high XPS atomic percent obtained for carbon atoms on this carbon-less ultrathin film is not related with high organic contamination but intrinsic properties of the chemicals bonds involved in this film creating a strong attenuation of the photoelectron underneath. Due to its unique depth-profiling features, the gas cluster ion beam bombardment offers new insights in the chemical and physical analysis of sensitive surfaces as ultrathin covering layers.

References

[1] Gonçalves et al. App. Surf. Sci. 2016 , 391, 44-48

SS1.2-5O342

MOLECULAR DEPTH PROFILING WITH A NEW HYBRID SIMS INSTRUMENT FOR IMPROVED MOLECULAR IDENTIFICATION

S. Kayser, A. Pirkl, R. Moellers, H. Arlinghaus, E. Niehuis
ION-TOF GmbH - Muenster (Germany)

The characterisation of organic layer systems is of increasing interest in many research areas. Since the application of large argon clusters as sputter species in SIMS, depth profiling of almost all organic materials has become feasible whilst retaining the intact molecular information during the profile.

However, molecular identification of unknown substances, e.g. contaminants, can be hampered by constraints in mass resolution and mass accuracy of a standard TOF analyser. To overcome this problem, we have developed a new Hybrid SIMS instrument, which uniquely combines all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of a Q Exactive^{TM} HF mass analyser. The Q Exactive^{TM} HF provides a mass resolution of more than 240,000 @ m = 200 u, < 1 ppm mass accuracy, and full MS/MS capabilities for structural analysis of complex molecules.

In this contribution, we will introduce the new instrument and discuss applications from various fields including organic electronics. We will demonstrate how the extremely high mass resolution of the Q Exactive^{TM} HF mass spectrometer can be used to resolve essential peak interferences which cannot be separated in a standard TOF-SIMS instrument. We will also show examples of structural analysis using the high-performance MS/MS capabilities and discuss the new possibilities of the unique TOF / Q Exactive^{TM} HF combination.

SS1.2-4O402

DETERMINING BULK AND INTERFACE CHEMICAL DAMAGE REGIMES IN XPS DEPTH PROFILING USING CLUSTER ION BEAMS

B. Schmidt, J. Newman, J. Moulder, J. Mann
Physical Electronics - Chanhassen, Mn (United States of America)

The development of gas cluster ion beams (GCIB) has provided fresh opportunities to study materials that exhibit chemical changes under monatomic argon ion bombardment during surface cleaning or depth profiling. This is especially important as mixed inorganic/organic structures are increasingly used in applications such as OLED display devices and medical implants.

Several variables are available to fine tune cluster energy and size, which provides high levels of control to the user, but can present an overwhelming parameter space for practical use. Previous studies have shown that there is a relationship between the GCIB energy/atom and observed chemical changes. In the case of bulk HfO_2, Barlow [1] observed that no change in Hf 4f peaks was detected for argon GCIB settings of 6 eV/atom, whereas a decrease to 2 eV/atom was required to minimize reduction in InAs. In a similar study on HfO_2, we observe similar results. By varying beam conditions, no Hf 4f reduction is observed at nominal 5.6 eV/atom, but reduction is seen while profiling with a nominal 8 eV/atom beam. We discuss bulk and interface effects under these various conditions. For example, while no reduction is observed in bulk HfO_2 at 5.6 eV/atom, reduced Hf oxide species are observed near the Si substrate, broadening the observed HfO_2/Si interface. We have investigated several other material systems, including Ti compounds and polymers, to provide guidance on general user settings.

References

[1] AJ Barlow, JF Portoles, PJ Cumpson. Observed damage during Argon gas cluster depth profiles of compound semiconductors. J App Phys 116, 054908 (2014)

SS1.1-3O219

HIGH RESOLUTION SECONDARY ION MASS SPECTROMETRY ON THE HELIUM ION MICROSCOPE: APPLICATIONS AND CORRELATIVE ASPECTS

P. Philipp, J.N. Audinot, F. Vollnhals, D. Dowsett, T. Wirtz
Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, Luxembourg Institute of Science and Technology (LIST), 41 rue du Brill, L-4422 Belvaux, Luxembourg (Luxembourg)

High resolution imaging and nanofabrication became possible with the development of the helium ion microscope (HIM) with ultimate resolutions down to 0.5 nm for the He+ beam and few nm for the Ne^+ beam.[1] With the development of a compact mass spectrometer as an add-on tool for the HIM, the lack of analytical techniques on the latter could be overcome by allowing secondary ion mass spectrometry to be performed. By adding reactive gas flooding, high resolution and high sensitivity can be obtained at the same time.[2]

We will present the progress in instrument and method development for HIM-SIMS as well as the newest data for several applications related to thin films and coatings, batteries, solar cells, hard materials and wear protection solutions, and soil. Lateral resolutions below 15 nm and hence approaching the dimensions of the collision cascade have been obtained[3,4] (see as an example Figure 1 showing Co distributions obtained from a WC-Co sample with 10 µm and 3 µm fields of view). Correlating secondary ion images with secondary electron (SE) images allows to improve or facilitates data analysis by gaining topography information and higher resolution structural information from the SE images, but goes along with possible pitfalls depending on the approach which is chosen for image fusion. This will also be discussed in detail.

References

[1] L. Scipioni, C.A. Sanford, J. Notte, B. Thompson, and S. Mcvey, J. Vac. Sci. Technol. B 27, 3250 (2009).

[2] T. Wirtz, P. Philipp, J.-N. Audinot, D. Dowsett, and S. Eswara Moorthy, Nanotechnology 26, 434001 (2015).

[3] T. Wirtz, D. Dowsett, and P. Philipp, in Helium Ion Microsc., edited by G. Hlawacek and A. Golzhäuser (Springer Berlin / Heidelberg, 2016), pp. 297–323.

[4] P. Gratia, G. Grancini, J.-N. Audinot, X. Jeanbourquin, E. Mosconi, I. Zimmermann, D. Dowsett, Y. Lee, M. Grätzel, F. De Angelis, K. Sivula, T. Wirtz, and M.K. Nazeeruddin, J. Am. Chem. Soc. jacs. 6b10049 (2016).

SS1.1-2O352

HOW TO OBTAIN SPATIAL CHEMICAL INFORMATION FROM TITANIUM OXIDE HYBRID FILMS MEASURED BY X-RAY PHOTOELECTRON IMAGING WITH NOVEL DATA TREATMENT METHODS?

V. Fernandez [1], S. Bechu [1], J. Walton [2], N. Fairley [3], M. Richard-Plouet [1]
[1]Institut des Matériaux Jean Rouxel (IMN), CNRS, University of Nantes - Nantes (France), *[2]TSTC Ltd, TQ14 8NE - Teignmouth* (United kingdom), *[3]Casa Software Ltd, Bay House, TQ14 8NE - Teignmouth* (United kingdom)

Understanding the chemical information at the surface of thin films is key to predict the behavior of materials, especially where the surface evolves under different stimuli. A hybrid gel [1,2] based on titanium oxide was deposited as thin films and shows evolution under in situ UV illumination with the reduction of Ti(IV) to Ti(III) and the appearance of an intermediate band in its band gap. We measured the relevant XPS core levels using a parallel XPS analyzer. Due to the very low intensity by each pixel, data were analyzed using an outlier filter, Singular value decomposition (SVD), conversion image to spectrum, adding together spectrum from pixels with similar chemical information, fitting and converting components back into images Fig [1]. Mathematic tools and time saving computational procedures were developed to improve the quality of data sets partitioned into spatial and energetic data bins allowing successful improvement of spectroscopy and both elemental and chemical mapping of the surface [3].

References

[1] T. Cottineau, M. Richard-Plouet, A. Rouet, E. Puzenat, H. Sutrisno, Y. Piffard, P.-E. Petit, L. Brohan, Photosensitive Titanium Oxo-polymers: Synthesis and Structural Characterization, Chem. Mater. 20 (2008) 1421–1430.

[2] T. Cottineau, A. Rouet, V. Fernandez, L. Brohan, M. Richard-Plouet, Intermediate band in the gap of photosensitive hybrid gel based on titanium oxide: role of coordinated ligands during photoreduction., J. Mater. Chem. Mater. Energy Sustain. 2 (2014) 11499–11508.

[3] S. Béchu, M. Richard-Plouet, V. Fernandez, J. Walton, N. Fairley, Developments in numerical treatments for large data sets of XPS images, Surf. Interface Anal. 48 (2016) 301–3090

SS1.1-1O354
XPS IMAGING OF 2D-MATERIALS

O. Renault [1], H. Kim [2], M. Frégnaux [3], D. Ferrah [1], M. Gay [1], N. Fairley [4], M. Jamet [5]
[1]Univ. Grenoble Alpes, F-38000 Grenoble, France - CEA, LETI, MINATEC Campus, F-38054 Grenoble, France (France), *[2]EPFL* (Switzerland), *[3]UVSQ* (France), *[4]Casa Software* (United kingdom), *[5]Univ. Grenoble-Alpes, F-38000 Grenoble, France - CEA-SPINTEC, F-38054 Grenoble, France* (France)

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as MoS_2, WSe_2, …) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and kPEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection). The examples will range from graphene doping [1] and cleaning [2], to single layer MoS2 [3-4], including also novel materials and 2D heterostructures.

Thanks/Acknowledgement

This work was performed at the Platform For Nano-Characterization of CEA-MINATEC.

References

[1] H. Kim, O. Renault et al., Appl. Phys. Lett. 105, 011605 (2014).
[2] D. Ferrah, O. Renault et al., Surf. Interface Anal. 2016, 48, 451-455.
[3] M. Frégnaux, O. Renault et al., Surf. Interface Anal. 2016, 48, 465-469.
[4] H. Kim, M. Frégnaux, A. Kis, O. Renault, et al., Phys. Rev. B 34, 081401 (R) (2016).

SS2.2-5O125

A NEW INSTRUMENTATION FOR COMBINED XRF AND XPS ANALYSIS FOR A QUANTITATIVE SURFACE CHARACTERIZATION OF SILICON SPHERES

E. Beyer [1], M. Kolbe [2], M. Müller [2], R. Fliegauf [2]

[1]*Physikalisch-Technische Bundesanstalt - Braunschweig* (Germany), [2]*Physikalisch-Technische Bundesanstalt - Berlin* (Germany)

The SI unit kilogram will be redefined in terms of fundamental constants based on the Planck constant h, whose numerical value can be obtained through the Avogadro constant N_A. For this reason N_A is determined through the number of atoms in two isotopically enriched monocrystalline ^{28}Si-spheres. For an accurate result the mass of the surface layer on the ^{28}Si-spheres has to be determined.

A novel instrumentation built up by the Physikalisch-Technische Bundesanstalt combines X-ray fluorescence spectroscopy and X-ray photoelectron spectroscopy [1] in order to enable the characterization and quantification of the oxide layer and unintentional contaminations. The instrumentation is equipped with a ball manipulator, giving the opportunity to measure on each point of a spherical sample surface.

The absolute quantification of the mass deposition of the full sample surface is achieved by reference-based XRF. Reference samples with various oxide layer thicknesses have been characterized with synchrotron radiation based reference-free X-Ray Spectrometry [2] and a calibration curve for the mass deposition of oxygen was derived. Comparing the measurements to the calibration curve gives information about the mass deposition of oxygen on the sphere. Since the surface layer consists not only of silicon oxide but also of carbonaceous contamination and water, information about the chemical binding states of the elements and the elemental composition gained from the XPS is used to determine the value of the surface layer mass. Measurements on spheres have been carried out including a mapping of the complete surface of a sphere. The distribution of the individual surface layer components (e.g. oxygen mass deposition cf. the figure) has been determined as well as the total mass of the surface layer.

References

[1] Müller M, Beckhoff B, Beyer E, Darlatt E, Fliegauf R, Ulm G, and Kolbe M 2017 Quantitative surface characterization of silicon spheres by combined XRF and XPS analysis for determination of the Avogadro constant *Metrologia* (submitted March 2017)

[2] Hönicke P, Holfelder I, Kolbe M, Lubeck J, Pollakowski-Herrmann B, Unterumsberger R, Weser J, Beckhoff B 2017 Determination of SiO2 and C layers on a monocrystalline silicon sphere by reference-free X-ray fluorescence analysis to be submitted to Metrologia

SS2.2-4O357

WORK FUNCTION MEASUREMENT BY PHOTOELECTRON SPECTROSCOPY

J. Kim
Korea Research Institute of Standards and Science - Daejeon (Korea, republic of)

VAMAS TWA2 (Surface Chemical Analysis) has several on-going projects in three different subjects such as Scanning probe microscopies, Electron optical spectroscopies, and Mass spectroscopies. Among them, the work function (WF) measurement (Project A20) was initiated two year ago.

The WF is the minimum energy to remove an electron from solid to vacuum, ie. energy difference between vacuum level (E_{VAC}) and Fermi level (E_F). The value is not a characteristic of bulk material but rather a surface property determined by crystal face or surface condition. This is one of the reasons to deal with under the guideline of TWA2 or ISO-TC201 (Surface Chemical Analysis). The application of WF measurement is wide among many optical and electronic devices because the WF controls charge injection/collection efficiency at interfaces as well as emission properties of conventional electron emitters. This is why many scientific and technical research papers often refer to the WF. There are several different ways of the WF measurement, such as thermionic emission, photoelectric effect, and Kelvin probe. Even though each method has strong and weak points, the photoelectron spectroscopy is the most primarily utilized one because of its reliability and versatility. Thus, the International Standard will provide the procedure of WF measurement of a specimen by photoelectron spectrometer such as ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

During the last years of inter-laboratory study, common materials (Au, Ag, and Cu foils) with measurement protocol were distributed to seven laboratories in four different countries. The comparison results will be summarized and presented in this talk. Finally the prospect of international standard establishment will be discussed in terms of reference sample and measurement method.

Thanks/Acknowledgement

This work is supported by Nano Material Technology Development Program (2014M3A7B6020163) of MSIP/NRF.

SS2.2-1O137

SCOPEFOUNDRY: AN OPEN ENVIRONMENT FOR EXPERIMENTAL MICROSCOPY AND SURFACE SPECTROSCOPY

D. Ogletree, E. Barnard, D. Durham
Molecular Foundry, Lawrence Berkeley National Lab - Berkeley (United States of America)

Spectromicroscopy methods, which combine microscopic or nanoscopic imaging with spectroscopic analysis, are critical tools in physics, chemistry, materials and nano science research. Both lab-designed and commercial instruments involve the integration of multiple software-controlled sub-systems, and overall system performance is often limited by software. The limits of vendor-provided software often make it difficult to fully exploit the technical capabilities of the hardware systems, while lab-developed software can have a steep learning curve, little or no documentation, and stability problems.

We are developing the “ScopeFoundry” software environment at the Molecular Foundry to address these challenges.[1] ScopeFoundry is an open-source, cross-platform project based on modern scientific Python, the Qt graphical environment, and HDF5 data storage. In this talk we will describe the architecture of ScopeFoundry and describe three different use-cases: Scanning Auger Microscopy, Scanning Cathodoluminescence Microscopy, and 3-Dimensional Optical Lifetime Tomography.

ScopeFoundry is based on Hardware Components and Measurements. The Hardware Component (HC) wraps an instrument or subsystem with Python. We have HCs for lasers, optical and electron spectrometers, SEMs, CCD cameras, data acquisition and FPGA devices. A Measurement uses one or more HCs, includes a Qt graphical interface and HDF5 datafiles. The framework automates many aspects of HC initialization, user interface generation and saving of metadata.

The Scanning Auger Microscope is a commercial system. With ScopeFoundry we have taken over control the SEM column and electron energy analyzer. We capture raw analog and digital data. This allows us to add new capabilities such as drift correction, hyperspectral Auger imaging and reflection electron-energy loss mapping.

The Cathodoluminescence system combines a commercial SEM with lab-designed in-vacuum nano-positioned collection optics and external detectors and spectrometers, all of which can be controlled by ScopeFoundry for advanced materials characterization.[2]

The 3D lifetime microscope is a lab-built system for 2-photon photoluminescence lifetime tomography [3] combining an ultrafast laser system, optics and sample scanning stages, photon counting detectors and PicoHarp timing electronics, again controlled by ScopeFoundry.

Thanks/Acknowledgement

This work was supported by the Molecular Foundry, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

1) Introduction at www.scopefoundry.org, source code at https://github.com/ScopeFoundry

2) Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites, C.G. Bischak et al., Nanoletters 17 (2017) doi: 10.1021/acs.nanolett.6b04453

3) 3D Lifetime Tomography Reveals How CdCl2 Improves Recombination Throughout CdTe Solar Cells, E.S. Barnard et al., Adv. Mat. 29 (2017) doi: 10.1002/adma.201603801

SUF - Surface functionalization

SUF2-2O042

OXIDATIVE TREATMENT EFFECTS ON TIH2 POWDERS

P. Soltani [1], **S. Kaciulis** [1], **A. Mezzi** [1], **G. Lapi** [2], **R. Montanari** [2], **M. Richetta** [2], **A. Varone** [2], **G. Barbieri** [3]

[1]ISMN–CNR, P.O. Box 10, 00015 Monterotondo Stazione - Rome (Italy), [2]Department of Industrial Engineering, University of Rome "Tor Vergata", 00133 - Rome (Italy), [3]ENEA, Centro di Ricerche Casaccia, 00123 - Rome (Italy)

Metal hydrides are used in a wide variety of technological applications: hydrogen storage, recovery and separation of hydrogen, in energy conversion systems based on thermo-chemical cycles. Titanium hydride (TiH_2) is a brittle powder, which is highly reactive when exposed to heat or strong oxidizers. Namely due to its high reactivity, TiH_2 powder is widely applied in pyrotechnics, initiator squibs and igniters. In addition, TiH_2 is used as a blowing agent to prepare aluminium foams and to bond metals with non-metals [1,2]. All the industrial applications of TiH_2 are based on its decomposition and consequent hydrogen release. Since TiH_2 phase transformations strongly affect its decomposition and the hydrogen release rate depends on the surface structure of TiH_2 particles [3], the knowledge of these aspects is of basic importance to control hydrogen desorption and consequently the industrial processes.

In present work, the surface of TiH_2 powders has been analyzed after different heat treatments in air realized by changing time and temperature. Hydrogen release during heating was investigated by temperature programmed desorption (TPD), whereas the crystalline phases were examined by X-ray Diffraction (XRD). X-ray Photoelectron Spectroscopy (XPS) was used to characterize the chemical states of the surface layers of the treated TiH2 particles. By using the XPS depth profiling focused onto only one selected particle of about 40 microns in diameter was determined the oxide thickness after different heat treatments. Obtained results permitted to determine the oxide layer thickness and its dependence on the parameters of oxidative treatment.

Keywords: titanium hydride, oxidative heat treatment, XPS, XRD.

References

[1] M. Gambini, M. Manno, M. Vellini, *Int. J. Hydrogen Energy*, **33** (2008) 6178.

[2] H.T. Hall, U.S. Patent, 2728651, 1955.

[3] G. Lapi, C. Alvani, F. Varsano, et al., *Mat. Sci. Forum*, **879** (2017) 2032.

SUF1-4O085

BIODEGRADABLE SURFACE MODIFICATION BY POLYMERIZATION PERFORMED BY INK-JET PRINTING FOR THE DEVELOPMENT OF BIODETECTION SYSTEMS.

A. Forget, G. Mattana, G. Anquetin, B. Piro, V. Noël
Laboratoire Interfaces, Traitements, Organisation et Dynamiques des systèmes, UMR CNRS 7086, Université Paris Diderot, 15 rue Jean Antoine de Baïf, 75205 Paris Cedex 13, France. - Paris (France)

Biosensors are nowadays essential tools for health and environmental applications. Organic Field-Effect Transistors (OFETs) have been extensively used for the fabrication of biosensors.[1,2] Since most of the materials used for the fabrication of OFETs is solution-processable, fabrication of OFET-based biosensors becomes particularly attractive if realized on low-cost substrates using ambient-conditions printing techniques.

Cellulose is an inexpensive, biodegradable and renewable resource present in numerous daily life items. Nevertheless, this porous, hydrophilic substrate needs several treatments to be used as a substrate for the fabrication of electronic devices. Dip-coating, a treatment commonly employed to obtain cellulosic printable substrates, compromises the cellulose biodegradability and leads to undifferentiated surface modification, preventing printing of inks with different wetting characteristics. To finely and locally tune both cellulose porosity and surface energy, we propose to develop an ink-jet printing (IP) methodology based on reactive inks. We developed an innovative cellulose functionalization method that benefits from IP coupled to Atom Transfer Radical Polymerization (ATRP). IP permits the cellulose substrate local modification while ATRP is compatible with different monomers and leads to controlled molecular weight polymers.[3]

Cellulose functionalization is performed by employing diazonium chemistry under ambient conditions and low time scale using IP process. The grafted diazonium gives an initiator coat thanks to a photoactivatable bond to realize a grafting-from polymerization (ATRP) of hydrophobic monomers (Figure 1). The efficiency of monomer grafting and controlled radical polymerization is evaluated by XPS and MEB studies. Our preliminary results show that localized tuning of cellulose surface properties is possible and pave the way for the fabrication of all-IP biodetection systems entirely realized on biodegradable, bulk cellulosic substrates.

Thanks/Acknowledgement

We thank the LabEx SEAM (Science and Engineering for Advanced Materials and Devices) of Sorbonne Paris Cite in the frame of the project P2M, CNRS and the University Paris Diderot.

References

[1] D. Wang et al., Electronics, 2016, 5, 9.
[2] L. Kergoat et al., Adv. Mater. 2014, 26, 32.
[3] J.-S. Wang et al., 1995, 28, 7901-7910.

SUF1-1O118

LOW PRESSURE PLASMA, UV PHOTO AND WET CHEMICAL MODIFICATION OF GRAPHENE AND CARBON NANO TUBES

W. Unger [1], A. Lippitz [1], R. Illgen [1], C. Ehlert [2], P.L. Girard-Lauriault [3], I. Donskyi [4], R. Haag [5], M. Adeli [5]

[1]BAM - Berlin (Germany), [2]BAM/University of Potsdam - Berlin (Germany), [3]BAM/McGill University Montreal - Berlin (Germany), [4]BAM/Free University Berlin - Berlin (Germany), [5]Free University Berlin - Berlin (Germany)

Graphene is a two-dimensional carbon network with unique properties, including high mechanical stiffness, strength, and elasticity, outstanding electrical and thermal conductivity, and many others. Despite these advantages, its low solubility, poor reactivity and the limited accessibility of a well-defined basal plane are major challenges for applications. An ideal method to overcome these problems is the covalent attachment of functional molecules to its surface which enables further reactive modifications for specific applications. There is a number of different technologies for surface functionalization of graphene and related CNT materials. However, to get control on the functionalization process and to optimize the performance of the modified surfaces analytical tools for surface chemical characterization are required. X-ray absorption (NEXAFS) and photoelectron spectroscopy (XPS) have been identified to be rather powerful here [1-3]. Specifically NEXAFS spectroscopy underpinned by quantum chemical spectrum simulations [4] is unique in a way to address changes of aromaticity and defect formation at the graphene surface during functionalization.

For relevant surface modification technologies, we present examples on how NEXAFS and XPS can perform well. All presented modifications aim on the production of platforms for defined functional 2D nanomaterials, as for example multifunctional hybrid architectures. In detail, we investigated:

- Graphene and carbon nanotube functionalized by a Vacuum-Ultraviolet (VUV) induced photochemical process in NH_3 or O_2 atmospheres in order to introduce amino or hydroxy functionalities, respectively.

- Br bonding on r.f. cw low pressure plasma brominated graphite surfaces by using Br_2 and bromoform as plasma gases.

- A wet chemical method for covalent functionalization of graphene sheets by a one-pot nitrene [2+1] cycloaddition reaction under mild conditions. Here a reaction between 2,4,6-trichloro-1,3,5-triazine and sodium azide with thermally reduced graphene oxide (TRGO) results in defined dichlorotriazine-functionalized graphene sheets.

Thanks/Acknowledgement

We acknowledge support by the team at the BESSY II synchrotron radiation facility in Berlin, Germany as well as Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group.

References

[1] P.-L. Girard-Lauriault et al., Appl. Surf. Sci., 258 **2012** 8448-8454, DOI: 10.1016/j.apsusc.2012.03.012

[2] A. Lippitz et al., Surf. Sci., 611 **2013** L1-L7, DOI: 10.1016/j.susc.2013.01.020

[3] A. Faghani et al., Angew. Chemie (International ed.), 56 **2017** 2675-2679, DOI:10.1002/anie.201612422

[4] C. Ehlert et al., Phys.Chem.Chem.Phys., 16 **2014** 14083-14095, DOI: 10.1039/c4cp01106f

SUF2-4O135

EFFECTS OF NANOPORE CONFINEMENT ON THE SUPERCRITICAL CO2 GRAFTING OF ORGANIC MOLECULES ON SILICA SURFACES

S. Sananes Israel [1], D. Rébiscoul [1], A. Ayral [2]
[1]Institut de chimie séparative de Marcoule (ICSM) - Bagnols-Sur-Cèze (France), [2]Institut Europeén des Membranes (IEM) - Montpellier (France)

Surface functionalization of silica has been widely studied for microelectronics, chromatography and wastewater treatment. Moreover, supercritical carbon dioxide (SC CO_2) is a good solvent for grafting a large variety of organic molecules. In fact, its high diffusivity and its zero surface tension provide a significant advantage over liquid solvents facilitating the access to nanostructures and to nanoporous media. This is of great interest for applications related to selective retention of heavy metal cations.

In this study, we have grafted three molecules in nanoporous silica materials: (3-mercaptopropyl)trimethoxysilane, N-(3-(trimethoxysilyl)propyl)ethylenediamine and (3-iodopropyl)trimethoxysilane. However, this last molecule is very interesting since it can be post-functionalized in many ways [1]. Our approach summarized in the figure below, was first to develop the grafting process on silicon wafer activated by a HNO_3 pretreatment. Afterwards, ordered nanoporous silica thin films (S2D) and powders (SBA-15), having 2D hexagonal mesostructures and synthetized by a sol-gel method, were grafted using the optimized experimental protocols.

The efficiency of the grafting process was controlled by X-ray reflectivity and contact angle measurement for thin film samples and by Small Angle X-ray Scattering (SAXS), N_2 adsorption-desorption, FTIR and solid-NMR spectroscopies for powder samples.

Results showed that a complete grafted silica surface on silicon substrate is obtained at 60°C, 100 bars and 15 minutes. For S2D thin films the grafting process was extended to 24 hours. The increase of critical angle in the X-ray reflectivity curves enable to attest of a partial or complete surface functionalization of the nanopores wall. Similar conditions were used for SBA-15 powder. N_2 isotherms and SAXS show that the grafting on SBA-15 does not modify the porous structure but decreases the main pore size in agreement with the length of the grafted molecules. Also, it is the first time that the SC CO_2 grafting process of (3-iodopropyl)trimethoxysilane is performed in nanoporous silicas. Thus opens new perspectives for post-grafting of other moieties such as highly selective phosphonate groups

References

[1] R. Corriu, J. Alauzun, A. Mehdi, C. Reye, New J. Chem. 31 (2010) 911–915

SUF2-3O148

EXPLORING THE NATURE OF THE SUBSTRATE-MOLECULE INTERFACE IN SAMS BY DFT CALCULATIONS AND ARXPS EXPERIMENTS

C. Passiu [1], A. Rossi [2], M.T. Weinert [3], W.T. Tysoe [4], N.D. Spencer [1]

[1]ETH Zürich, Department of Materials - Zürich (Switzerland), [2]Università degli Studi di Cagliari, Dipartimento di Scienze Chimiche e Geologiche - Cagliary (Italy), [3]University of Wisconsin-Milwaukee, Department of Physics - Milwaukee (United States of America), [4]University of Wisconsin-Milwaukee, Department of Chemistry - Milwaukee (United States of America)

The formation of self-assembled monolayers (SAMs) is among the simplest and most versatile of methods for surface functionalization. A commonly studied system is that formed by alkanethiols on gold. Despite the great insights gained in the last decades about its properties, there is still a lack of understanding of the S-Au adsorption site and geometry.

The difficulty in identifying the S-Au interface structure is due to the interface being buried below the SAM alkyl chains and therefore not directly observable. The large number of atoms in the system and the presence of complex van der Waals' interactions make it problematic to draw reliable conclusions from DFT optimizations or energy comparisons. Other commonly used methods for adsorption geometry identification, such as the simulation of STM images and comparison with experiments, are useful in the case of small adsorbed molecules, but cannot unambiguously be applied to large ones.[1]

In the present study, we used DFT to calculate the core-level shifts (CLSs) of Au4f electrons of SAMs adsorbed on Au(111) according to different geometries, in order to compare them to experimental angle-resolved X-ray photoelectron spectroscopy (ARXPS) values. This method has the advantages of not completely relying on geometry optimizations and of considering an experimental property that is directly measurable, such as the Au4f binding energy.

Three different geometries have been modelled using methylthiolate as the adsorbed molecule. Bare Au(111) surfaces were also modelled for comparison(Fig.1).

ARXPS spectra were acquired on both bare gold surfaces and SAM-functionalized gold surfaces. The former showed the presence of the two expected components at positions that were in perfect agreement with the DFT results.

The latter, when fitted with two components without position constraints, showed a different CLS for the second component with respect to the case of bare gold, indicating that such a difference is detectable. The resolution achieved by laboratory XPS does not allow an unambiguous three-component fitting as suggested by the DFT results.

This method is not limited to thiols on gold but could find application for interface structure identification of any other system of molecules adsorbed on a solid surface.

References

(1) Hakkinen,H. Nat.Chem 2012,4,443-455.

SUF1-3O207

FUNDAMENTAL INVESTIGATIONS ON THE REACTIVITY OF IMINE GROUPS WITH TFAA

M. Kehrer [1], **J. Duchoslav** [2], **C. Munise** [1], **H. Andreas** [1], **A. Mehic** [3], **T. Stehrer** [3], **D. Stifter** [1]
[1]Center for Surface and Nanoanalytics (ZONA), Johannes Kepler University - Linz (Austria), [2]Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH (CEST) - Wiener Neustadt (Austria), [3]Fronius International GmbH - Wels (Austria)

Chemical derivatization (CD) is known as a powerful method for advanced surface characterization with X-ray photoelectron spectroscopy (XPS), especially when functional groups with similar binding energies coexist on the surface (e.g. after plasma treatment) [1]. One of the best-known CD agents is trifluoracetic anhydride (TFAA), typically used for labeling hydroxyl groups. Unfortunately, TFAA features a very low selectivity and in addition reacts with several other functional groups, including amine, epoxy or imine groups. Due to the very limited knowledge on this topic [2], the reaction of imine groups with TFAA was investigated in detail.

For this study, surfaces with two different types of imine were prepared from poly(allyl amine) using a vapor phase reaction with a fluorine tagged aldehyde and for the first time with a fluorine tagged ketone, as depicted in the given reaction scheme. The prepared imine samples were initially characterized by XPS (reference samples) and then derivatized using TFAA. Interestingly, the performed derivatization reaction did not lead to the formation of simple N-trifluoroacetamides. Instead, rather complicated products containing in addition trifluoroacetoxy (for imine derived from the aldehyde) or 3,3,3-trifluoro-1-propen-2-yl groups (imine from ketone) were identified by us, considering data from [3]. Nevertheless, these products prove useful for selective identification of imine groups in XPS. An essential part of the presented work was also denoted to substantial improvements of the individual derivatization reactions, i.e. for converting the amine into imine groups and to the reaction of TFAA with amine and imine groups. In this context, a yield of almost 100% could now be reached for both reaction types by using a proper catalyst and optimized reaction conditions. Thus, the gained complex knowledge on the improved individual derivatization reactions as well as on the imine reaction products is now applicable for a more efficient characterization of surfaces by CD-XPS.

References

[1] Batich, C. D. (1988). Applied Surface Science, 32(1–2), 57–73

[2] Klages, C. P., Khosravi, Z., & Hinze, A. (2013). Plasma Processes and Polymers, 10(4), 307–312.

[3] Breederveld, H. (1960). Recueil, 79(4), 401–407

SUF2-5O212

PROBING CHEMICAL INTERACTIONS BETWEEN ORGANIC CONVERSION COATINGS AND ALUMINIUM OXIDE WITH HIGH LATERAL RESOLUTION: AN

F. Cavezza [1], S. Pletincx [1], M. Boehm [2], H. Terryn [1], T. Hauffman [1]

[1]Department of Materials and Chemistry, Research group Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2 - 1050 Brussels (Belgium), [2]C-TEC Constellium Technology Center, 725 rue Aristide Bergès, Centr'Alp - 38341 Voreppe (France)

The use of aluminium in the automotive industry has increased tremendously in the last years. Due to its low density, this metal has a high potential for weight saving, thus improving vehicle fuel efficiency while reducing the total greenhouse gas emission throughout the life of the vehicle. To enhance adhesion and improve the corrosion resistance, the aluminium oxide surface is commonly treated with a conversion coating. Among the different conversion coatings, organophosphorus and acrylic based coatings are used. However, what type of bonds aluminium oxide is forming with the organic overlayer is not clear yet. Obtaining more information on these interfacial interactions is necessary for the further understanding and optimisation of these hybrid systems.

Industrial organic conversion coatings contain a wide mixture of different monomer compounds. In this work, a model system of acrylic and phosponic monomers of interest were deposited separately on a well-characterized reference substrate. Infrared spectroscopy (IR) is commonly used to probe the interaction between the substrate and an organic film [2] [3]. However, due to the optical diffraction limit, the lateral resolution of a conventional IR spectroscopy is in the order of tens of µm in the mid-IR range. The use of an AFM probe to obtain spectroscopic data (AFM-IR) provides a powerful tool to obtain chemical analysis and compositional mapping on the nanoscale level . By comparing AFM-IR spectra from the bare aluminium oxide and the monomer-coated aluminium oxide, it is possible to pinpoint the interfacial interactions of the substrate and the different functional groups in the final system. AFM-IR is used to identify how the different functional groups are binding with the aluminium oxide at the interface with nanoscale lateral resolution. We show topographic and chemical maps obtained with resonance-enhanced AFM-IR to characterise thin organic layers.

The ability to locally probe the interaction between the organic coating and the aluminium oxide, without the need of vacuum surface sensitive techniques, increases the understanding, and hence the tuneability, of the organic coatings/aluminium-oxide interface.

References

[1] Karl Wefers, et al. U.S. Patent, US5132181 A (1990)

[2] Pletincx, S.; Trotochaud, L.; Fockaert, L.-L.; Mol, J. M. C.; Head, A.; Karslıoğlu, O.; Bluhm, H.; Terryn, H.; Hauffman, T. Sci. Rep. 2017, 7 (45123).

[3] M. Brogly, Y. Grohens, C. Labbe, J. Schultz, International Journal of Adhesion and Adhesives, Volume 17, Issue 3, 1997, 257-261,

SUF1-2O289

SELF-ASSEMBLED MONOLAYERS ON MGO - BRIDGING THE GAP FROM UHV TO REAL LIFE APPLICATIONS

M. Killian, E. Anastasiou, P. Schmuki
Friedrich-Alexander University Erlangen-Nürnberg - Erlangen (Germany)

The lightweight material magnesium exhibits excellent physical and mechanical properties which make it valuable in a number of applications. These include automotive, aerospace, audio and electronic industries as well as implant technology. One of the main challenges in the use of pure magnesium is its poor corrosion resistance. An effective solution to prevent corrosion is coating the material to provide protection by forming a barrier layer between the metal and its environment. The surface can be protected without altering the material's general properties, e.g., by applying a protective self-assembled monolayer (SAMs) of organic molecules.

The surface of Mg materials will consist of MgO under atmospheric conditions. Most studies on the adsorption of molecules to MgO are conducted in ultra-high vacuum,[1] few on polished, oxidized Mg discs.[2] We observed in our initial experiments that the self-assembly of molecules on sputtered MgO samples significantly differs from the adsorption to polished MgO, which is likely to be caused by the hydroxylation of the latter. Thus, we studied the hydration of sputtered layers of MgO to $Mg(OH)_2$ by exposure to water vapor under controlled conditions and performed modification of the hydrated samples with functional organic molecules comprising carboxylic acid anchor groups. The adsorption of a Co-porphyrin (Co-TCPP) and stearic acid to samples of different hydration grade was investigated with the surface analytical techniques time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-Ray photoelectron spectroscopy (XPS) as well as contact angle measurements. The adsorption showed to be strongly dependent on the degree of hydration.

Thanks/Acknowledgement

The authors would like to thank the DFG research unit FOR1718 FunCOS "Functional Molecular Structures on Complex Oxide Surfaces" for funding.

References

1 e.g., Mohr, S.; Döpper T.; Xu, T.; Tariq, Q.; Lytken, O.; Laurin, M.; Steinrück, H-P.; Görling, A.; Libuda, J., Organic Linkers on Oxide Surfaces: Adsorption and Chemical Bonding of Phthalic Anhydride on MgO(100). Surface Science 2016, 646, 90-100.

[2] M.S. Killian, S. Seiler, V. Wagener, C. Ebensperger, B. Meyer, P. Schmuki, "Attachment of ethoxysilanes to hydroxylated magnesium surfaces", ACS Appl. Mat. Interf. 2015, 7, 9006.

SUF2-1O356

LIQUID-PHASE MONOLAYER DOPING OF INGAAS WITH SI-, S- AND SN-CONTAINING ORGANIC MOLECULAR LAYERS

J. O'connell, R. Duffy, J.D. Holmes
Department of Chemistry, University College Cork, Ireland - Cork (Ireland)

InGaAs is a promising potential future channel material for complementary metal-oxide semiconductor (CMOS) applications due to its direct band gap and high electron mobility. These materials require shallow and abrupt dopant profiles. S, Si and Sn are typical dopants of choice for n-type doping of InGaAs. Monolayer doping (MLD) is a relatively new technique that has been applied to materials such as Si and Ge.[1-3] A schematic depicting a general MLD process is shown in **Figure 1**. Conventional doping methods e.g. ion implantation can cause crystal lattice damage that is difficult to rectify. Additionally, ion-implantation is incompatible with tightly-pitched 3D nanodevices such as FinFETs.

The functionalization and subsequent monolayer doping of $In_{0.57}Ga_{0.43}As$ substrates using a Sn-containing molecule and a compound containing both Si and S was investigated. Epitaxial InGaAs layers were grown on InP waters and functionalised with both S and Si using mercaptopropyltriethoxysilane (MPTES) and with Sn using allyltributylstannane (ATBS). The surfaces were characterized using X-ray photoelectron spectroscopy (XPS). The surfaces were capped and subjected to rapid-thermal annealing to cause in-diffusion of dopant. Dopant diffusion was monitored using secondary ion mass-spectrometry (SIMS). Due to the As-dominant surface chemistry, the resistance of the functionalized surfaces to oxidation in ambient conditions over periods of 24 hours and 1 week was elucidated using XPS by monitoring the As 3d core-level for the presence of oxide components.

Thanks/Acknowledgement

We acknowledge financial support from Science Foundation Ireland (Grant: 14/IA/2513). We thank Dr Emanuele Pelucchi and the EPN Group at the Tyndall National Institute for providing InGaAs substrates and for helpful discussions.

References

1. O'Connell, J.; Biswas, S.; Duffy, R.; Holmes, J. D. Chemical Approaches for Doping Nanodevice Architectures. Nanotechnology **2016**, 27 (34), 342002
2. O'Connell, J.; Collins, G.; McGlacken, G. P.; Duffy, R.; Holmes, J. D. Monolayer Doping of Si with Improved Oxidation Resistance. ACS Appl. Mater. Interfaces **2016**, 8 (6), 4101–4108
3. O'Connell, J.; Verni, G. A.; Gangnaik, A.; Shayesteh, M.; Long, B.; Georgiev, Y. M.; Petkov, N.; McGlacken, G. P.; Morris, M. A.; Duffy, R.; and Holmes, J.D. Organo-Arsenic Molecular Layers on Silicon for High-Density Doping. ACS Appl. Mater. Interfaces **2015**, 7 (28), 15514–15521

TFC - Thin films and coatings

TFC2.3-4O005

PLASMA POLYMER FILMS EXHIBITING VERTICAL CHEMICAL GRADIENTS

P. Rupper [1], M. Vandenbossche [1], L. Bernard [2], D. Hegemann [1], M. Heuberger [1]
[1]Laboratory for Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology - St. Gallen (Switzerland), *[2]Laboratory for Nanoscale Materials Science, Empa, Swiss Federal Laboratories for Materials Science and Technology - Dübendorf* (Switzerland)

Controlling the balance between stability and functional group density in plasma polymer films (PPF) is the key to diverse applications such as drug release, tissue-engineered implants, filtration, sensors. The usage of highly functional PPF is often limited by their stability in air or aqueous environments due to mechanisms like molecular reorganization, oxidation and hydrolysis [1,2,3]. Stabilization is achieved by enhancing cross-linking at the cost of the terminal functional groups. To overcome such limitations, a structural and chemical gradient was introduced perpendicular to the surface plane [4,5]. This vertical gradient is composed of a highly cross-linked subsurface structure, gradually changing into a more functional nanoscaled surface termination layer (see Figure).

The gradient layer was achieved using CO_2/C_2H_4 discharges with decreasing power input and increasing gas flow ratio during plasma polymer deposition. Aging behavior and stability was studied in air and in different aqueous environments using complementary characterization methods including angle-resolved X-ray photoelectron spectroscopy (ARXPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Simple models for the oxygen depth distributions were studied. A fast hydrophobic recovery, followed by midterm radical reactions and progressive hydrolysis reactions under non-neutral pH conditions were identified.

Compared to homogeneous plasma polymer structures, it was found that in air and in neutral water, the gradient films are stabilized over a period of at least one week. Changes in the oxygen depth profiles have been observed at pH 4 and pH 10 showing structural and chemical aging effects on different time scales. The use of vertical gradient plasma polymer nanofilms represents a novel approach providing improved surface hydrophilicity with significant reduced aging effects, thus opening the possibility for applications in diverse changing environments.

References

[1] S.Swaraj, U.Oran, A.Lippitz, J.F.Friedrich, W.E.S.Unger, Plasma Processes Polym. 4 (2007) S784-S789.

[2] C.López-Santos, F.Yubero, J.Cotrino, A.R.González-Elipe, ACS Appl. Mater. Interfaces 2 (2010) 980-990.

[3] M.Drabik, J.Kousal, C.Celma, P.Rupper, H.Biederman, D.Hegemann, Plasma Processes Polym. 11 (2014) 496-508.

[4] D.Hegemann, E.Lorusso, M.I.Butron-Garcia, N.E.Blanchard, P.Rupper, P.Favia, M.Heuberger, M.Vandenbossche, Langmuir 32 (2016) 651-654.

[5] P.Rupper, M.Vandenbossche, L.Bernard, D.Hegemann, M.Heuberger, Langmuir, DOI:10.1021/acs.langmuir.6b04600.

TFC2.3-3O034

CHIRAL X-RAY DICHROISM AND INDUCED SPIN FILTERING EFFECTS IN ORGANIC THIN FILMS

M. Niño Orti [1], F.J. Luque [2], P. Gargiani [3], I.A. Kowalik [4], D. Arvanitis [5], J.J. De Miguel [2]

[1]Instituto Madrileño de Estudios Avanzados IMDEA-Nanoscience - Madrid (Spain), [2]Dpt. Física de la Materia Condensada - Madrid (Spain), [3]ALBA-CELLS Synchrotron - Barcelona (Spain), [4]Polish Academy of Sciences - Warsaw (Poland), [5]Dpt. Physics - Uppsala University - Uppsala (Sweden)

Chiral surfaces open the door, from a technological point of view, to use different properties like chiral selectivity, enantiospecific chemical reactions [1] or the possibility to use these materials as spin filters [2]. Chiral structures, and in particular chiral molecules, are fascinating objects in many areas: in Physics the relationship between chirality and magnetism has puzzled researchers since the 19th century, and only in the 21th century we have learn to make use of this relationship, for example using the ability of chiral layers to scatter electrons differently depending on their spin.

We have used synchrotron based spectroscopic techniques (XAS, XPEEM, spin polarized UPS) to study the influence of the chirality on the magnetism. We have grown monolayer-thick films of 1,2-diphenyl-1,2-ethane diamine (DPEDA) and 1,2-diphenyl-1,2-ethane diol (DPED) on Cu(001) and on Co/Cu(100) surfaces in UHV by Molecular Beam Epitaxy (MBE). This molecule has two chiral centers and presents two enantiomers, which are designated according to their conformation and optical activity as (R,R)-(+)-DPED/A and (S,S)-(–)-DPED/A. We observe clearly dichroic features (natural circular dichroism) by measuring the absorption by the molecular film of circularly polarized X-rays (XAS) of opposite helicity, at the carbon K edge. This dichroic asymmetry depends on the chirality (opposite sign for the two enantiomers) showing the preservation of the chiral character of these molecular thin films in the electronic structure upon adsorption.

The effect of this chiral molecular film adsorbed on ferromagnetic cobalt has been measured though XMCD at the Co L-edges, showing a change in the magnetic moment in the cobalt atoms at the surface, with the implication of a charge transfer with spin polarization.

More indeed, we have observed macroscopic spin polarizations in electron currents photoemitted from molecular films of DPED and DPEDA adsorbed on Co/Cu(100) surfaces, showing that chiral molecules in a non-spiral geometry can filter spin electrons [2]. These measurements also show that the different enantiomers of the same molecule can produce spin polarizations oriented along different directions in space [3].

Thanks/Acknowledgement

We acknowledge to MAX-lab staff for their help, the support from ALBA Synchrotron for the experiments performed at Boreas beamline (proposal ID 2016021627), and the support of the MICCINN/MINECO (Spain) through the program MAT2014-59315-R.

References

[1] A. Gellman et al., J. Am. Chem. Soc. **135**, 19208 (2013).

[2] B. Göhler et al., Science **331**, 894 (2011).

[3] M. A. Niño et al., Adv. Mat. **26**, 7474 (2014).

TFC1-1O062

STUDY OF THE AU-CR BILAYER SYSTEM USING X-RAY REFLECTIVITY, GDOES AND SIMS

P. Jonnard [1], M.H. Modi [2], K. Le Guen [1], N. Aneshwari [2], M. Sinha [2], M. Idir [3], P. Chapon [4], A. Galayries [5]

[1]LCPMR / UPMC / CNRS - Paris (France), [2]Raja Ramanna Centre for Advanced Technology - Indore (India), [3]Brookhaven National Laboratory - NSLS II - Upton (United States of America), [4]Horiba Jobin Yvon - Longjumeau (France), [5]Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP) - Paris (France)

Gold thin films are used in grazing incidence x-ray reflectivity mirrors in the 100-1500 eV soft x-ray region on synchrotron beamlines because gold presents a flat reflectivity performance. In order to provide a good adhesion with silicon or fused silica substrates, a binding layer of chromium is often used. These mirrors should exhibit no interdiffusion in order to get high and stable optical performances.

We study, as a model, a Au/Cr bilayer system deposited by electron beam evaporation technique on a float glass substrate. An as-deposited sample is characterized by using three complementary techniques: soft x-ray reflectivity (XRR), glow discharge optical emission spectrometry (GDOES) and time of flight secondary ion mass spectroscopy (ToF-SIMS). XRR informs about the thickness and roughness of the different layers while GDOES is used to obtain the elemental depth profile of the stack, with a nanometer depth resolution and SIMS to obtain the elemental and chemical depth profile with a nanometer depth resolution also.

The XRR measurements shown in Figure 1 confirm that the sample is a bilayer stack with Au and Cr layer thicknesses of 24.2 and 10.3 nm respectively and interface roughnesses of 0.55 and 0.83 nm. The depth profiling is obtained from the SIMS measurements and is shown in Figure 2. From the SIMS data one infers that:

- a contaminated exits at the top of the stack;
- at the interfaces between the Au and Cr layers, a possible AuCr solid solution is evidenced;
- between the Cr layer and the glass substrate, Cr is oxidized.

Such a study shows the interest of combing complementary techniques in order to determine the in-depth composition of multilayer stacks of nanometer thickness.

Fig. 1 (left): Measured and fitted SXR curves of the as-deposited sample.

Fig. 2 (right): ToF-SIMS depth profiles of the as-deposited sample.

TFC2.2-4O074

NOVEL PATHWAYS IN REACHING BURIED INTERFACES OF ORGANIC/INORGANIC HYBRID SYSTEMS: A MECHANISTIC UNDERSTANDING OF POLYMER ADSORPTION ON PASSIVATED METAL OXIDE SURFACES

<u>T. Hauffman</u>, S. Pletincx, K. Marcoen, F. Cavezza, H. Terryn
Department of Materials and Chemistry, Research group Electrochemical and Surface Engineering, Vrije Universiteit Brussel - Brussels (Belgium)

The interface between a metal oxide and its coating is of great importance for the durability and efficiency of the entire organic/inorganic hybrid system. However, the analysis of such solid/solid interfaces is challenging, as they are masked by a µm-thick polymer layer on one side and a thick metal oxide matrix on the other side. The main difficulty will be to investigate buried interfaces non-destructively with conventional surface analysis techniques.[1,2]

In this work, we characterize interfacial interactions of several ultrathin polymeric films with aluminum and zinc oxides by utilizing novel methodologies, leading to the characterization of a realistic model interface. The adsorption mechanisms are established by using XPS for chemical state information and ToF-SIMS for direct molecular information of these ultrathin organic overlayers.

The use of these nanometer thin films opens up the possibility of an in situ characterization of environmental influences such as water ingress. The use of Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) is employed to describe the adsorption mechanism in the presence of water vapor. Furthermore, ATR-FTIR Kretschmann is utilized to obtain a near-interface infrared spectrum while simultaneously, the influence of an above-the-polymer electrolyte (such as water) on the interface is characterized.[3]

The homogeneity of these interfacial interactions is characterized on the nanoscale using nano-infrared spectroscopy. This novel technique allows to conduct infrared spectroscopy on the nanoscale by using an AFM tip, which probes the expansion of the material due to IR absorbance. This results in a local vibrational spectrum.

This work comprises novel synthesis routes and methodologies, which enable to probe interfacial changes in hybrid systems non-destructively and in situ. As such, coatings systems can be optimized with respect to the bare substrate.

References

(1) van den Brand, J.; Blajiev, O.; Beentjes, P. C. J.; Terryn, H.; de Wit, J. H. W. Interaction of Anhydride and Carboxylic Acid Compounds with Aluminum Oxide Surfaces Studied Using Infrared Reflection Absorption Spectroscopy. Langmuir 2004, 20 (15), 6308–6317.

(2) Hinder, S. J.; Lowe, C.; Maxted, J. T.; Watts, J. F. A ToF-SIMS Investigation of a Buried Polymer/polymer Interface Exposed by Ultra-Low-Angle Microtomy. Surf. Interface Anal. 2004, 36 (12), 1575–1581.

(3) Pletincx, S.; Trotochaud, L.; Fockaert, L.-L.; Mol, J. M. C.; Head, A.; Karslıoğlu, O.; Bluhm, H.; Terryn, H.; Hauffman, T. In Situ Characterization of the Initial Effect of Water

on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. Sci. Rep. 2017, 7 (45123).

TFC3-1O097

COMBINED XPS AND KINETIC STUDY OF PASSIVATING GAN THIN FILM ELABORATED ON GAAS

H. Mehdi [1], C. Robert-Goumet [1], G. Monier [1], P. Hoggan [1], V. Dubrovkii [2]

[1]Institut Pascal, CNRS UMR 6602 - Clermont-Ferrand (France), [2]St. Petersburg Academic University,Ioffe Physical Technical Institute of the Russian Academy of Sciences - St. Petersburg (Russian federation)

The high density of interface and surface states that cause the strong Fermi pinning observed on GaAs surface is reduced by passivating GaN thin film on GaAs. To further develop this passivation, it is necessary to investigate the nitridation phenomena by identifying the different steps occurring during the process and to understand and quantify the growth kinetics of GaAs nitridation under different conditions. Nitridation of cleaned GaAs substrate was performed using a N_2 plasma produced by an electron resonance cyclotron source and a glow discharge source. Two approaches have been combined. Firstly, AR-XPS study is carried out to determine the chemical environments of the Ga, As and N atoms and the composition depth profile of the elaborated ultra-thin films through the schematization described in Fig 2. This study allowed us to summarize the nitridation process in three steps. The second approach is a refined kinetic model which better describes the GaN growth as function of the nitridation time. Figure 1 shows the best fits of the experimental data obtained with Eq. (1) for different nitridation conditions at T=500°C. This model clarifies the exchange mechanism of arsenic with nitrogen atoms at the GaN/GaAs interface and the phenomenon of quasi-saturation of the process.

$$t = \beta . x^2 - \frac{K}{\delta} \ln(1 - \frac{x}{\delta}) \qquad (1)$$

where $K = k . c_N^*$ is the true rate constant of the reactive step at the GaN/GaAs interface,

$(1/\beta) = 2 D_N c_N^*$ is the transport of the nitrogen by diffusion and δ describing the characteristic width of the arsenic-rich layer at the interface.

TFC2.3-5O111

NANO-ANALYSIS OF OXIDES ON ZNMGAL SURFACES AFFECTED BY DIFFERENCES IN THE ALLOY COMPOSITION

J. Duchoslav [1], T. Truglas [1], H. Groiß [1], C.K. Riener [2], M. Arndt [2], K.H. Stellnberger [2], G. Luckeneder [2], G. Angeli [2], D. Stifter [3]

[1]Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH (CEST) - Wiener Neustadt (Austria), [2]voestalpine Stahl GmbH - Linz (Austria), [3]Johannes Kepler University in Linz, ZONA - Linz (Austria)

ZnMgAl alloys have been established for advanced coating systems bringing superior corrosion protection to steel [1]. Knowledge on the structure and properties of several ZnMgAl coating types is already available, however with only limited attention paid to the surface [2,3]. Thus, the current study aims at a fundamental investigation of the alloy composition and the subsequent surface oxide formation, which can help for future developments of advanced industrial coatings. For that purpose, three different alloys – Zn1.5Mg2.5Al (i.e. 1.5 weight% Mg and 2.5 weight% Al in Zn bath), Zn1.5Mg1.5Al and Zn3.0Mg3.7Al – were prepared in a laboratory hot-dip galvanizing facility and investigated using X-ray photoelectron and Auger electron spectroscopy (AES) as surface sensitive methods, together with high resolution transmission electron microscopy for analysis down to the atomic scale.

The obtained results confirmed that the alloy composition affects the overall microstructure. The Zn1.5Mg2.5Al alloy is constituted of primary zinc dendrites and a ternary eutectic phase. In this case the chemical composition of the surface oxides is rather uniform and does not reflect the underlying phase distribution. A different behavior is found for Zn1.5Mg1.5Al which comprises primary zinc dendrites as a major component, a binary and a ternary eutectic phase. Here the chemical composition and the spatial distribution of the oxides noticeably follow changes in the structure and composition of the alloy (Fig. 1a: electron micrograph; Fig. 1b: corresponding AES mapping). For Zn3.0Mg3.7Al samples with dominant ternary eutectic phase, the surface layer becomes again spatially uniform, but exhibits a different composition. The discrepancy between the results of new laboratory samples on a microscopic level and earlier findings of line materials on a macroscopic level shall also be explained in this work [2].

References

[1] N. LeBozec, D. Thierry, M. Rohwerder, D. Persson, G. Luckeneder, L. Luxem, Corrosion Sci. 74 (2013) 379-386.

[2] Riener C. K., Arndt M., Duchoslav J., Itani H., Stifter D., Hingerl K., Preis K., Achammer E., Angeli G., Proceedings of Galvatech `11, Genua, Italy, (2011).

[3] Arndt M., Duchoslav J., Itani H., Hesser G., Riener C.K., Angeli G., Preis K., Stifter D., Hingerl K., Anal. Bioanal. Chem. 403 (2012) 651-661.

TFC2.2-2O112

DESIGN AND APPLICATION OF A NEW LABORATORY HAXPES INSTRUMENT

R. Inoue [1], H. Yamazui [1], K. Watanabe [1], J. Newman [2], J. Mann [2]
[1]ULVAC-PHI, INC. - 370 Enzo, Chigasaki, Kanagawa 253-8522, (Japan), [2]Physical Electronics, Inc. - 18725 Lake Drive East, Chanhassen, Mn 55317 (United States of America)

Hard X-ray Photoelectron Spectroscopy (HAXPES), available in synchrotron radiation facilities, is widely used in the research field of materials and electronic thin film devices. HAXPES utilizes x-rays typically defined as having energies greater than 5 keV and can excite deeper core-level photoelectrons not excited by soft x-rays such as Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) commonly used in conventional XPS instruments. More importantly, the information depth into a sample using HAXPES is greater than conventional soft x-ray XPS [1]. From these characteristics, HAXPES can obtain spectra which are coming from deeper (bulk) compositions with less signal originating from atmospheric and other surface contamination. Combining both soft and hard x-ray analyses, we can expect to gain an even better understanding of composition with depth and information at buried interfaces [2] [3].

This presentation will describe a newly developed instrument, the PHI Quantes, which is equipped with monochromated scanning Al Kα (1486.6 eV) and Cr Kα (5414.9 eV) x-ray sources, thus enabling both soft and hard x-ray analysis in the same instrument. The dual scanning x-ray sources can automatically be switched by UHV robotics technology. The scanning x-ray beams enable the generation of x-ray induced secondary electron images (SXI) which allow easy alignment of the two x-ray beams to the same analysis point. This makes it possible to perform the sequential measurement of the same analysis point or area with the hard and soft x-ray beams. In combination with a high sensitivity electrostatic electron analyzer, dual scanning x-ray sources enable not only micro-area analysis capability but also large area analysis.

In initial application studies on the instrument, thin film multiple-layered samples and the chemical states of transition metal oxide films were compared with Al and Cr x-rays. While charge neutralization of insulating samples can be very difficult on synchrotron HAXPES instruments, the PHI Quantes employs a combination of low energy ions and electrons for charge neutralization [4]. This enables chemical state analysis of organics, metal oxides, and other insulating materials with either the hard or soft x-ray source.

References

[1] H. Shinotsuka, S. Tanuma, C. J. Powell and D. R. Penn, Surf. Interface Anal. 47(9), 871 (2015).

[2] K. Kobayashi et al., Appl. Phys. Lett., 83, 1005 (2003).

[3] M. Kobata et al., J. Surf. Sci. Soc. Jpn, Vol. 31, pp. 487-492, 2010

[4] P. E. Larson, M. A. Kelly: J. Vac. Sci. Technol. A16, 3483, (1998)

TFC2.2-5O119

THE EFFECT OF WATER ON CHEMICAL INTERACTIONS AT THE INTERFACE OF ULTRATHIN POLYMERIC FILMS AND ALUMINUM OXIDE: AN IN SITU CHARACTERIZATION

S. Pletincx [1], L. Trotochaud [2], L.L. Fockaert [3], A. Mol [3], H. Bluhm [2], H. Terryn [1], T. Hauffman [1]

[1]Department of Materials and Chemistry, Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel - Brussels (Belgium), *[2]Chemical Sciences Division, Lawrence Berkeley National Laboratory - Berkeley* (United States of America), *[3]Department of Materials Science and Engineering, Delft University of Technology - Delft* (Netherlands)

Probing interactions at the interface of acrylic polymers and a hydroxylated aluminum oxide surface under humid conditions has the potential to reveal the local chemical environment at solid/solid interfaces under real-world, technologically relevant conditions. Although this region is very important for understanding adhesion and de-adhesion of the polymer coating, it is very challenging to get useful information directly from the interface, let alone characterize the effect of water on formed chemical bonds. Common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*.[1]

Due to recent developments in the field of ambient-pressure photoelectron spectroscopy (APXPS), a novel approach with respect to interface studies can be set up. A broad range of relative humidities can be simulated in the analysis chamber, making it possible to unravel interfacial chemistry changes of the hybrid system *in situ*.[2] Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. This is done by making the polymer layer sufficiently thin to probe the interface non-destructively.

An integrated setup of *in situ* ATR-FTIR Kretschmann and Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) on a complementary model system is used to characterize the formed bonds at the metal oxide/polymer interface. A nanometer thin aluminum layer is sputtered on an IR transparent crystal, such that the IR signal from the oxide/polymer interface is amplified as a result of the Kretschmann effect, obtaining a near-interface spectrum.[2] This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H_2O) can be probed. Simultaneously the protective properties and corrosion processes of the overall hybrid system are monitored by ORP-EIS.[3]

References

(1) Leadley, S. R.; Watts, J. F. The Use of XPS to Examine the Interaction of PMMA with Oxidised Metal Substrates. J. Electron Spectros. Relat. Phenomena 1997, 85 (1–2), 107–121.

(2) Pletincx, S.; Trotochaud, L.; Fockaert, L.-L.; Mol, J. M. C.; Head, A.; Karslıoğlu, O.; Bluhm, H.; Terryn, H.; Hauffman, T. In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. Sci. Rep. 2017, 7 (45123).

(3) Öhman, M.; Persson, D. An Integrated in Situ ATR-FTIR and EIS Set-up to Study Buried Metal-Polymer Interfaces Exposed to an Electrolyte Solution. Electrochim. Acta 2007, 52 (16), 5159–5171.

TFC3-3O120

ION IMPLANTATION OF ERBIUM INTO AND CUTS OF SINGLE-CRYSTAL DIAMOND AND A STUDY OF POST-IMPLANTATION ANNEALING

J. Cajzl [1], **B. Akhetova** [1], **P. Nekvindová** [1], **A. Macková** [2], **P. Malinský** [2], **R. Böttger** [3], **J. Oswald** [3]

[1]University of Chemistry and Technology - Prague (Czech republic), *[2]Nuclear Physics Institute, Czech Academy of Sciences, v. v. i. - Prague* (Czech republic), *[3]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research - Dresden* (Germany)

Diamond is an extraordinary material due to its outstanding physical and chemical bulk properties such as the highest thermal conductivity, extreme hardness, broad optical transparency, bio-compatibility, physical and chemical inertness, and excellent electrical insulation, which can be tailored to become semiconducting or normal conducting by doping with various ions. In photonics diamond is mainly used due to its high refractive index and low optical absorption scattering. The photoluminescence in diamond can be enabled thanks to the colour-defect centres created by doping with various ions, e.g. Si, O, N, Cr, Eu, Er. For the doping of materials, ion implantation is one of the most used technique. Ion implantation, however, causes changes in the crystal structure, both wanted and unwanted. Unwanted implantation-induced damage to the diamond crystal structure is difficult to repair or recover. Regarding these points, it is necessary to choose right implantation and annealing conditions and appropriate base.

Here we report on the results of erbium ion implantation into <100> and <110> cuts of single-crystal diamond and study of subsequent annealing at the temperatures of 400, 600 and 800 °C in vacuum. Ion implantation was performed with an energy of 190 keV and a fluence of $1\mathrm{x}10^{15}$ ions.cm^{-2}. Erbium concentration depth profiles and degree of crystal damage (structural ordering) were measured using Rutherford Backscattering spectroscopy (RBS) and RBS/Channeling, respectively. Structure changes were also studied with Raman spectroscopy and Atom Force Microscopy (AFM). From the results it turned out that the choice of diamond crystallographic cut orientation plays important role. Significant strengthening of the luminescence after annealing at 800 °C in vacuum was able to achieve in <110> cut sample (see Fig. 1). In the luminescence spectra 4 bands at the wavelengths of about 1.5 µm that are typical for $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er ions are evident. Thereby <110> cut showed to be more suitable for erbium ion implantation doping than <100> cut which was having almost no luminescence.

Thanks/Acknowledgement

We acknowledge the Czech Science Foundation project GA 15-01602S.

TFC1-4O142

TI, TIN AND TIO2 ARCHITECTURED COATINGS ON STAINLESS STEEL WIRES: STRUCTURAL PROPERTIES VS MECHANICAL AND CORROSION BEHAVIOR

S. Grosso [1], T. Le Coz [2], G. Berthomé [1], L. Latu-Romain [1], M. Mantel [2]
[1]*Univ. Grenoble Alpes, SIMAP - Grenoble* (France), [2]*Ugitech SA - Ugine* (France)

Titanium-based architectured coatings are grown by PVD in an inverted cylindrical magnetron (ICM) thanks to an innovative industrial process corresponding to a continuous reactive deposition on moving 316L stainless steel wires [1].
Thin films are fully characterized by Xray Photoelectron Spectroscopy, Electron Probe Micro Analysis, Transmission Electron Microscopy coupled with Energy Dispersive Spectroscopy and Orientation Phase Mapping (ASTAR) [2].
Chemical compositions of coatings have been linked to CIELAB color measurement. Under-stoichiometric TiN (N/Ti<1) present greyish color with low oxygen content, stoichiometric TiN is golden whereas brown TiN contains around 8 at% of oxygen. Titanium oxynitride and TiO_2 coatings show interferometric optical behavior.
During deposition, a low substrate temperature inferior to 650 °C is needed to avoid chemical diffusion from the substrate into the films, to prevent intermetallic phase formation. However, whatever the substrate temperature, the PVD process leads to grains refining of the stainless steel surface (see Fig.1a). TiN presents an equiaxis microstructure for thickness inferior to 50 nm whereas columnar microstructure with <111> texturation appears for greater thicknesses (see Fig.1a) [3]. Ti-TiN coatings promote <111> texturation in the TiN layer (from 60 % to 83 %, see Fig.1b). Mechanical properties of the coatings were investigated by *in situ* SEM tensile test. Ti, TiN and Ti-TiN coatings have a high adhesion on stainless steel whereas TiO_2 coatings spallate. The adhesion is improved by growing a titanium interlayer between the substrate and TiO_2 coating. Finally, the corrosion behavior of simple and architectured coatings was studied and compared. TiN coatings are more protective than Ti and TiO_2 coatings. Defects like porosity coupled with the high roughness of the substrate play a major role in the corrosion behavior which is, in the best case, identical to uncoated 316L.

References

[1] A. Todoran, M. Mantel, A. Bés, C. Vachey, A. Lacoste, Control of particle flux and energy on substrate in inverted cylindrical magnetron for plasma PVD, Plasma Sources Sci. Technol. 23 (2014)

[2] E.F. Rauch, M. Véron, Automated crystal orientation and phase mapping in TEM, Mater. Charact. 98 (2014)

[3] G. Abadias, Stress and preferred orientation in nitride-based PVD coatings, Surf. Coatings Technol. 202 (2008)

TFC1-2O146

IN-LINE METROLOGY OF TE-BASED ULTRA-THIN FILMS FOR MEMORY APPLICATIONS

W. Pessoa [1], C. Sabbione [1], A. Roule [1], M.C. Lépy [2], M. Bernard [1], E. Nolot [1]

[1]CEA, LETI, MINATEC Campus, 17 rue des Martyrs, 38054 - Grenoble (France), *[2]CEA-LIST, Laboratoire National Henri Becquerel (LNE-LNHB) - Saclay* (France)

Telluride alloys are chalcogenides able to change from amorphous to crystalline phase (reversibly) when an electric current is applied, such phenomena makes them essential in advanced memory applications (e.g. Phase Change RAM and Conductive Bridge RAM) [1]. The properties of thin telluride alloys are deeply influenced by their chemical composition whereas surface/interface effects may become preponderant for ultrathin films. In this paper, we'll first comment on the performances of both wavelength-dispersive X-ray fluorescence (WD-XRF) and angle-resolved X-ray photoemission spectroscopy (ARXPS) to non-destructively characterize and monitor the deposited mass and the composition of ultrathin GeSbTe films. ARXPS analysis was based on Ge-3d, Sb-4d and Te-4d environments that feature close kinetic energies and similar probing depths. However, ARXPS data may rapidly degrade due to aging/oxidation (Fig.1) thereby limiting the accuracy of the composition information. In this paper, we'll then discuss inline measurement strategies that aim to master aging-induced surface effects for various Te-based thin films. We'll evaluate two complementary protocols based on (i) the transfer of wafers from deposition tool to inline metrology tool using dedicated vacuum carriers or (ii) the optimization and use of ultrathin capping layers deposited in situ (Fig.2) in the Physical Vapor Deposition equipment. We'll show that Ta-Te intermixing makes SiN a better candidate than Ta as a passivation layer for TiTe thin layered systems.

Key-Words: In-line X-Ray metrology; XPS; WDXRF; Telluride thin films; Chalcogenides; Memories.

References

[1] Tanaka, Keiji, and Koichi Shimakawa. Amorphous chalcogenide semiconductors and related materials. Springer Science & Business Media, 2011.

TFC2.1-4O157

XPS ANALYSIS OF MULTILAYER HFO2 USING HARD AND SOFT X-RAYS

J. Mann [1], R. Inoue [2], H. Yamazui [2], K. Watanabe [2], J. Newman [1]
[1]Physical Electronics, Inc - Chanhassen (United States of America), [2]ULVAC-PHI, Inc - Chigasaki (Japan)

Hard x-rays can generally be considered as having photon energies > 5 keV, while photon energies below 5 keV are described as soft x-rays. Hard x-ray photoelectron spectroscopy (HAXPS) is typically performed at large synchrotron facilities, while most commercial lab-scale XPS instruments use soft x-rays. The PHI *Quantes* is a new commercial laboratory instrument equipped with two scanning microprobe, monochromated x-ray sources, Cr Kα (5414.9 eV) and Al Kα (1486.6 eV). Use of higher photon energies increases the mean free path of photoelectrons, resulting in an increased information depth obtained from the sample (~3x that of Al Kα). HAXPS measurements are therefore more sensitive to the bulk and contributions from the surface are minimized [1,2]. Toggling between x-ray sources allows non-destructive depth analysis of multilayer thin films and buried interfaces [1]. A more detailed description of the instrument will be presented in reference [3].

Initial analysis results on the high-k dielectric, HfO_2, obtained on the PHI Quantes using both hard and soft x-ray sources will be presented. Several samples of HfO_2 on SiO_2 on Si substrate with varying thicknesses of the HfO_2 and SiO_2 layers were analyzed. The HfO_2/SiO_2 thicknesses of the samples are as follows: 27Å/28Å, 80Å/22Å, 81Å/81Å and 263Å/22Å. Spectra were collected with a 90 degree take-off angle to maximize the information depth of each sample. As expected, the presence and relative intensities of SiO_2 and Si substrate peaks varied depending on the sample thickness, photon energy and photoelectron kinetic energy.

References

[1] Kobayashi, K. Hard X-ray photoemission spectroscopy, *Nucl. Instr. Meth. Phys. Res. A* **2009**, 601, 32-47.

[2] Fadley, C.S. Hard X-ray Photoemission: An Overview and Future Perspective. In Hard X-ray Photoelectron Spectroscopy (HAXPS); Woicik, J. C., Ed; Springer: Switzerland 2016.

[3] Inuoe, R., Yamazui, H., Watanabe, K., Newman, J., Mann, J. E., Design and Application of a New Laboratory HAXPES Instrument, ECASIA 2017.

TFC2.2-1O170

DEPTH PROFILE OF SODIUM WITHIN SILICA THIN LAYER DEPOSITED ON GLASS

H. Montigaud [1], J.T. Fonne [1], E. Gouillart [1], E. Burov [1], S. Grachev [1], T. Cretin [2], D. Vandembrouck [3]

[1]Surface du verre et interfaces, UMR125 CNRS/Saint Gobain - Aubervilliers (France), [2]Saint Gobain Recherche - Aubervilliers (France), [3]PMMH, UMR 7636 CNRS/ESPCI/Univ. Paris6 UPMC/Univ. Paris7 Diderot - Paris (France)

Silica doped with alumina thin films (SiO2: Al) are sometimes part of the layers stack of functionalized glazing for solar control or low emissivity applications. This layer is used to adjust the optical index and mostly to prevent the alkali diffusion (mainly Na) from the glass during post-treatments like glass tempering [1].

The estimation of the sodium profile through the depth of such very thin layer (in the range of 100nm) is thus a key parameter for the study of the behaviour of the stack when the whole system (substrate + layers) reaches temperature up to 700°C. However, the quantification of Na at the nano-scale is a very challenging task because of its mobility within silicate network mainly due to surface charging artefact directly induces by the analysis technique itself [2].

The present work compares various techniques to probe the layer composition like ToF-SIMS and XPS depth profiling operating in different conditions (nature of abrasion species, their energy, substrate temperature), Electron Probe MicroAnalysis (at different electron energies). The impact of different artefacts is discussed (sputtering damage on surface, charging effect [3], [4]) and a final composition profile of the main elements Na, Al, Si, O also including hydrogen is finally established.

References

[1] F. P. Fehlner, J. Non-Cryst. Solids 218 (1997) 360-367

[2] S. Krivec et al. Appl. Surf. Sci. 257 (2010) 25-32

[3] Y. Yamamoto et al. Optical Materials 33 (2011) 1927-1930

[4] D. Kobayashi et al. Surf. Interface Anal. 45 (2013) 113-116

TFC2.2-3O172

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) STUDY OF SIC(X)N(Y):H THIN FILMS ELABORATED BY ASSOCIATED RADIOFREQUENCY MAGNETRON SPUTTERING AND MICROWAVE PLASMA : EFFECT OF EXPERIMENTAL PARAMETERS ON THE FILM'S SURFACE

A. Bachar [1], H. Mehdi [2], A. Bousquet [1], C. Robert-Goumet [2], G. Monier [2], E. Tomasella [1]

[1]Université Clermont Auvergne, CNRS, Institut de Chimie de Clermont-Ferrand, F-63000 - Clermont-Ferrand (France), [2]Université Clermont Auvergne, CNRS, Institut Pascal, F-63000 - Clermont-Ferrand (France)

In the present study, hydrogenated silicon carbonitride SiCxNy:H thin films were elaborated combining radiofrequency magnetron sputtering and ECR plasma excitations. This material, which is a very interesting candidate as antireflective and passivation coating in photovoltaic devices, was obtained using a 99.99% purity silicon target under an Argon-nitrogen-methane gas mixture, and four coaxial microwave sources while the reactive gas flow ratio R = [FN2]/([FN2] + [FCH4]) was varied. In order to understand the effect of the different experimental parameters on the film composition, the chemical environment of each component especially at the surface, XPS analyses were performed and an optimization of the de-convolution parameters for XPS spectra allowed the identification of the different atom bonds.

In light of the binding energies obtained for different surface compositions, the results have shown the existence of a preferential bonding of silicon with carbon or nitrogen. A comparison of XPS and RBS results showed a slight change of the composition due to the high reactivity of the extreme surface of the deposited films. Thicknesses and refractive indexes (n) of the films were characterized using spectrometric ellipsometry and allowed us to emphasize the improvement of n values [1.8- 2.3] versus R by using additional microwave excitations instead of a conventional magnetron sputtering deposition, while no major changes were observed for the growth rates. Our process leads us to cover a wide range of optical band gap [2- 4.5 eV] versus R and the microwave power.

TFC1-5O185

LOW ENERGY ION SCATTERING FOR THIN FILM ANALYSIS

H. Brongersma [1], P. Brüner [1], T. Grehl [1], C. Hägglund [2], S.F. Bent [3], J.Z. Mundy [4], G.N. Parsons [4]

[1]ION-TOF GmbH - Münster (Germany), [2]Stanford University (now: Uppsala University, Sweden) - Uppsala (Sweden), [3]Stanford University - Stanford (United States of America), [4]North Carolina State University - Raleigh (United States of America)

The outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. Precisely these outer atoms can be selectively and quantitatively analyzed with Low Energy Ion Scattering (LEIS). Using He^+ ion scattering non-destructive in-depth information, with high depth resolution, is also obtained for the heavier elements (0 – 10 nm) [1]. This information is quantified with a Monte-Carlo type simulation (TRBS, [2]) with correction for the ion fraction of the backscattered He particles. Since LEIS is a fast analysis technique, following diffusion processes in-situ is possible.

In this study we use LEIS to analyze two low-temperature Atomic Layer Deposition (ALD) processes.

During the development of a new ALD process for 145 ºC deposition of Pd on ZnO, TMA was used as a co-reagent to enable the nucleation and growth of Pd at this lower temperature. However, the shift of the Zn sub-surface edge after 25 cycles shows (see Fig. 1) that a thick Al_2O_3 layer was deposited, while the Pd coverage was, typically, only 3 %.

In the exploration of new tailor made materials, the growth, lamination and intermixing of zinc oxide and tin oxide is studied [3]. The LEIS results (Fig. 2) show that upon annealing (sequence 1-7) of laminated zinc tin oxides (grown at 150 °C; bilayer period of 60 cycles and 45 cycle SnO_x termination) in air at 400 °C, the surface contamination is first removed (1-2). After longer annealing (2-7) ZnO segregates and an inverted spinel Zn_2SnO_4 is formed at the surface, while the surface density increases by 30 %.

References

[1] H.H. Brongersma, Low-Energy Ion Scattering, in "Characterization of Materials", Ed. E.N. Kaufmann, pp. 2024-2044, J. Wiley & Sons (2012)

[2] P. Brüner et al., JVST A 33 (2015) 122

[3] C. Hägglund et al., JVST A 34 (2016) 02156

TFC3-2O210

MEASUREMENT OF GAN/SINGLE-LAYER (SL) WSE2 HETEROJUNCTION BAND OFFSETS BY HIGH-RESOLUTION X-RAY PHOTOEMISSION SPECTROSCOPY

M. Hedhili [1], M. Tangi [2], P. Mishra [2], C.C. Tseng [3], T.K. Ng [2], D.H. Anjum [1], M.S. Alias [2], N. Wei [1], L.J. Li [3], B.S. Ooi [2]

[1]Imaging and Characterization Laboratory, King Abdullah University of Science and Technology - Thuwal (Saudi arabia), [2]Photonics Laboratory, Computer, Electrical, and Mathematical Sciences and Engineering (CEMSE) - Thuwal (Saudi arabia), [3]Physical Science and Engineering (PSE) Division - Thuwal (Saudi arabia)

Electrical and optical properties of heterojunction semiconductors are heavily influenced by the relative alignment of their energy band edges at the interface [1]. That is why the knowledge of this alignment is crucial for the design of heterostructure devices. In this regard, high-resolution X-ray photoemission spectroscopy (HR-XPS) has been shown to measure the valence band offset of heterojunction semiconductors quite accurately [2]. In this report, we present a study that contains the characterization of GaN/single-layer (SL) WSe2 heterojunction semiconductor material done by using a myriad of techniques including HR-XPS, scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), micro-Raman, absorbance, and microphotoluminescence spectroscopy. The samples for this study were prepared by depositing an epitaxial GaN thin layer with molecular beam epitaxy (MBE) on chemically vapor deposition (CVD) grown SL-WSe2/c-sapphire substrates. The formation of SL of WSe2 was crucial to device properties and hence was confirmed by using both STEM and AFM techniques. HR-XPS analysis of samples was performed in two-steps to measure the valence band discontinuity for GaN/single-layer (SL) WSe2 heterojunction interface. In first step, the core level binding energies with respect to the valence band maximum in both GaN and WSe2 bulk films were measured. Second, the subsequent measurements on the separation between Ga and W core levels for GaN thin layer grown SL-WSe2 was measured. The valence band and conduction band offset values are determined to be 2.25 ± 0.15 eV and 0.80 ± 0.15 eV, respectively, with type II band alignment. The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling of their heterojunction-based electronic and optoelectronic devices.

References

[1] U. Gnutzmann and K. Clausecker, Appl. Phys. 3, 9 (1974).

[2] J. C. Bernède, L. Cattin, P. Predeep, XPS Study of the Band Alignment at the Interface ITO/CuI, Technology Letters 1 (1), 2 (2014).

TFC2.1-5O214

THE USE OF FE-AES AND FE-SEM TO CHARACTERISE THE SUB-MICROMETRE DISTRIBUTION OF A ZR-TI NO-RINSE CONVERSION COATING APPLIED ON AUTOMOTIVE ALUMINIUM COILS

P. Bouckenooge [1], O. Bauer [2], K. Eckhard [2], H.J. Brinkman [2], H. Terryn [1]
[1]Department of Materials and Chemistry, Research group Electrochemical and Surface Engineering, Vrije Universiteit Brussel, Pleinlaan 2 - 1050 Brussels (Belgium), [2]Hydro Aluminium Rolled Products GmbH, Research & Development Bonn, Georg-von-Boeselager-Str. 21 - 53117 Bonn (Germany)

Since several years the importance of aluminium in the automotive industry is growing, due to its lower density compared to steel. Before an aluminium sheet can be used in a car it needs to undergo several treatments and requires several successive coatings. The initial layer on the bare metal is conventionally a conversion coating. The purpose of this coating is two folded. First, it is applied to enhance of the adhesion properties of the aluminium surface towards the successive layers (e.g. zinc phosphate). Secondly, the conversion coating forms a first corrosion protection layer on top of the second phase particles at the surface. In the past these conversion coatings were chromium based but are now banned. Although new alternatives, like the Zr-Ti based coatings, are already commercially used, a lot of their behaviour and properties are still to be discovered.

Several techniques can be used to apply the conversion coating, divided in rinse (dipping) and no-rinse (spraying and roller coater) applications. Though published research was only focused on dip applications. In this literature it was already pointed out how the surface metallurgy, especially the second phase metallic particles, of the aluminium influence the formation and growth of the conversion coating.[1-3]

To analyse this 10-20 nm thick conversion coating the FE-AES system is an excellent tool. The nanometre depth and lateral resolution of the system makes it possible to investigate the coating distribution near the intermetallic particles on a sub-micrometre scale. Line scans, point analysis and depth profiling were used to reveal interesting coating concentration changings near the intermetallic particles. By data analysis of the semi-quantitative measurements, statistical conclusions could be obtained.

Also FE-SEM-EDS was used to investigate the conversion coating near the intermetallic particles. In this case point analysis, line scans and mappings were obtained. Although SEM-EDX is not the most recommended technique to analyse this nanometre thin coating, interesting results were obtained. This provides the possibility to do a comparison between the analysis possibilities of FE-AES and FE-SEM-EDS when investigating the conversion coating distribution near second phase surface particles.

All measurements were performed on mill-finished automotive aluminium alloys, coated with a Zr-Ti based conversion coating applied by an industrial spraying process.

References

1. Lunder, O. et al. Surf. Coatings Technol. 184, 278–290 (2004).
2. Andreatta, F. et al. Surf. Coatings Technol. 201, 7668–7685 (2007).
3. Cerezo, J. et al. Appl. Surf. Sci. 366, 339–347 (2016).

TFC2.1-3O249

IN-SITU NEAR AMBIENT PHOTOEMISSION STUDY OF THE GASOCHROMIC BEHAVIOR OF PT/WO3 THIN FILMS

A. González-Elipe [1], P. Castillero [1], V. Rico-Gavira [1], C. López-Santos [1], F. Yubero [1], A. Barranco [1], V. Perez-Dieste [2], C. Escudero [3], J.P. Espinós [1]

[1]Instituto de Ciencia de Materiales de Sevilla (CSIC-USE) - Sevilla (Spain), [2]ALBA Synchrotron Light Source. - Sevilla (Spain), [3]ALBA Synchrotron Light Source. - Barcelona (Spain)

M/WO3 (M: Pt, Pd) systems formed by a porous WO3 thin film decorated by metal nanoparticles are known for its reversible coloring upon exposure to H2 at room temperature. In this work, this gasochromic behavior is investigated “in situ” by means of near ambient photoemission (NAPP). Pt/WO3 systems formed by very small Pt nanoparticles (10 nm average size) incorporated in the pores of WO3 thin films prepared by magnetron sputtering at oblique angle, have been exposed to a small pressure of hydrogen. The recorded UV-vis transmission spectra showed the reversibly appearance of a very intense absorption band responsible for the blue coloration of these gasochromic films. In an equivalent experiment carried out in the NAPP spectrometer, W4f, O1s, Pt4f and valence band photoemission spectra have been recorded at various photon energies to follow the evolution of the reduced tungsten species and hydroxyl groups formed upon film exposure to hydrogen. The obtained results are compared with those of a conventional X-ray photoemission study after hydrogen exposure between 298 and 573 K. The gasochromic behavior at 298 K is accounted for by a reaction scheme in which hydrogen atoms resulting from the dissociation of H2 onto the Pt nanoparticles are spilt over to the WO3 substrate where they form surface –OH- /H2O species groups and W5+ cations, these latter preferentially located in buried layers of the oxide network.

Thanks/Acknowledgement

The authors thank the European Regional Development Funds program (EU-FEDER) and the MINECO-AEI (Projects MAT2013-40852-R, 201560E055 and MAT2016-79866-R)) for financial support

TFC2.3-2O258

EXPERIMENTAL AND SIMULATED XPS SPECTRA OF A METALLIZED POLY-EPOXY AMINE POLYMER SURFACE

A. Gavrielides, T. Duguet, M. Aufray, C. Lacaze-Dufaure
CIRIMAT, Université de Toulouse, CNRS-INPT-UPS - Toulouse (France)

Poly-epoxy polymers are used in the aerospace industry as the matrix of composite components. For specific applications, their surface must be metallized to achieve the desirable properties (e.g. electromagnetic shielding, permeation barrier, electrical conductivity). Methods that were used until now to ensure these properties and a proper interfacial adhesion have been efficient but highly empirical. Hence, there is a need to rationalize this knowledge. To that end, we decided to synthesize a model poly-epoxy and study its surface and the formation of an interface with Cu in model conditions. Our epoxy-amine thermoset is obtained by poly-addition of diglycidylether of bisphenol A (DGEBA) and ethylenediamine (EDA). In order to ensure a smooth and defect-free surface for thin film depositions, AFM and XPS characterizations, we use a slow polymerization protocol that takes place under inert atmosphere. The synthesis protocol is validated by bulk (DSC, FTIR), and surface characterizations, showing that roughness and defects density are extremely low, and that the composition is homogeneous [1]. Cu thin films are then evaporated in ultrahigh vacuum. In parallel, DFT calculations are performed on a dimer model of the polymer (1DGEBA-1EDA) with or without adsorbed Cu atoms. Simulations of the XPS spectra are achieved using the unrestricted Generalized Transition State (uGTS) theory; thus complementing our previous results in the Hartree-Fock framework [2]. The uGTS DFT calculations take initial and final states effects into account and provides binding energy shifts (ΔBE) of the 1s orbitals involved in the different bonds. These ΔBEs are used to decompose experimental XPS spectra. Results show an excellent correspondence between experiments and theory for both the bare surface and the metallized surface; therefore we are able to (i) decompose the XPS spectra of the poly-epoxy surface with a high accuracy and (ii) to identify preferential adsorption sites of Cu atoms. Preliminary results will also be presented about the simulation of a real surface model of the poly-epoxy based on molecular dynamics calculations.

References

[1] T. Duguet, C. Bessaguet, M. Aufray, J. Esvan, C. Charvillat, C. Vahlas, C. Lacaze-Dufaure, Toward a computational and experimental model of a poly-epoxy surface, Applied Surface Science, 324 (2015) 605.

[2] A. Gavrielides, T. Duguet, J. Esvan, C. Lacaze-Dufaure, P.S. Bagus, A poly-epoxy surface explored by Hartree-Fock ΔSCF simulations of C1s XPS spectra, The Journal of Chemical Physics, 145 (2016) 074703.

TFC2.3-1O272

A STUDY OF THE INTERFACE BETWEEN POLYMERIC METHYLENE DIPHENYL DIISOCYANATE AND METAL SURFACES BY TOF-SIMS AND MVA

J. Bañuls Ciscar [1], M.L. Abel [1], K. Marcoen [2], T. Hauffman [2], H. Terryn [2], T. Conard [3], J. Watts [1]

[1]University of Surrey, Department of Mechanical Engineering Sciences - Guildford (United kingdom), *[2]Vrije Universiteit Brussel, Department of Materials and Chemistry,Research Group SURF - Brussels* (Belgium), *[3]IMEC - Leuven* (Belgium)

Polymeric methyl diphenyl diisocyanate (pMDI) is a versatile isocyanate commonly used in coatings and adhesives applications because of its excellent mechanical properties. Expanding the knowledge of the chemistry involved at the interface between pMDI and metal surfaces will lead to an advance in existing applications.

To extend the understanding of the interaction of pMDI with metals surfaces, a thin layer of pMDI has been deposited on the surface of interest, followed by cluster ion profiling in conjunction with ToF-SIMS. Multivariate analysis (MVA) has subsequently been performed on the data acquired in order to obtain characteristic information of the studied interface. Preliminary work using XPS and ToF-SIMS has shown an interaction between nitrogen and chromium at the interface. A low binding energy peak (~397 eV) was identified in the N1s high resolution XPS spectrum. This peak represents nitrogen atoms which have a higher electronic density as a result of the electron withdrawing effect of the pMDI on the metal substrate. Furthermore, peaks of characteristic fragments of nitrogen-metal interactions were found in the ToF-SIMS spectra. Additionally, the benefits of Ar_n^+ profiling compared to C_{60}^+ profiling have been assessed by using two separate ToF-SIMS systems, one equipped with a C_{60}^+ source the other with Ar_n^+.

Thanks/Acknowledgement

The authors would like to thank Huntsman PU for supplying the samples and funding this work.

TFC2.1-2O308

SILICON NANOPARTICLES FORMATION IN A-SI/ZRO2 OR A-SIOX/ZRO2 MULTILAYERED NANOPERIODICAL STRUCTURES

D. Koyuda [1], S. Turishchev [1], V. Terekhov [1], D. Spirin [1], D. Nesterov [1], E. Parinova [1], A. Ershov [2], D. Grachev [2], A. Mashin [2], E. Domashevskaya [1]
[1]*Voronezh State University - Voronezh* (Russian federation), [2]*Lobachevsky State University of Nizhni Novgorod - Nizhny Novgorod* (Russian federation)

Silicon nanocrystals formation in dielectric matrix is promising direction for the opto- and nanoelectronics. One of the functional ways for nanocrystals size control and limitation is the formation of the multilayered nanoperiodical structures (MNS) with fixed thicknesses of nanolayers containing silicon nanoparticles located between nanolayers of different materials (e.g. ZrO_2). The redundant silicon in the SiO_2 matrix can be obtained by annealing of the SiOx films formed from SiO powder. Another way to form silicon nanoparticles can be annealing of amorphous silicon layers.

MNS were formed by SiOx or a-Si and ZrO_2 layer by layer deposition on to Si substrates with 8 and 2 nm thickness respectively of each layer type and totally 17 nanolayers pairs. The formed structures were annealed at 500–1100 C aimed at photoluminescent Si nanoparticles formation.

a-Si/ZrO_2 and a-SiOx/ZrO_2 multilayer nanoperiodical structures were studied by means of local atomic surrounding sensitive X-ray absorption near edge structure (XANES) spectroscopy and XPS techniques supported by XRD and SEM. XANES and XPS spectra were recorded at synchrotron radiation center SRC (University of Wisconsin-Madison, Stoughton, USA) and BESSY II (Helmholtz Zentrum Berlin, Germany). Different absorption edges photons energies allowed to probe local atomic surrounding specificity at different analysis depths while XPS was used to control surface properties of the first layer of MNS.

A noticeable changes of electronic structure and phase composition caused by transformation of the silicon atoms surrounding in investigated a-Si/ZrO_2 and a-SiOx/ZrO_2 MNS was shown. a-Si/ZrO_2 structures are partially oxidized at the formation stage. High temperature annealing do not lead to silicon nanoparticles formation in a-Si/ZrO_2 MNS. Moreover the highest temperature anneal of 1100 C leads to multilayers destruction and full silicon oxidation with possible Zr silicide formation. At the same time a-SiOx/ZrO_2 structures may contain silicon nanocrystals after annealing at 1100 C accompanied with the upper (first from the MNS top) ZrO_2 nanolayer disappearance.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh.

TFC1-3O374

EROSION AND NITRIDE FORMATION IN NANOSTRUCTURED TUNGSTEN FILMS EXPOSED TO NITROGEN SEEDED DEUTERIUM PLASMA OF THE LINEAR MACHINE GYM

F. Ghezzi [1], L. Laguardia [1], A. Uccello [1], R. Caniello [1], A. Cremona [1], D. Dellasega [2], F. Dell'era [1], D. Minelli [1], M. Passoni [2], M. Pedroni [1], A. Pezzoli [2], D. Ricci [1], E. Vassallo [1]
[1]CNR, Istituto di Fisica del Plasma "P. Caldirola" - Milan (Italy), [2]Dipartimento di Energia, Politecnico di Milano - Milan (Italy)

In the frame of magnetic confinement nuclear fusion, thin films of metals and composites have been extensively used as model systems to study the issue of plasma-material interaction in laboratory facilities. We focus the attention here on the interaction of a nitrogen (N) seeded deuterium (D) plasma with tungsten (W) coatings having different morphology and structure. This is a typical situation in operating full-metal tokamaks, like JET and ASDEX, where the formation of W nitrides with reduced melting temperature and increased physical sputtering than W, could be a source of plasma impurities [1]. W films were produced with two deposition techniques: magnetron sputtering (MS) and pulsed laser deposition (PLD) [2]. On one hand, thanks to their high density, MS films can simulate the virgin W coatings installed as plasma facing components in JET and ASDEX. On the other hand PLD films, that exhibit an amorphous-like structure, resemble W redeposited after plasma-material interaction in these tokamaks. MS and PLD W coatings were exposed to a N admixed D plasma in the linear machine GyM [3]. Samples were characterized before and after the exposures to study the influence of coating morphology and structure on the erosion by the plasma and nitride formation. The former was evaluated with a profilometer while the latter by X-ray photoelectron spectroscopy (XPS) depth profiles. Moreover, possible modifications of the surface of the films were investigated via scanning electron and atomic force microscopy.

The preliminary results are the following. The sputtering of the MS films is about a factor of 2 higher than that of PLD samples. The XPS analysis shows that the outermost layer of all the samples is characterized by components under the N1s core line that are fingerprints of the presence of ammonia. In the few nanometers subsurface region W nitrides were detected. However, the nitrogen retention of PLD films is much less than that of MS coatings.

References

[1] K. Schmid, et al., Nucl. Fusion 50(2), 025006 (2010)

[2] D. Dellasega, et al., J. Appl. Phys. 112, 084328 (2012)

[3] G. Granucci, et. al., 36th EPS Conference on Plasma Phys., Sofia, June 29 – July 3, 2009 ECA Vol. 33E, P-4.148 (2009)

TFC2.1-1O394

CRYSTALLIZATION OF PE-B-PEO COPOLYMER THIN FILMS EVIDENCED BY FTIR – PM-IRRAS AND AFM

M. Brogly, D. Fischer, S. Bistac
Université de Haute Alsace - Mulhousee (France)

This work focus on the understanding on how organization and crystallization of thin amphiphilic copolymer films[1] can be directed by the surface chemistry of a metal substrate. Various copolymers were adsorbed by spin-coating on metal substrates. The surface chemistry of the substrates was controlled by chemical grafting using thiols[2]. The influence of the hydrophilic or hydrophobic nature of the substrate on the organization and structuration of PE–b–PEO copolymers of different compositions was then studied.

Characterization of thin films of copolymers requires the use of specific characterization techniques. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) is an original vibrational spectroscopy that was used for "in situ" characterization of the polymers or copolymers. Indeed the polarization modulation of the incident IR wave increases the sensitivity of the spectral response, allowing determination of molecular orientation and structuring effects. Atomic Force Microscopy[3] (AFM) analyzes were also performed to access the surface morphology and distinguish amorphous and crystalline phases.

Chains orientations and conformations as well as surface morphologies were thus characterized in order to understand the competition between polymer/polymer and polymer/substrate interactions, as well as impact on the crystallization. This was explained by changes in the balance of polymer/polymer vs polymer/substrate interactions. Substrate surface chemistry alters the balance between these interactions significantly. In the case of amphiphilic PE-b-PEO diblock copolymers, an hydrophilic substrate favors the crystallization of the polar block whereas an hydrophobic substrate will favor the non-polar block crystallization. The modification of the crystalline phase content, morphology and molecular orientation of the crystalline structures of the adsorbed films reflects the strong competition between interfacial forces and intra and intermolecular forces.

Thanks/Acknowledgement

Authors thank Université de Haute Alsace and MENESR for financial support.

References

1. Friction of PE-b-PEG diblock copolymers on model substrates, S. Bistac, D. Fischer, M. Brogly, in Surfactants in Tribology, Vol. 5, Section 1, G. Biresaw and K. L. Mittal Eds., CRC Press, Taylor and Francis Group, Boca Raton (2017)
2. Adsorption of Alkanethiols on Gold Surfaces: PM-IRRAS Study of the Influence of Terminal Functionality on Alkyl Chain Orientation, T. Elzein, A. Fahs, M. Brogly , A. Elhiri, B. Lepoittevin, P. Roger, V. Planchot, The Journal of Adhesion, 89, 416-432 (2013)
3. Surface Morphology and Crystallinity of Polyamides Investigated by Atomic Force Microscopy, T. Elzein , M. Brogly , S. Bistac, in Scanning Probe Microscopy in Nanoscience and Nanotechnology, Vol. 3, NanoScience and Technology, Springer-Verlag Ed., Berlin Heidelberg, p. 235-247 (2013)

TRI - Tribology

TRI-1O016

TRIBOLOGICAL BEHAVIOUR OF LOW-TEMPERATURE CARBURISED AUSTENITIC STAINLESS STEELS

G. Maistro [1], M. Esneider [2], S.A. Pérez-García [2], L. Nyborg [1], Y. Cao [1]

[1]Department of Materials and Manufacturing Technology, Chalmers University of Technology - Gothenburg (Sweden), [2]Centro de Investigación en Materiales Avanzados, S.C. Unidad Monterrey, Parque PIIT, Alianza Norte 202, Apodaca, N.L. CP 66628 - Monterrey (Mexico)

Low-temperature thermochemical surface treatments were developed in order to improve surface hardness of austenitic stainless steels while maintaining their corrosion resistance [1]. However, the tribological behaviour of the treated materials is not well understood. Therefore, in the present work, we investigate the wear mechanisms of low-temperature carburised 304L and 904L steels by means of surface analytical techniques.

Pin-on-disk tests were performed at low-load (0.5N, 1.5N and 3N) conditions in dry and wet (3% NaCl in water) environments for the as-received and carburised materials using an Al_2O_3 ball as static partner. Stylus profilometry was used to measure the wear scar profiles and the worn volume was calculated accordingly by integration. Morphology of the wear tracks was studied using optical and electron microscopy. Energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were used to characterise the nature of the tribo-surfaces and of the wear debris.

In dry conditions, oxidative wear was the dominant wear mechanism. For as-received materials, the total worn volume of 304L varied insignificantly with loads, while 904L suffered severe wear (Fig. 1a) at higher loads due to increased adhesion. The low-temperature carburising process reduced the friction coefficient of both materials due to formation of a continuous, low-friction oxide scale. Consequently, the worn volume was decreased by one order of magnitude.

In wet conditions, three-body abrasive wear was the main mechanism acting on both as-received and carburised materials. Small Fe/Cr-oxide particles (< 1 µm) and fragments from the Al_2O_3 counter-surface were found impinged on the material surface in correspondence of well-defined grooves along the sliding direction. The increase in hardness of the low-temperature carburised materials provides protection against abrasive wear (Fig. 1b).

Thanks/Acknowledgement

The authors are grateful for the financial support from the National Graduate School of Materials Science, hosted by Chalmers University of Technology and the Svenska Föreningen för Materialteknik.

References

[1] S.K. Balijepalli et al. , Surf. Interface Anal. 46 (2014) 731–734.

Posters

ADH - Adhesion

P02.001-ADH013
DEPTH-PROFILING

S. Oswald, E. Lattner, M. Seifert, S. Menzel
IFW Dresden - Dresden (Germany)

AES and XPS Depth-profiling of annealed AlN/Ti-Al/AlN Films for High-temperature Applications in SAW Metallization

For the application of surface acoustic wave sensors at high temperatures, both, a high-temperature stable piezoelectric substrate as well as a suitable metallization are needed. In the past we studied intensively the behavior of Ru-Al thin films on different substrates with various diffusion barriers and different Ru/Al stoichiometry [1-3]. Another attempt is the use of TiAl thin films also known as high temperature resistant.

Al/Ti multilayers have been prepared by electron beam evaporation (10 nm/10nm, 20 layers) on oxidized Si and CTGS substrates. Sputtered AlN cover and buffer layers have been applied as oxidation barriers. To form the TiAl g-phase thermal treatment was done in vacuum up to 800 °C. While phase formation was followed by XRD, we used AES and XPS depth-profiling to investigate film composition and oxidation behavior.

AES is the easiest and fastest way for concentration analysis with sputter depth-profiling of thin films. For the AlN/TiAl system both the complete overlap of the spectra of Ti and N and the highly-insulating substrate CTGS is challenging. By means of data analysis (LLS, factor analysis) the elemental composition can be followed; extreme sample tilting and high ion beam energy helps to overcome the problems of surface charging by the electrons and ions respectively.

XPS has the advantage of easier identification of chemical state changes, however, because of the low lateral resolution of lab systems a much higher measuring (resp. sputtering) time for depth profiling is necessary. Also here the highly-insulating character of the CTGS substrate was challenging: beside the use of non-monochromatic excitation and optimized charge compensation, data treatment by shifting the BE scale using reference peaks was necessary.

The results show a starting intermixture of Al and Ti at 600 °C, accompanied by TiAl formation. The AlN buffers (containing residual O) are stable, however, at 800 °C an oxidation starting from the surface is observed, which can be identified as preferential Al oxidation.

References

[1] M. Seifert, G.K. Rane, S. B. Menzel, T. Gemming, J. Alloys Compd. 664 (2016) 510-517.

[2] M. Seifert, G.K. Rane, S. B. Menzel, T. Gemming, J. Alloys Compd. 688, Part A (2016) 228-240.

[3] M. Seifert, G. K. Rane, S. Oswald, S. B. Menzel, T. Gemming, Materials (2017) accepted

P02.080-ADH463

INFLUENCE OF ORGANIC SURFACE CHEMISTRY ON THE NUCLEATION AND ADHESION OF PLASMA DEPOSITED SIOX FILMS

T. De Los Arcos [1], C. Hoppe [1], F. Mitschker [2], P. Awakowicz [2], D. Kirchheim [3], R. Dahlmann [3], I. Giner [1], G. Grundmeier [1]

[1]*University of Paderborn - Paderborn* (Germany), [2]*Ruhr-University Bochum - Bochum* (Germany), [3]*RWTH - Aachen* (Germany)

Thin silica like films (SiOx) have attracted much interest as coating on plastic materials in the last decades. For the deposition process, the high throughput of plasma enhanced chemical vapor deposition (PECVD) has distinctly established itself for applications on an industrial scale. The nucleation and film growth of PECVD deposited SiOx films as a function of the substrate surface chemistry (Self-assembled monolayers (SAMs) acting as a polymeric model system) was investigated. Ultra-thin SiOx films were deposited by microwave plasma in a mixture of HMDSO and O2. The changes in surface, interface and thin film chemistry were characterized by PM-IRRAS. Cyclic voltammetry with ferricyanide as a redox system was used to probe the defect density of the bare SAMs and the SiOx-covered SAMs. Furthermore, the evolution of the SiOx surface morphology for increasing film thickness as function of the substrate chemical termination is investigated by AFM. A strong influence of the surface chemistry on the SiOx nucleation and film growth was observed. While methyl and carboxyl terminated SAMs were degraded during the nucleation leading to defect rich ultrathin films, the trimethoxysilane group protects the aliphatic chain of the SAM and leads to much better barrier properties of the ultra-thin SiOx-films. A mechanistic explanation of the results was provided. Following, the results were transferred to the adhesion of a SiOx coating, also deposited by a PECVD process, deposited onto injection-molded polypropylene (PP). The surface chemistry was modified by the by-mixture of polypropylene with small amounts of polydimethylsiloxane (PDMS) to create a Si-enriched top layer. The substrates were characterized by X-ray photoelectron spectroscopy, attenuated infrared reflection and time of flight spectroscopy. The adhesion of the SiOx coatings to the PP/PDMS substrates (Si-enriched top layer about 1 nm thick) was greatly enhanced with respect to the non-functionalized PP, which shows that adhesion to polymer substrates can be improved without the need to deposit intermediate adhesion layers, and without the need to include a plasma pre-treatment step into the process.

Thanks/Acknowledgement

We acknowledge the support of the German Research Foundation (DFG) within the framework of the Transregional Collaborative Research Center TRR 87/1 (SFB-TR 87) “Pulsed high power plasmas for the synthesis of nanostructured functional layers”.

References

Influence of organic surface chemistry on the nucleation of plasma deposited SiO_x *films.* Hoppe et al. *J. Phys. D: Appl. Phys.* **50** (2017) 204002 (9pp)

BIO - Bio-interfaces & biomaterials

P01.002-BIO033

FUNCTIONALIZATION OF ZWITTERIONIC BRUSHES, DO THEY REMAIN ANTIFOULING?

M. Ramstedt, S. Hakobyan, O. Rzhepishevska, D. Barbero
Umea University - Umea (Sweden)

Polymer brushes are surface coatings that can be tailored in many ways to suit specific demands including reduction of protein and bacterial fouling of biomaterials. Previously, we reported that antifouling poly (2-(methacryloxy)ethyl)dimethyl-3-sulphopropyl ammonium hydroxide) (MEDSAH) brushes dramatically reduced formation of bacterial biofilm [1]. We hypothesized that this brush could be efficiently functionalized with a small molecule (2-oxo-2-[*N*-(2,4,6-trihydroxybenzylidene)-hydrazino]-acetamide, ME0163) and that the antifouling property would remain also after functionalization. Diblock co-polymer brushes of MEDSAH and GMA were formed by surface-initiated atom transfer radical polymerization (SI-ATRP) and the ME0163 hydrazone was covalently bound to the surface via a ring-opening reaction. Functionalization of the surfaces was followed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The influence of temperature, reaction time and reagent concentrations on the immobilization process was investigated. Surfaces with high degree of functionalization could be made in this way. However, the functionalization rendered the surface more hydrophobic and the antifouling property of the brush was lost. Thus, disproving the second of our starting hypotheses but not the first.

References

1. O. Rzhepishevska, S. Hakobyan, R. Ruhal, J. Gautrot, D. Barbero, M. Ramstedt, Biomaterial Science, vol. 1, 2013, pp. 589-602.

P01.003-BIO115

IMPLEMENTATION OF A PDMS MICRODEVICE FOR THE IMPROVED PURIFICATION OF CIRCULATING MICRORNAS

L. Vanzetti [1], G.C. Santini [2], C. Potrich [3], L. Lunelli [3], S.L. Marasso [4], M. Cocuzza [4], F.C. Pirri [5], C. Pederzolli [2]

[1]Fondazione Bruno Kessler, CMM-MNF - Trento (Italy), [2]Fondazione Bruno Kessler, LaBSSAH - Trento (Italy), [3]Fondazione Bruno Kessler, LaBSSAH; CNR-Institute of Biophysics - Trento (Italy), [4]Department of Applied Science and Technology, Politecnico di Torino; CNR-IMEM, Parma - Torino; Parma (Italy), [5]Department of Applied Science and Technology, Politecnico di Torino - Torino (Italy)

Circulating microRNAs (miRNAs) are considered relevant, non-invasive biomarkers of several pathologies. Simply, rapid and standardised analyses, such as microdevice-based analyses, are highly required. A promising polydimethylsiloxane (PDMS)-based microdevice which integrates the complete processing of the biological sample was previously developed in our lab[1,2]. Here we improved the performances of our microdevice acting on PDMS mold casting, curing and functionalisation, modulating the surface roughness and charge.

Atomic force microscopy was employed to estimate changes at the nanometric scale, while the surface chemical composition modified by functionalisation with different mixes of positively charged 3-aminopropyltrimethoxysilanes (APTMS) and neutral poly(ethylene glycol) silane (PEG), was characterized by X-ray photoelectron spectroscopy. Moreover, the number of exposed primary amines introduced by functionalization was quantified with the reagent sulfosuccinimidyl-4-o-(4,4-dimethoxytrityl) butyrate (s-SDTB). Finally, the miRNAs adsorption rate of the differently modified surfaces was assessed by fluorescence microscopy by incubating a synthetic fluorescently-labelled miRNA.

The functionalisation of PDMS resulted as a necessary step to significantly increase the amount of microRNA captured by the surface. The modulation of the surface charge provided a much more relevant improvement in miRNA capture over roughness modulation (i.e. mold casting strategies). 0.1% APTMS and 0.9% PEG was found as the best mixture to obtain a functional positively-charged coating, able not only to capture miRNAs but also to make miRNA available for further analysis steps, such as on-chip reverse transcription of both synthetic and natural miRNAs. PDMS properties were stable for over two months and PDMS functionalisation lasted up to 48 hours.

The increased functionality of the PDMS surface resulted in the doubling of the purification efficiency of the microdevice which reached a detection limit of about 0.01 pM, starting from human plasma. This sensitivity allows to confidently perform the analysis of the most relevant populations of circulating miRNAs (e.g. miR-21) directly from a few µl of blood plasma. This improvement lays the foundation for the development of an efficient, rapid and user-friendly assay able to exploit the great potentialities of circulating miRNAs.

Thanks/Acknowledgement

This work was accomplished in the framework of NEWTON (Advanced nanosystems for a new era in molecular oncology) funded by MIUR (RBAP11BYNP) Grants-FIRB2012-2016.

References

[1]C. Potrich et al. (2014) Lab Chip 4(20): 4067-75

[2]V. Vaghi et al. (2016) Biophys Chem 208: 54-61

P01.004-BIO130

THE ANALYSIS OF THERMAL AND ANODIC OXIDE LAYERS ON SELECTED BIO-COMPATIBILE TITANIUM ALLOYS

J. Krcil [1], Z. Rafaj [2], S. Krum [1], V. Mára [1], V. Starý [1], V. Nehasil [2]

[1]Department of Materials Engineering, Faculty of Mechanical Engineering, Czech Technical University in Prague - Prague (Czech republic), [2]Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University - Prague (Czech republic)

The bio-compatibility is the important factor regarding implants and bone replacements. In the case of titanium alloys, the oxide layers on their surfaces influence strongly both the bio-compatibility and corrosion resistance. In order to improve these properties the effects and results of oxidizing procedures are studied. The difference in growth, properties and effects of oxide layers prepared by various methods on different base materials are examined [1].

In this work we compared samples of widely used biomaterials: Commercially Pure (CP) titanium grade 2 and titanium alloy Ti6Al4V with recently developed β-titanium alloy Ti-39wt.%Nb (Ti39Nb). We prepared the thermal (600 °C for period of 8 hours in the presence of atmospheric air) and anodic (in 1 M H_2SO_4 with voltage app. 110 V for 1 hour) oxide layer on the samples from these materials. The results of oxidation process were compared using several methods.

Firstly, we observed the change of surface color; also the surface roughness was measured. The surface morphology of oxidized samples was observed using scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) which was used for chemical analysis of the samples. The thickness and structure of oxide layers was measured and observed on the cross-section samples. The further analysis of the surface of oxide layers was carried out using x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The growth of hydroxyapatite for further comparison of oxide layers was realized in Hank's balanced salt solution (HBSS). The results were compared with results in article [2] where the similar procedures were carried out on Ti45Nb alloy samples.

Thanks/Acknowledgement

This work was supported by the Grant Agency of the Czech Republic, grant No. 15-01558S; by the Ministry of Education, Youth and Sport of the Czech Republic, program NPU1, project No. LO1207 and by the Grant Agency of the Czech Technical University in Prague, grant No. SGS16/216/OHK2/3T/12.

References

[1] OSHIDA, Yoshiki. Bioscience and bioengineering of titanium materials. 2nd ed. Elsevier, Waltham, MA : 2013. Elsevier insights. ISBN 978-0-444-62625-7.

[2] ZORN G, LESMAN A. and GOTMAN I., Surface and Coatings Technology. 2006, 201(3-4) 201 (2006) 612–618. DOI: 10.1016/j.surfcoat.2005.12.009. ISSN 02578972.

P01.005-BIO141

SURFACE CHARACTERIZATION AND CORROSION BEHAVIOR OF TINB THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING

D. Tallarico [1], N.T.C. Oliveira [2], A.L. Gobbi [3], P.I. Paulin Filho [4], P.A.P. Nascente [4]
[1]UFSCar - Sorocaba (Brazil), [2]USP - São Carlos (Brazil), [3]CNPEM - Campinas (Brazil), [4]UFSCar - São Carlos (Brazil)

Titanium and niobium metals are promising in applications including, but not limited to, cardiovascular/dental/orthopedic implants, bone fixation devices, joint replacement parts, and surgical instruments due to the combination of good biocompatibility, high mechanical strength, excellent thermal stability, and optimal corrosion behavior. Actually, most of the metallic implants are produced with stainless steel (SS) because it has adequate bulk properties to be used as biomaterials for orthopedic or dental implants and is less expensive than Ti and its alloys, but it is less biocompatible than them. The coating of this SS implants with Ti thin film alloys may be one alternative to improve the biomaterial properties at a relatively low cost. TiNb thin films were deposited in stainless steel substrates using a DC magnetron sputtering equipment, under an argon atmosphere. The chemical composition, roughness, grain size, elastic moduli, hardness, and corrosion resistance of the coating films were analyzed by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), nanoindentation, and potentiodynamic polarization method. The TiNb thin films presented oxidized surface, low roughness, nanostructured grain sizes, as well as elastic modulus smaller than the SS substrate. Open-circuit potential values indicated that the TiNb alloys studied underwent spontaneous passivation due to spontaneously formed oxide film passivating the metallic surface, under the chloride-containing solution. Electrochemical impedance spectroscopy (EIS) tests showed high impedance values for all samples, increasing with immersion time, indicating an improvement in corrosion resistance of the spontaneous oxide film. In all cases, the passive current values were quite small. All these electrochemical results suggest that the TiNb alloy is a promising material for implants devices.

Thanks/Acknowledgement

This work received financial support from FAPESP (proposal 2009/17055-7), CAPES, CNPq, and LNLS (proposals LMF-8912 and LMF-10475).

P01.006-BIO262

XPS STUDY ON ADHESION OF BIOMOLECULES FROM LURIA BERTANI MEDIUM ON DIAMOND FILMS

O. Romanyuk [1], P. Matyska Lišková [2], A. Artemenko [1], I. Gordeev [1], P. Jirícek [1], J. Beranová [2], M. Marton [3], E. Ukraintsev [1], A. Kromka [1]

[1]Institute of Physics, AVCR - Prague (Czech republic), [2]Charles University - Prague (Czech republic), [3]Institute of Electronics and Photonics - Bratislava (Slovakia)

Nanocrystalline diamond (NCD) films are increasingly studied due to their potential biomedical applications, especially as antibacterial coatings. Numerous reports focused on the investigation of film morphology and NCD surface termination for the attachment of organic molecules, cells or bacteria [1,2]. X-ray photoelectron spectroscopy (XPS) is as one of the essential tools for deeper understanding the interaction between functionalized film surfaces and biomolecules.

NCD films were grown using the large area linear antenna microwave plasma system and terminated by H, O, and F employing radio frequency plasma in appropriate gas atmosphere (hydrogen, oxygen or carbon tetrafluoride). All investigated samples were sterilized in autoclave (121 °C, 101.5 kPa). The sterilized samples were exposed (immersed) to the Luria Bertani (LB) medium at 37 °C for 24 hours. The LB-treated samples were washed in DI water prior loading into XPS spectrometer. The C 1s, O 1s, and N 1s core level peaks were measured by AlKα source. Untreated NCD samples and a glass substrates were used as references.

XPS measurements revealed a presence of amino groups of peptide molecules only on the LB-treated samples and AFM measurements confirmed an increased surface roughness. The N 1s core level peak consisted of NH_2 (400 eV binding energy) and NH_3 (401.7 eV) components. While the NH_2/NH_3 ratio was found to be different for the LB-treated glass and NCD samples, it remained rather constant for various NCD surface terminations [Fig. (a)]. In contrast, a significant change in LB film structure was observed for differently terminated NCD surfaces [Fig. (b)]: The O=C (530.8 eV – 531.4 eV) to the H_2O (532.5 eV – 533.3 eV) peak component area ratio depends on NCD surface termination. Here, the selective adhesion of biomolecules from the LB medium on NCD surfaces is possible. A partial change of LB structure at the diamond interface should be expected too. Finally, we will also discuss the influence of liquid/solid interface morphology and chemistry on bacteria attachment.

Thanks/Acknowledgement

This work was supported by project GACR 15-01687S.

References

[1] O. Babchenko, et.al., Phys. Stat. Sol. B 250 (2013) 2717.

[2] A. Kromka, et.al., Phys. Stat. Sol. B 1-5 (2016).

P01.007-BIO410

SELF-ASSEMBLING PEPTIDES FOR REGENERATIVE MEDICINE: STRUCTURAL CHARACTERIZATION AND BIOLOGICAL PROPERTIES

V. Secchi, S. Franchi, M. Santi, G. Iucci, C. Battocchio
Roma Tre - Roma (Italy)

The main object of regenerative medicine is to develop novel therapies to replace or restore the functionality of tissues and organs within the human body [1]. In this context, self-assembling peptides (SAPs) are an appealing class of materials due to their ability to organize in nanostructures that can be successfully anchored to appropriate substrates or directly injected into a lesion [2]. SAPs are able to mimic the structure of the extra-cellular matrix (ECM), offering tridimensional support for cell growth [3]. Indeed these nanomaterials, eventually functionalized with signalling biomolecules (growth factors, small adhesive peptidic sequences, glycans) may constitute a biomimetic matrix with the ability of surrounding cells and promoting specific interactions with them, in order to control and conduct their behavior by mimicking their native environment. The ideal matrix must have a 3D geometry similar to the extracellular matrix and must be able to promote cell adhesion, proliferation, infiltration and differentiation aimed at new tissue formation.

The realization of self-assembling peptides should include a first step of chemical and structural characterization, to check the stability of the molecular structure following the scaffold's development. In the present study we have chemically characterized different type of peptides using X-ray Photoelectron Spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) techniques with the aim to probe the chemical composition, molecular structure and conformation of the proposed materials.

The second step of this work consists in an accurate investigation of the biological properties of SAPs and their interaction with cells. For this reason cells were cultured in the presence of the SAPs in order to assess if peptides exert cytotoxic effect and to evaluate biocompatibility, cellular adhesion and proliferation.

References

[1]Kobolak J., Dinnyes A., Memic A., Khademhosseini A., Mobasheri A.; Mesenchymal stem cell: identification, phenotypic characterization, biological properties and poteintial for regenerative medicine through biomaterial micro-engineering of their niche; Methods; 2015

[2] Dettin M., Zamuner A., Iucci G., Messina G.M.L., Battocchio C., Picariello G., Gallina G., Marletta G., Castagliuolo I., Brun P. Journal of Peptides Science 2014

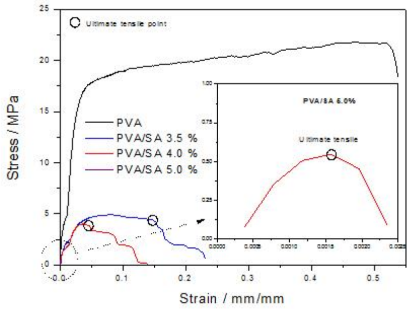
[3] Flamia R., Salvi A.M., D'Alessio L., Castle J.E., Tamburro A.M. Biomacromolecules 2007,8, 128-38.

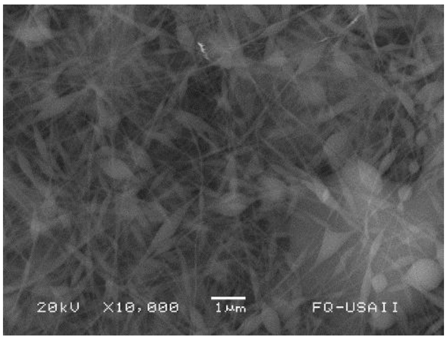
P01.008-BIO450

CHARACTERIZATION OF SODIUM ALGINATE NANOFIBERS FOR BIOMATERIAL APPLICATION

M. Hernandez, P. Corona-Lira, A. Ramírez-Reivich, K. Gómez, C. Gayosso, A. Covelo
Universidad Nacional Autónoma de México - Cdmx (Mexico)

Sodium alginate (SA) is a linear polysaccharide with a negative charge derived from brown seaweed. The SA, in its different forms such as gels, beads or sponges, is commonly used for tissue engineering [1]. One of the main challenges of using SA for tissue engineering relies on the fabrication of nanoparticles or nanofibers for cell culture scaffolds. Since SA has been developed for medical purposes it is necessary to measure, among other properties, the physical-chemical and mechanical properties in order to characterize real conditions of application. This work mainly focuses on the measurement of the electrochemical and mechanical properties of SA by means of electrochemical impedance spectroscopy (EIS) and tensile testing (TT), respectively, of SA electrospunned fibers mixed with poly(vinyl alcohol) (PVA) at different SA/PVA concentration ratios (3.5, 4, and 5 wt. %). The EIS results show that SA/PVA nanofibers immersed in a calcium chloride solution react instantly and change its dielectric properties until the crosslinking process is stabilized in time. The overall crosslinking time is a function of the SA/PVA ratio which means, the more SA concentration mixed in PVA solution, the shorter crosslinking time needed for the stabilization plateau. On the other hand, mechanical testing depicts (Fig. 1) that the higher the PVA/SA ratio, the lower the tensile stress needed for the ultimate tensile point. In addition, a decrement in the ductile behavior at higher SA concentrations was observed and thus, the fracture observed for each case was brittle-like. Additional characterizations such as infrared spectroscopy and scanning electron microscopy were used for further analysis of both electrochemical and morphology assessment (Fig. 2 -PVA/SA_4%).





Thanks/Acknowledgement

M. Hernandez gratefully acknowledges the PAPIIT project, DGAPA, IN114316 (2016-2018), Universidad Nacional Autonoma de Mexico, Mexico.

References

1] N. B. Shelke, R. James, C. T. Laurencin, S. G. Kumbar, Polym. Adv. Technol. 2014, 25, 448.

P01.109-BIO476

PHYSICO-CHEMICAL CHARACTERIZATION OF SELECTED NANOMATERIALS STORED AT THE EC-JRC REPOSITORY

G. Ceccone, G. Cotogno, G. Buti, D. Mehn, J. Ponti, H. Crutzen, D. Gilliland
Joint Research Centre - Ispra (Italy)

It is widely recognized that the use of nanomaterials will strongly impact many research and industrial fields ranging from biomedical to electronics energy and transport. However, it is also widely accepted that in order to profit of the peculiar properties of nanomaterials a careful characterisation and classification is also necessary. In particular, in case of application in medical devices, the knowledge of the surface composition and chemistry is of a paramount importance to avoid possible adverse effects of nanomaterials in biological environment.

The Joint Research Centre of the European Commission (EC-JRC) hosts the repository of representative nanomaterials (JRC Repository) metal oxides and metals and (e.g. TiO_2, SiO_2, CeO_2, ZnO and gold) and industrial scale bare and chemically functionalized single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).[1] These materials are and will be in the future made available to research groups in Europe and globally for benchmarking in research and in regulatory studies. In particular, the JRC established the Repository in order to support programs such as the OECD Working Party on Manufactured (WPMN)[2] for "Testing a Representative set of Manufactured Nanomaterials". The JRC Repository also addresses the need for availability of nanomaterials from a single batch which is preferable in order to enhance the comparability of results between different laboratories and research projects. It is also important to address uncertainties related to whether a nanomaterial tested in a project is the same or similar to a nanomaterial tested in other project(s).

In this work, physico-chemical properties (e.g. size, morphology, dispersivity, surface composition and chemical functionalization) of selected nanomaterials, namely coated and uncoated TiO_2, ZnO and CeO_2 nanoparticles and MWCNTs, investigated using different techniques such as transmission electron microscopy (TEM), dynamic light scattering (DLS), centrifugal sedimentation (DSC), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS), will be presented and discussed.

References

[1] https://ec.europa.eu/jrc/en/scientific-tool/jrc-nanomaterials-repository

[2] http://www.oecd.org/science/nanosafety/

CAT - Catalytic materials

P01.009-CAT056

A STUDY ON THE ETHYLENE-TO-PROPYLENE REACTIONS OVER SSZ-13 ZEOLITES CONVERTED Y ZEOLITES

C. Kim, J.W. Jun, J.W. Kim, T.W. Kim
KRICT - Daejeon (Korea, republic of)

Y zeolites having wide SiO_2/Al_2O_3 ratios (silica/alumina ratios or SARs) were converted into SSZ-13 zeolites in the presence of N,N,N-trimethyl-1-adamantanamine iodide (TMAda-I) as a template. SSZ-13s with increased SARs could be obtained from Y zeolites having SAR of 5.1-80 and sodium silicate by both conventional electric (CE) and microwave (MW) heating. The syntheses were completed in 2 h and 5 d by MW and CE heating, respectively, at 140 oC, because of accelerations by MW both in nucleation and crystal growth stages. The obtained yields of SSZ-13 decreased with increasing the SARs of starting Y zeolites, showing the relatively easy conversion of aluminous Y into SSZ-13. The obtained SSZ-13s with wide SARs (19 – 287) were applied as catalysts in the direct conversion of ethylene-to-propylene (ETP) to understand the effect of SARs on the ETP performances including conversion of ethylene and propylene selectivity. The stability of ETP was highly dependent on the SAR of SSZ-13 zeolites. SSZ-13s with too high and low SARs caused low ethylene conversion (from the beginning of the reaction) and rapid deactivation in the conversion, respectively. The propylene selectivity or yield (at a fixed ethylene conversion of 80%) generally increased with decreasing the SARs (up to 19) of SSZ-13s under the studied conditions because of steady increase in the selectivities for butenes and higher products with increasing SARs of SSZ-13s.

Thanks/Acknowledgement

We would like to acknowledge the financial support from the R&D Convergence Program of MSIP (Ministry of Science, ICT and Future Planning) and NST (National Research Council of Science & Technology) of Republic of Korea (CRC-14-1-KRICT).

P01.010-CAT107

TEXTURAL CHARACTERISTICS OF DESILICATED AL RICH BETA ZEOLITE

A. Benamar, **K. Djenaidi**
USTHB university Algiers Algeria - Algiers (Algeria)

It is well known that Beta zeolite is very sensitive to alkaline treatment than ZSM-5 owing to its unstable structure [1, 2]. Optimal desilication conditions of ZSM-5 are not adapted to prepare hierarchical Beta zeolites[1, 2]. In this work, commercial NH4Beta zeolite with low Si/Al molar ratio of 12.5 is treated at 100°C for different times of 0.5, 4 and 24 h with 0.1 M NaOH aqueous solution. The obtained samples denoted Batx (x: time of alkaline treatment) are characterized by several techniques and N2 sorption.

Data obtained from N2-isotherms of samples show that both low (0.5 h) and long (24 h) alkaline treatment times led to minor changes in the meso- and microporous volumes with respect to the Beta parent while particular behavior is observed for sample treated during 4h. Bat4 displays a relatively high total pore volume determined at 0.987 of P/P0 which corresponds to the mesoporous volume. Micropores seem to be absent over Bat4. The characteristics of the samples follow the order:

Vmesopore (cm3/g) : Bat24 Bparent (0.6) Bat0.5 (0.7) <Bat4 (1.42);

Vmicropore (cm3/g): Bat4 (0)<<<<Bat0.5=Bat24(0.16) Bparent (0.17);

SBET(m2/g): Bat24(524)<Bat0.5(540)<Beta parent (564)<Bat4(830);

Sexternal(m2/g): Bat24 (212)<Bat0.5(227) = Beta parent (228)<Bat4(840)

(Numbers in brackets correspond to either volume or surface).

Our results let suggested that a long alkaline treatment time of 24 h at 100 °C allows to the recrystallization of the Beta zeolite after its dissolution in the NaOH solution.

For the treatment time of 4 h, addition of cethyltrimethylammonium bromide (CTAB, 0.05 %) to NaOH solution, allows to a small increase in the mesoporous volume while maintaining he microporous volume of the Beta parent. The surfactant protects the zeolite from a non controlled desilication.The mesopores size distribution evidenced the benefic effect of the surfactant in NaOH solution on mesopores size around that of CTAB micelles.

Key words : hierarchical zeolite, Beta zeolite, desilication

References

[1] J.C. Groen, S. Abelló, L.A.A. Villaescusa, J. Pérez-Ramirez, Micropor. Mesopor. Mater. 114 (2008) 93

[2] V. Valtchev, G. Majano, S. Mintova, J. Pérez-Ramirez, Chem. Soc. Rev. 42 (2013) 263

P01.012-CAT140

SYNTHESIS OF CARBON-SUPPORTED PT NANOPARTICLES BY GALVANIC REPLACEMENT FOR DEHYDROGENATION REACTION OF DECALIN

H. Na, D. Kim, J.Y. Kang, K.M. Kim, J.C. Jung
Department of Chemical Engineering, Myongji University - Yongin (Korea, republic of)

Highly dispersed Pt nanoparticles were synthesized by galvanic replacement reaction between platinum ion and copper nanoparticles on a carbon support. Galvanic replacement reaction offered a facile preparation of Pt nanoparticles supported onto activated carbons in mild aqueous conditions without any surfactants. In particular, the degree of platinum dispersion and resulting active surface area were controlled by modifying replacement conditions. Prepared catalysts were characterized by TEM, ICP-AES, XRD, and CO-chemisorption analyses. They were applied to hydrogen production through catalytic dehydrogenation of decalin. Then, the relation between physical property and catalytic activity of catalysts was studied. The smaller use of platinum ion in galvanic replacement resulted in Pt nanoparticles of 2.04 nm which showed higher catalytic performance (Figure 1). This investigation on the characterization and activity of nanocatalysts revealed that galvanic replacement process endows noble metal based catalysts with economic feasibility by less use of costly noble metal maintaining a catalytic performance.

P01.014-CAT177

PREPARATION AND PHOTOCATALYTIC STUDY OF ZNO/META- AND AB-PBI POLYMER HYBRID NANOMATERIALS FOR REMOVAL OF DYES FROM AQUEOUS SOLUTIONS UNDER UV-LIGHT

I. Avramova [1], K. Zaharieva [2], H. Penchev [3], K. Milenova [2], F. Ublekov [3], S. Dimova [3], D. Budurova [3], M. Staneva [3], I. Stambolova [1], V. Sinigersky [3], V. Blaskov [1]

[1]*Institute of General and Inorganic Chemistry, BAS, “Acad. G. Bonchev” St., Bl. 11, 1113 - Sofia* (Bulgaria), [2]*Institute of Catalysis, BAS, “Acad. G. Bonchev” St., Bl. 11, 1113 - Sofia* (Bulgaria), [3]*Institute of Polymers, BAS, “Acad. G. Bonchev” St., Bl.103A, 1113 - Sofia* (Bulgaria)

Here we report the results of an extensive investigation on the use of photocatalysts for degradation of organic compounds in polluted water or air, converting them into harmless substances, protecting in this way the environment [1]. The nanocomposites - inorganic particles incorporated in a polybenzimidazole polymer matrix (m- or AB PBI) - exhibit unexpected properties, which considerably differ from these of conventional materials [2]. The combination of inorganic oxide/conjugated polymer enhances the degradation rates of the pollutants due to synergistic effect. For the preparation of nanocomposite powders and films - 2.5 wt. % and 5 wt. % ZnO/meta-PBI and in situ obtained 2.5 wt. % and 5 wt. % ZnO/AB-PBI two approaches have been applied. Commercial ZnO nanoparticle powder was redispersed in DMAc and mixed with commercially available solution of meta-PBI in dimethylacetamide/LiCl (PBI S-26). For the second material ZnO nanoparticles were synthesized in situ in alkali-ethanol AB-PBI solution. The materials were studied by FTIR, XPS, PXRD, thermal analysis and were tested as photocatalysts in the reaction of degradation under UV-light of Malachite Green (MG), Methylene Blue (MB) and Methyl Orange (MO), as model pollutants in aqueous solutions. The photocatalytic tests established that the degradation degree of the dyes decreases in the following order: 2.5 wt. % ZnO/meta-PBI, MG (98%) > 2.5 wt. % ZnO/AB-PBI, MG (91%) > 2.5 wt. % ZnO/meta-PBI, MB (90%) > 2.5 wt. % ZnO/meta-PBI, MO (86%) > 2.5 wt. % ZnO/AB-PBI, MB (67%) > 2.5 wt. % ZnO/AB-PBI, MO (33%). The results show that the photocatalytic activity of 2.5 wt. % ZnO/meta-PBI for degradation of MG, MB and MO is higher than that over the 2.5 wt. % ZnO/AB-PBI.

References

[1] V. Eskizeybek, F. Sarı, H. Gülce, A. Gülce, A. Avc, Applied Catalysis B: Environmental 119– 120 (2012) 197.

[2] A. Matei, I. Cernica, O. Cadar, C. Roman, V. Schiopu, International Journal of Material Forming 1(Supplement 1) (2008) 767.

P01.015-CAT192

SURFACE AND REDOX CHARACTERIZATION OF NEW NANOSTRUCTURED ZRO2@CEO2 SYSTEMS WITH POTENTIAL CATALYTIC APPLICATIONSP

G. Blanco, **A. Barroso-Bogeat, B. Núñez-Pérez, J.M. Pintado, J.J. Calvino**
Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz - Puerto Real (cádiz) (Spain)

Ceria and ceria-zirconia have been widely employed in catalytic applications, where their surface and redox properties play a key role [1]. In the last years, an effort to decrease ceria content in catalysts, while keeping their good performance, has lead to different synthesis strategies [2,3]. In this work, we have deposited ceria over a zirconium oxide, to obtain a well dispersed and thin layer of this material. Surface, structural and redox characterization of the as-prepared samples have been performed by photoelectron spectroscopy (XPS), x-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 physisorption, and thermal-programmed reduction followed by mass spectrometry (TPR-MS) experiments.

As can be seen in Figure 1, the obtained material show a core-shell like structure, wih spherical nanoparticles with an average size from 300 to 400 nm, and ceria covering its surface in the form of nanometric crystallites well dispersed all over the ZrO_2 particles. XPS analysis showed a Ce 4d/Zr 3d atomic ratio of 1.33, far from the average bulk composition expected to be 0.09 (corresponding to 8% mol CeO_2 over ZrO_2). This suggest that ceria is well dispersed over the surface of ZrO_2 particles in a first stage.

The as-prepared ZrO_2@CeO_2 sample was submitted to succesive reduction and reoxidation cycles, and the redox behaviour followed by TPR-MS. These high temperature reduction treatments lead to a progressive incorporation of the CeO_2 surface layer into the ZrO_2 nanoparticles, affecting the redox properties of the system. This CeO_2 integration could be followed by XPS.

Thanks/Acknowledgement

This work has been supported by the Ministry of Science and Innovation of Spain, project MAT 2013-40823-R. A. Barroso-Bogeat acknowledges Juan de la Cierva Contracts MICINN/FEDER Program, and B. Nuñez-Perez thanks the grant from the “Programa Iberoamericano de Formación Doctoral en Ciencias Básicas” (2015-2018) received.

References

1.- A. Trovarelli, Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002

2.- M.P. Yeste, J.C. Hernández-Garrido, D.C. Arias, G.Blanco, J.M. Rodríguez-Izquierdo, J.M. Pintado, S. Bernal, J.A. Pérez-Omil, J.J. Calvino, J. Mater. Chem. A, **1** (2013) 4836-4844

3.- I.Cabeza, L.G. Souto, J.M. Pintado, C. Pereira, C. Freire, G. Blanco, Surf. Interface Anal., **46** (2014) 712-715

P01.016-CAT220

STUDY OF THE CATALYTIC ETHYLENE HYDROGENATION OF NOBLE-METAL FREE CERIA-ZIRCONIA-YTTRIA CATALYTS

G. Blanco, M.P. Yeste, M.A. Muñoz, J.J. Sanchez, A. Barroso-Bogeat, J.M. Pintado, M.A. Cauqui

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz - Puerto Real (cádiz) (Spain)

Ceria-zirconia mixed oxides and related materials are of key importance in catalytic applications, being used either as catalysts or as catalytic support for metal nanoparticles [1]. Due to economic and geo-strategic issues, reducing ceria contents in the catalysts and avoiding the use of noble metals in their formulations, while maintaining good performances, has become a key point in current research [2]. In this sense, we obtained a set of noble-metal free ceria/yttria-stabilized zirconia systems (CYSZ) with very good H_2 reducibility and low ceria content [3]. It is also well known that ceria-zirconia systems can modulate their redox properties depending on the chemical-thermal treatment applied [4]. For this reason, we prepared two different samples: CYSZ with a conventional redox response, and CYSZ-SRMO with enhanced redox properties.

Related with the H_2 reduction mechanism for this kind of oxides, the first step that should be considered refers to the dissociative adsorption and activation of H_2 on the oxide surface. To study the reactivity of that adsorbed hydrogen, we selected ethylene hydrogenation as a test reaction where activated hydrogen plays a key role. The catalytic behaviour of the CYSZ systems was studied both by gas chromatography and near ambient pressure XPS (NAPP-XPS).

The catalytic behaviour of CYSZ and CYSZ-SRMO was significantly different, so the latter reached 100% conversion at 150ºC, whereas CYSZ worked below 30%. The reduction degree of surface ceria was followed by NAPP-XPS (Figure 1), giving a correlation between the oxidation state and the redox performance of the samples.

Thanks/Acknowledgement

This work has been supported by the Ministry of Science and Innovation of Spain (MAT 2013-40823-R). NAPP-XPS experiments were performed at BL24-CIRCE beamline at ALBA Synchrotron (proposal ID: 2015071317). Thanks in particular are given to ALBA beamline scientists Dra. Virginia Perez-Dieste and Dr. Carlos Escudero for their valuable support during the experiments.

References

1.- A. Trovarelli, Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002

2.- N.R. Collins, M.V. Twigg, Top. Catal. **42-43** (2007) 323-332.

3.- M.P. Yeste et al., J. Mater. Chem. A, **1** (2013) 4836-4844.

4.- R.T. Baker et al., Chem. Commun. (1999) 149-150

P01.018-CAT255

INVESTIGATION OF THE MECHANISM OF PEROXIDASE-LIKE ACTIVITY OF CERIUM OXIDE NANOPARTICLES

Y. Kosto, M. Dubau, M. Vorokhta, O. Leiko, N. Tsud, V. Matolin
Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science - Prague (Czech republic)

In recent decades, some nanomaterials have been found to exhibit enzyme-like activities. One of such nanozymes are cerium oxide nanoparticles, which are very promising in biomedicine, drug delivery, biological sensors and have ability to mimic properties of different enzymes, including superoxide dismutase, catalase, peroxidase, oxidase, hydroxyl and nitric oxide radical scavengers.

Many in vivo and in vitro studies of enzyme-like activities of cerium oxide nanoparticles had been already performed. The results show a strong dependency of enzymatic properties of nanoscale cerium oxide on its chemical and physical properties, surface properties, synthesis conditions, exposition method, cell type and other characteristics. Depending on all these parameters, cerium oxide nanoparticles can have healthy effect, be neutral or even be toxic. Ambiguity in understanding of the reasons of increase and decrease of enzyme mimetic activity of ceria nanoparticles leads to necessity to study thoroughly the mechanism of antioxidative properties of cerium oxide.

In our work, we are investigating the mechanism of peroxidase-like activity of cerium oxide. For this purpose, the interaction between CeO_{2-x} thin films and aqueous solutions of hydrogen peroxide (and pure water for reference) is studied.

Two types of CeO_{2-x} thin films with different oxidation state were used. First type of samples was prepared by depositions of cerium oxide 5 nm thick film on copper foil at room temperature under 4×10^{-3} mbar of Ar by means of magnetron sputtering. For obtaining partially reduced surface, glancing angle deposition method was used. Second type of samples was prepared by normal angle deposition of cerium oxide film onto 200 nm CN_x buffer deposited on Si wafer. Deposition was carried out at room temperature in $Ar+O_2$ atmosphere (3.99×10^{-3} mbar Ar + 0.01×10^{-3} mbar O_2).

Experiment was performed at MSB beamline at synchrotron Elettra (Italy). To characterize the surface changes in Ce^{3+}/Ce^{4+} ratio, Ce4f valence band states in off- and on-resonance of Ce^{3+} and Ce^{4+} states were measured by means of Resonance photoelectron spectroscopy. High resolution O1s spectra were recorded (hv=630 eV) to observe changes in concentrations of hydroxyl groups, lattice oxygen and water after treatment by water and hydrogen peroxide solutions with molar concentrations 0.1 M and 1 mM in glove-bag.

Thanks/Acknowledgement

The study was supported by the Charles University, project GA UK No. 1054217.

P01.019-CAT267

UNRAVELING THE ROLE OF IRON IN CRYPTOMELANE CATALYST BY TOF-SIMS FOR TRICHLOROETHYLENE ABATEMENT IN HUMID AIR

N. Nuns [1], S. Sultana [2], J.M. Giraudon [1], N. De Geyter [2], R. Morent [2], J.F. Lamonier [1]

[1]Université Lille1 Sciences et Technologies, Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, 59655 Villeneuve d'Ascq - Lille (France), [2]Ghent University, Faculty of Engineering, Department of Applied Physics, Research Unit Plasma Technology, Sint-Pietersnieuwstraat 41, 9000 Ghent, Belgium - Lille (France)

Trichloroethylene (TCE) is mainly used for the vapor degreasing of metals. Due to the increased awareness to ensure and improve air quality, the need for remediation technologies more sustainable than existing methods has encouraged researchers to explore new innovative processes. Post-plasma catalysis has been shown to be a promising alternative: Coupling a Non Thermal Plasma (NTP) with a catalytic reactor downstream [1]. It has been reported [2] that environmentally and eco-friendly cryptomelane of ideal formula KMn8O16 can be a potential candidate for TCE abatement in humid air as it is an efficient O3 decomposition catalyst. The strategy to improve the performances of the NTP assisted catalyst has been to add Fe to cryptomelane (Figure 1) in order to enhance the electronic, catalytic and possible O3 degradation efficiency. The adding of iron has been carried out by co-precipitation and by impregnation of the cryptomelane followed by calcination at 450°C to be compared with a conventional cryptomelane synthesized by a refluxing method in acidic media.

In this work Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) allow to (i) get more insight in the possible interaction between iron and manganese in the fresh samples and (ii) shed light on the detection of organic ad-species on Fe ions in the course of the PPC experiments. Additionally ToF-SIMS results provide crucial information about the extent of chlorination on the first layers of the studied surfaces. Such results emphasize the crucial role of the mode of preparation of the catalysts to be correlated to the PPC performances in the TCE abatement.

Thanks/Acknowledgement

The research has been partially supported by a French-Belgian research project (PHC FL n°25462PJ). PICS n°6913 (Preparation of catalysts and catalytic depollution assisted by plasma) from CNRS is acknowledged for financial support. Chevreul institute (FR 2638), Ministère de l’Enseignement Supérieur et de la Recherche, Région Nord – Pas de Calais and FEDER are acknowledged for supporting and funding this work.

References

[1] A. M.Vandenbroucke, R. Morent, N. De Geyter, and C. Leys, J. Adv. Oxid. Technol. 14 (2011) 165-173.

[2] V.P. Santos, M.F.R. Pereira, J.J.M. Órfão, J.L. Figueiredo, Appl. Catal. B Environ. 99 (2010) 353–363.

P01.020-CAT268

HYDROGEN INTERACTION WITH CEOX(100)/STO(100) MODEL CATALYST

K. Veltruska, **T. Duchon, J. Schusser**
Faculty of Mathematics and Physics, Charles University - Prague (Czech republic)

Cerium and titanium mixed oxides are excellent candidates for processes connected with hydrogen storage, production and conversion, including reaction such as photodecomposition of water, water- gas shift reaction and conversion of hydrogen to water. Both oxides exhibit exceptional reducibility and oxygen storage capacity facilitated by cycling between stable stoichiometries (Ce3+/Ce4+, Ti3+/Ti4+). The combination of both, a cerium-titanium mixed oxide, has been shown to exhibit remarkable activity in de-/hydrogenation reactions, which has been attributed to stabilization of Ce3+ ions at the interface of the two oxides [1]. Strontium titanate (STO) is an attractive substitute for TiO2 in forming the cerium-titanium oxide interface, offering unique electronic properties while retaining the photocatalytic capability of TiO2. The affinity for charge uptake at the interface allows STO to support polar structures and electrostatically influence interaction with adsorbates [2]. Furthermore, the STO(100) surface provides excellent epitaxial parameters for CeO2(100) growth.

Here we present results obtained on model CeOx(100)/STO(100) catalyst. Reduced ceria layers were prepared using Ce-ceria interfacial reaction [3]. During ultra-high vacuum experiments, we have observed oxidation of these reduced ceria layers under H2 exposition at elevated temperatures. Because thermal activation alone did not reproduce the effect, this indicates a significant hydrogen dissociation and hydrogen induced oxygen transport from STO to cerium oxide. Change of cerium oxidation state was followed by XPS Ce 3d region and XAS at Ce M5 edge. Influence of hydrogen pressure was studied using Near Ambient Pressure XPS.

Thanks/Acknowledgement

The study was supported by the Charles University in Prague, project GA UK No. 472216 and No. 448216. We acknowledge CERIC-ERIC consortium for open access to instrumentation.

References

[1] J. Graciani, K. Mudiyanselage, F. Xu, a. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J.Hrbek, J. F. Sanz, and J. a. Rodriguez, Science (80-.). 345, 546 (2014).

[2] W. Son, E. Cho, J. Lee, and S. Han, J. Phys. Condens. Matter 22, 315501 (2010).

[3] T. Duchoň, F. Dvořák, M. Aulická, V. Stetsovych, M. Vorokhta, D. Mazur, K. Veltruská, T. Skála, J. Mysliveček, I. Matolínová, and V. Matolín, J. Phys. Chem. C 118, 357 (2014).

P01.021-CAT311

AUGER ELECTRON SPECTROSCOPY ANALYSIS OF FRESH AND AGED ALUMINA SUPPORTED AG CATALYSTS

J. Newman [1], D. Paul [1], W. Suchanek [2]

[1]Physical Electronics - Eden Prairie, Mn (United States of America), [2]Scientific Design Company - Little Ferry, Nj (United States of America)

Auger Electron Spectroscopy is a well known surface analysis method optimized for characterization of very small features. The technique has an inherent depth of analysis of ~5 nm and can provide analysis of features as small as ~20 nm. While Auger works well on conducting and semiconducting materials, it is much more challenging to analyze insulating samples due to uncompensated charge buildup that occurs during electron bombardment. Thus, for catalyst analysis on insulating supports (typically metal oxides) Auger can be extremely difficult. However, with careful sample preparation and appropriate Auger operating conditions, excellent data can still be obtained from these challenging materials.

In this investigation Auger elemental mapping and small area spectroscopy were used to study the changes that occur between fresh and aged Cs-promoted, alumina-supported Ag catalyst samples. The results show that while the size of the alumina support particles remains roughly the same during extended use, the Ag catalyst morphology has changed dramatically with the particle size increasing by over an order of magnitude (Figure 1). Conversely, the Cs Auger maps from the Fresh and Aged catalysts show that this constituent remains dispersed across the alumina support during the aging process.

Figure 1. Auger maps for Ag on Fresh and Aged catalyst samples at a field of view (FOV) of 10 µm. The maps show the dramatic change in Ag catalyst localization. Ag map 1A (Fresh Catalyst) shows the Ag particles to be ~0.05 – 0.1 µm in size while Ag map 1B (Aged Catalyst) shows that many of the Ag particles have agglomerated to ~1 µm in size.

P01.022-CAT370

LOW-PRESSURE PLASMA DEPOSITION OF PT/C AND BIMETALLIC CATALYSTS FOR EFFICIENT PEM FUEL CELLS

Y. Busby
University of Namur - Namur (Belgium)

Yan Busby1, Vaios Stergiopulos2, Nathalie Job2, Mathieu da Silva Pires1, Emile Haye1, Jean-Jacques Pireaux1 and Laurent Houssiau1.

1 Research Center in Physics of Matter and Radiation (PMR), Laboratoire Interdisciplinaire de Spectroscopie Electronique (LISE), University of Namur, rue de Bruxelles 61, B-5000 Namur, Belgium

2 University of Liège, Department of Chemical Engineering – Nanomaterials, Catalysis, Electrochemistry (NCE), Building B6a, Sart-Tilman, B-4000 Liège, Belgium

Low-pressure plasma deposition of catalysts materials has been recently shown as a highly-promising way to prepare catalysts materials for proton exchange membrane (PEM) fuel cells.[1] Starting materials are (i) a high-surface area carbon support (graphene, nanotubes or mesoporous carbon xerogels[2]) and (ii) an organometallic solid precursor (Pt or Ni acetylacetonate). Compared to the conventional wet chemistry approaches, dry synthesis by plasma processing offers the advantage of reducing the environmental impact of the catalysts thanks to the lower energy consumption and for being a solvent-free and waste-free process. Furthermore, plasma deposition of catalysts may be more easily scaled in in-line processing. In this work we have studied in details the nanoparticles nucleation process, starting from the creation of an anchoring defect, the nucleation of small nanoparticles and the particle growth. Each step required an optimization of the plasma conditions (discharge power, treatment time, pressure, plasma chemistry) to finally reach the desired catalyst morphology and chemical state.

Catalysts have been systematically characterized by STEM-EDX, XRD and XPS, the electrochemical activity versus the oxygen reduction reaction show equal or superior performances of plasma catalysts with respect to commercial Pt/C catalysts. Moreover, the simultaneous N-functionalization of the carbon support has been successfully achieved by exploring N2 and NH3 plasma treatments.

Finally, bimetallic Pt-Ni/C catalysts have been realized by mixing the respective organometallic precursors. Interestingly, bimetallic Pt-Ni/C catalyst showed a catalytic activity comparable to that of Pt/C catalysts made with a higher Pt content.[3]

References

[1] M Laurent-Brocq, N Job, D Eskenazib, J-J Pireaux, Pt/C catalyst for PEM fuel cells: Control of Pt nanoparticles characteristics through a novel plasma deposition method, Applied Catalysis B: Environmental 147, 453–463, 2014

[2] N. Job; S Lambert; A Zubiaur; C Cao; J-P Pirard, Design of Pt/carbon xerogel catalysts for PEM fuel cells. Catalysts, 2015, 5, 40-57

[3] Y. Busby, V. Stergiopulos, N. Job, M. da Silva Pires, E. Haye, J.-J. Pireaux and L. Houssiau (in preparation)

P01.023-CAT378

XPS STUDY OF SURFACE MODIFICATION ON NICEO2-HMS AFTER INTERACTION WITH CH4.

V. La Parola [1], A. Emamdoust [2], G. Pantaleo [1], S. Farjami Shayesteh [3], A.M. Venezia [1]
[1]ISMN-CNR - Palermo (Italy), [2]Nanostructure Lab., Department of Physics, University of Guilan, Guilan, Iran - Guilan (Iran, islamic republic of), [3]Nanostructure Lab., Department of Physics, University of Guilan, Guilan, Iran - Guila (Iran, islamic republic of)

Natural gas, whose main constituent is methane, is one of the cheapest source of energy available on the planet. Besides its use as fuel, transformation reactions of methane into syngas, building block for high added value chemicals, are widely studied.

Nickel based catalysts are suitable for methane partial oxidation (CPO) reactions, however they suffer from lack of stability generally attributed to carbon deposition or sintering.

In order to elucidate the factors influencing the nickel activity and stability we investigated the changes of the nickel structural and chemical properties after different pretreatment and upon interaction with methane.

Ni(6wt%) and Ni(6wt%)CeO2(20wt%) on HMS, prepared by microwave assisted synthesis, were exposed to different gas atmospheres and their modifications were studied by means of XRD and XPS.

By temperature programmed CH4 decomposition on the reduced catalysts, it was found that the presence of ceria increases the temperature of methane activation by more than 100 °C, from 350°C of NiHMS to 480°C for NiCeHMS. On the contrary no modification of the oxygen activation is observed. This implies that, if we start a reaction involving oxygen below the temperature of methane activation, metallic nickel will be easily reoxidized, becoming inactive (Fig.1a). On the contrary, if we start above the activation temperature, the oxygen would preferentially react with the activated methane, while nickel would remain in a reduced state maintaining a high catalytic activity (Fig.2b). The changes in the nickel and cerium oxidation states are confirmed by XPS analysis, as evidenced in Fig.2, were reduced nickel and cerium are found after CPO when the feed is introduced at 550 °C.

In conclusion, depending on the activation and operative procedure, the methane CPO activity drastically changes. A preliminary study on the interaction of the catalyst surface with methane is essential for the correct assessment of a catalyst activity.

P01.024-CAT414

PHOTOSTIMULATED OXYGEN ISOTOPE EXCHANGE BETWEEN N18O AND TIO2

R. Mikhaylov, N. Glazkova, K. Nikitin

Laboratory "Photoactive Nanocomposite Materials", Saint Petersburg State University - Saint Petersburg (Russian federation)

TiO_2 is one of widely investigated UV photocatalysts owing to its high activity, versatility, non-toxicity and low cost. The interest to TiO_2 is related to the search for ways of photocatalytic removal of organic and inorganic pollutants from indoor air and water. In particular, emissions of oxides of nitrogen NOx (N_2O, NO and NO_2) are of importance for the atmospheric pollution problem. Photocatalytical decomposition of NO on TiO_2 and the understanding the mechanisms of processes, occurring on the surface, are widely investigated. One of the processes occurring under UV or VIS irradiation is intense photostimulated oxygen isotope exchange (POIEx) between $N^{18}O$ and TiO_2 [1, 2]. It occurs *via* interaction of $N^{18}O$ with surface hole center $^{16}O_{cus}^-$, where $^{16}O_{cus}^-$ is coordinatively unsaturated surface oxygen captured a photogenerated hole [1]. But the mechanism of formation of $N^{18}O$ - $^{16}O_{cus}^-$ intermediate has not been investigated in detail. The intermediate may result either from a collision of the gaseous NO molecule with the $^{16}O_{cus}^-$ center or from a contact of weakly adsorbed NO species with the one.

The present work is devoted to the investigation of POIEx between $N^{18}O$ and TiO_2 Hombifine N (anatase) at T = 293 K by means of kinetic mass-spectrometry and TPD spectroscopy.

From the linear dependence of the POIEx rate on $N^{18}O$ pressure, combined with results of computing simulation of $N^{18}O$ – TiO_2 exchange *via* intermediate formation of abovementioned types, it was shown that the exchange occurs *via* the collision interaction of gaseous NO molecule with the surface active site $^{16}O_{cus}^-$. The activation energy (E_a = 0.221 ±0.003 eV) of oxygen exchange step $N^{18}O$ - $^{16}O_{cus}^-$ → $N^{16}O$ - $^{18}O_{cus}^-$ was calculated basing on the dependence of the exchange rate on the temperature in the 150 – 300 K range.

The results may be useful for investigation of the processes occuring in "NO - TiO_2" systems with ^{18}O label participation.

Thanks/Acknowledgement

The present study was performed within the Project "Establishment of the Laboratory of Photoactive Nanocomposite Materials" financed by a Grant (No. 14.Z50.31.0016) from the Government of the Russian Federation. We are grateful to the Resource Centers "Nanophotonics", "Centre for X-ray diffraction Studies" and "Centre for Innovative Technologies of Composite Nanomaterials" of SPbSU.

References

1. Courbon, H.; Pichat, P. J. Chem. Soc., Faraday Trans. 1, 1984, 80, 3175-3185.
2. Lisachenko, A.A.; Mikhailov, R.V.; Basov, L.L.; Shelimov, B.N.; Che, M. J. Phys. Chem. C, 2007, 111, 14440-14447

P01.103-CAT456

THE ROLE OF RUTHENIUM ON CARBON-SUPPORTED PTRU CATALYSTS FOR ELECTROCATALYTIC GLYCEROL OXIDATION UNDER ACIDIC CONDITIONS

C. Kim, B.T. Yoon, T.W. Kim, H.J. Kim, S.Y. Jeing
Korea Research Institute of chemical Technology - Daejeon (Korea, republic of)

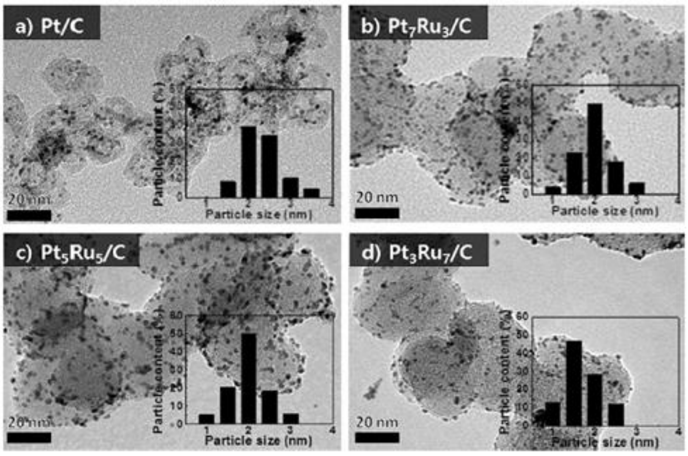


Figure 1. TEM images of carbon-supported Pt and PtRu catalysts with different Pt/Ru atomic ratios, together with corresponding histograms of particle size.

The electrooxidation of glycerol was investigated on a series of Ru-modified Pt/C catalysts. The XRD and TEM results indicate that bimetallic PtRu nanoparticles with different atomic ratios (Pt/Ru=7:3, 5:5, 3:7) are well alloyed and uniformly dispersed on the carbon support, with an average particle size of approximately 2 nm (Figure 1). X-ray photoelectron spectroscopy (XPS) and X-ray absorbtion near-edge structure (XANES) analyses revealed that the Pt electronic structure was significantly modified through the formation of the PtRu alloy (Table 1). The electrochemical measurements showed more enhanced catalytic activities for the glycerol electrooxidation on the bimetallic PtRu/C catalysts than for the Pt/C catalyst in acidic media. In the electrocatalytic batch reactor, the PtRu/C catalyst produced more oxidized products, such as glycolic acid, at higher glycerol conversion than the Pt/C catalyst. DFT calculations revealed that there exists a volcano-type relation between the glycerol binding energy and the catalytic activity for glycerol electrooxidation. This study thus highlights that glycerol molecules on the structurally and electronically modified PtRu surface can be efficiently oxidized by controlling the adsorption/desorption properties of glycerol and by breaking more C-C, C-H, and O-H bonds.

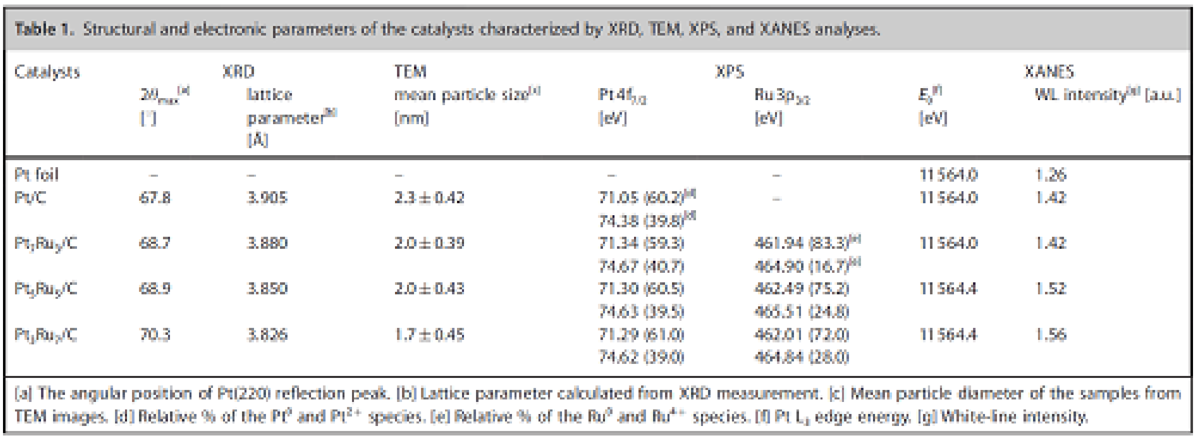


Table 1. Structural and electronic parameters of the catalysts characterized by XRD, TEM, XPS, and XANES analyses.

Catalysts	XRD		TEM	XPS		XANES	
	$2\theta_{max}$[a] [°]	lattice parameter[b] [Å]	mean particle size[c] [nm]	Pt $4f_{7/2}$ [eV]	Ru $3p_{3/2}$ [eV]	E_0[f] [eV]	WL intensity[g] [a.u.]
Pt foil	–	–	–	–	–	11564.0	1.26
Pt/C	67.8	3.905	2.3 ± 0.42	71.05 (60.2)[d] 74.38 (39.8)[d]	–	11564.0	1.42
Pt_7Ru_3/C	68.7	3.880	2.0 ± 0.39	71.34 (59.3) 74.67 (40.7)	461.94 (83.3)[e] 464.90 (16.7)[e]	11564.0	1.42
Pt_5Ru_5/C	68.9	3.850	2.0 ± 0.43	71.30 (60.5) 74.63 (39.5)	462.49 (75.2) 465.51 (24.8)	11564.4	1.52
Pt_3Ru_7/C	70.3	3.826	1.7 ± 0.45	71.29 (61.0) 74.62 (39.0)	462.01 (72.0) 464.84 (28.0)	11564.4	1.56

[a] The angular position of Pt(220) reflection peak. [b] Lattice parameter calculated from XRD measurement. [c] Mean particle diameter of the samples from TEM images. [d] Relative % of the Pt^0 and Pt^{2+} species. [e] Relative % of the Ru^0 and Ru^{4+} species. [f] Pt L_3 edge energy. [g] White-line intensity.

CER - Ceramics

P02.002-CER156

IMPACT OF SURFACE MODIFICATIONS OF POLISHED ZERODUR® ON THE GENERATION OF DEFECTS : A SURFACE ANALYSIS STUDY

B. Henault [1], A. Garnier [2], B. Letourneur [2], V. Lena [2], P. Robert [2], J.M. Nedelec [1]
[1]Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF - Clermont-Ferrand (France), *[2]Safran Electronics & Defense - Montluçon* (France)

Chemical mechanical polishing (CMP) is a technology used in many fields such as optronics and integrated circuits. It enables processes to achieve high removal rates with a nano-roughness.

Surface defects such as scratches (e.g. figure 1) or cracks limit the performances of polished products. The comprehension of CMP mechanisms is a key to understand the defects generation.

The studied process includes samples made of Zerodur®, which are polished on a pitch platen with ceria particles as abrasive.

The penetration depth of Ce on polished Zerodur® samples was characterized using Secondary Ion Mass Spectroscopy (SIMS). It was found to be 40 to 80 nm deep depending on the process parameters. This statement was similar to Suratwala et al. in 2015 on fused silica[1].

Following this statement, nanoindentation tests were performed on polished Zerodur® and showed an increase of 20% of the extreme surface hardness (~50 first nanometers) in comparison to the bulk. A link may be established between chemical modifications and mechanical variations.

This phenomenon could be explained with a specific interaction between ceria and silica[2], which may lead to the formation of cerium silicate and modify the mechanical properties.

In order to prove this hypothesis, cerium silicate samples were prepared by sintering and were compared with polished Zerodur® by photoemission using HAXPES (HArd X-ray PhotoElectron Spectroscopy) on the Synchrotron Soleil beamline.

Thanks/Acknowledgement

Team GALAXIES from Synchrotron Soleil

References

[1] T. Suratwala et al., “Chemistry and Formation of the Beilby Layer During Polishing of Fused Silica Glass,” J. Am. Ceram. Soc., vol. 98, no. 8, pp. 2395–2402, Aug. 2015.

[2] L. M. Cook, “Chemical processes in glass polishing,” J. Non-Cryst. Solids, vol. 120, no. 1–3, pp. 152–171, 1990.

P01.109-CER426

FERROELECTRIC AND PHOTOELECTROCHEMICAL INVESTIGATIONS IN LEAD-FREE BA(TI0.950SC0.025NB0.025)O3 CERAMICS

K. Taïbi, N. Haddadou, N. Bensemma
LCT Faculté de Chimie USTHB - Alger (Algeria)

Industrial effluents containing different types of hazardous products to the environment are discharged without strict control in watercourses leading to constant water pollution. Various types of treatments were used to remove such pollutants. Among these, photocatalysis is an inexpensive technique easy to implement and economically attractive. It is a new approach to eradicate pollution by means of abundant solar energy [1]. The current challenge is to increase the photocatalytic efficiency by means of new materials having mainly low band gap (<3e.V) and eco-friendly. Taking account of the considerations mentioned above, the lead-free ferroelectric compounds of perovskite structure appear to be potential candidate to increase the photocatalytic efficiency. In fact, ferroelectric material is good candidate for photocatalysis applications because its nature spontaneous polarization results in reduce the time recombination electron–hole pair, which is generated from photon energy [2]. In this way, we have previously explored several compositions regarding these conditions [3-4] and we present hear the photoelectrochemical investigations in a new lead-free ferroelectric compositions derived from BaTiO3 by the simultaneous substitution of Ti by Sc and Nb.

In the first part of this work, the temperature and frequency dielectric responses of Ba(Ti0.950Sc0.025Nb0.025)O3 ceramics are exposed and correlated with the structural results obtained by X-ray powder diffraction. The samples showed normal ferroelectric behavior with a slight deviation from the Curie-Weiss law.

The second part deals with the photoelectrochemical (P.E.C) characterization of Ba(Ti0.950Sc0.025Nb0.025)O3 in order to assess its photocatalytic feasibility. It was observed that this ferroelectric perovskite showed P.E.C properties with an optical gap of 2.60 e.V n-type conduction and a flat band potential of -0.58 VSCE. As application, the oxide is tested for the amoxicillin oxidation under solar light.

References

[1] I.K Konstantinou and T.A Albanis, Appl. Catal. B Environ. 49 (2004)1.
[2] Y. Lin, C.W. Nan, J. Wang, H. He, J. Zhai, L. Jiang, Mater. Lett., 58 (2004) 829.
[3] A. Kerfah, K. Taibi, S. Omeiri, M. Trari, Sol. Energy 85 (2011) 443
[4] N. Boutal, G. Rekhila, K. Taibi, M. Trari, Sol. Energy 99 (2014) 291

COR - Corrosion

P01.026-COR168

EVALUATION OF CORROSION INHIBITION OF THE MILD STEEL IN 1 M HCL USING SOME INORGANIC PHOSPHATES GLASSES

E. Mouloud, L. Mohammed, B. Abdelkbir, G. Abdallah
Mohammed V University, Faculty of Sciences - Rabat (Morocco)

Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acid media are the major obstacles for its use on larger scale [1]. Many inhibitors have been used in order to protect metals in acid environments. However, the use of inorganic inhibitors, for corrosion inhibition has received considerable attention [2]. In the present work, we prepare and characterize the syntheses glasses using X-ray diffraction, and infrared spectroscopy. In order to inhibit the mild steel corrosion in 1 M HCl, we study the effect of P_2O_5 and Bi_2O_3 in the glasses structure using electrochemical measurement. The results obtained from the potentiodynamic polarization measurements in 1 M HCl solution at different contents of P_2O_5 and Bi_2O_3 oxides in the glass network [PB], show that the current densities values decrease with increasing inhibitor concentration and reaches a minimum at 200 ppm and its inhibition efficiency reaches more than 90%. This result confirms that the phosphorus present in the glass is the important element in the system for inhibition. Also, the electrochemical parameters derived from the Nyquist plots and inhibition efficiencies values, show that the charge transfer resistance increase comparing to blank solution. This change can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer suggests that the inhibitor [PB] molecules function by adsorption at the metal–solution interface. Optical microscopy image confirmed the absence of corrosion product on the metal surface in the presence of inhibitor. This states that the glass system (PB) possess inhibition efficiency against mild steel in acidic medium.

Mots-clés- Steel, EIS Spectrometry, Corrosion inhibition, Electrochemistry, Phosphate Glasses

References

1-S.Bilgic,N.Caliskan,J.Appl.Electrochem.31(2001)79–83.

2- H.P.Sachin, M.H.Moinuddin,N.S.Bhujangaiah,Int.J.Electrochem.Sci.4(2009) 134–143

P01.028-COR202

ON THE INFLUENCE OF THE EQUAL-CHANNEL ANGULAR PRESSING PROCESS ON ELECTROCHEMICAL PROPERTIES OF ELECTROLYTIC COPPER

A. Covelo [1], E. Mota [1], J.M. Cabrera [2], A. Barba [1], R.G. Valdez [1], M.Á. Hernández[1]

[1]Centro de Ingeniería de Superficies y Acabados (CENISA), Dpto. de Materiales y Manufactura, Facultad de Ingeniería, UNAM - Ciudad De México (Mexico), [2]Department of Materials Science and Metallurgical Engineering ETSEIB, Universidad Politecnica de Catalunya - Barcelona (Spain)

Over the past few years a great number of investigations were carried out to improve the mechanical properties of traditional metals applying the Equal-Channel Angular Pressing process, ECAP [1, 2]. However, many unanswered questions concerning electrochemical behaviour must be studied and thus, clarified. For this reason, the objective of this work is to analyse the effects of the ECAP process on the electrochemical properties of electrolytic copper using different surface finishes (as received and polished finish with 1 µm) in a dissolution of 0.01 % NaCl and 0.1 M Na_2SO_4. For this purpose samples of electrolytic copper with eight passes of ECAP were tested using electrochemical noise (EN) and electrochemical impedance spectroscopy (EIS). Electrochemical results indicate that samples with and without ECAP process showed two time constants; the first process at high-frequency (10^5-10^1 Hz) is associated to the electrochemical response of the rusted sample whereas the second process, located between 10^1-10^{-1} Hz, is ascribed to the oxide-reduction process of copper. At the as received condition, samples with ECAP showed high impedance modulus around $2x10^4$ ohm·cm^2 at the end of the testing (216 hours) while samples without ECAP exhibited $9x10^3$ ohm·cm^2. On the other hand, polished samples exhibited lower impedance resistances with and without ECAP, which rapidly decreased their corrosion resistance as a function of time. In addition, morphological characterization in conjunction with X-ray analysis and Differential Scanning Calorimetry (DSC) demonstrated that samples subjected to the ECAP process suffered a modification of their thermal properties even though their crystalline structure did not change. As expected, microstructure of the ECAP samples revealed an average grain size in the order of nanometres.

Thanks/Acknowledgement

A. Covelo acknowledges PAPIME PE100916, DGAPA, UNAM, 2016, Mexico

References

[1] H. Gleiter. Prog Mater Sci 33,223–315 (1989).

[2] J. M. Cabrera, B. R. Rodriguez. Scientia et technica. 38 (1) 165-169 (2008).

P01.030-COR290

CORROSION OF CHALCOGENIDE GLASSES IN BASIC AQUEOUS SOLUTIONS

J. Conde Garrido, J.M. Silveyra, O. Cuellar Rodrigues, M.A. Ureña
Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Sólidos Amorfos / CONICET, INTECIN - Buenos Aires (Argentina)

Chalcogenide glasses are amorphous materials used in great variety of applications: infrared optics, chemical sensors, gas sensors, phase change memories, solid-state electrolytes, etc.

In previous works, our group has discovered that Agx(Ge0,25Se0,75)1−x (at. %) bulk glasses are heterogeneous and consist of two phases: a Ag-rich phase and a Ag-poor phase. In the range of compositions $0.08 < x < 0.1$, the glasses suffer a spinodal decomposition upon solidification. Outside this range, a binodal decomposition takes place.

A high resistance to acidic media characterizes these materials but they are corroded by basic solutions. Our group has shown in previous works that the Ag-poor phase is more easily corroded than the Ag-rich phase.

In this work, we studied bulk AgGeSe glasses with $x = 0$ and 10 by immersing them in KOH (0.3M) solutions at various temperatures. We observed the samples by SEM, measured the mass loss as a function of time, and estimated the reaction order and the activation energy.

Thanks/Acknowledgement

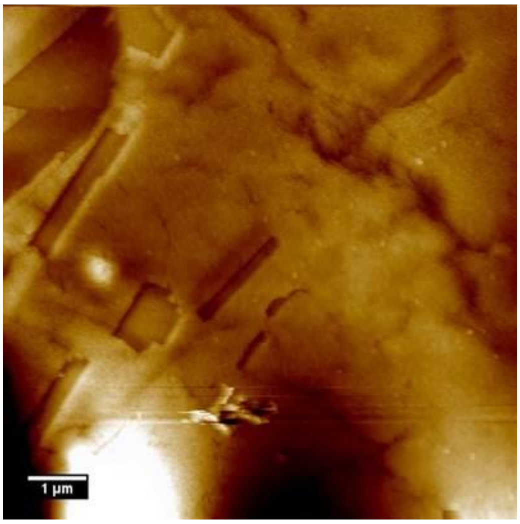
The authors would like to acknowledge the financial support of Universidad de Buenos Aires, CONICET and ANPCyT.

P01.104-COR461

COMBINED ECSTM AND EBSD STUDY OF THE EFFECT OF GRAIN BOUNDARY TYPE ON INTERGRANULAR CORROSION OF COPPER

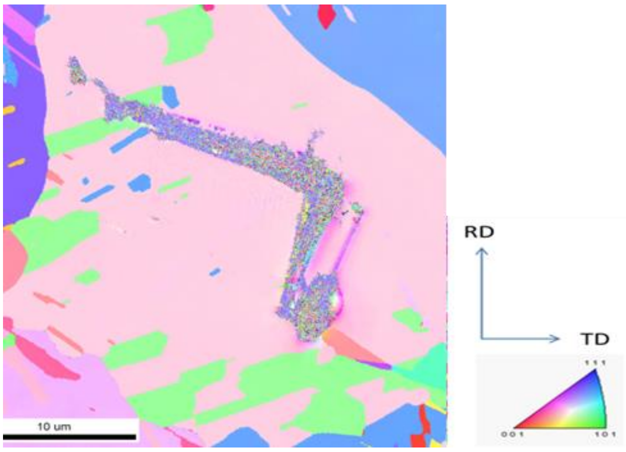
M. Bettayeb [1], V. Maurice [1], P. Marcus [1], L. Klein [1], L. Lapeire [2], K. Verbeken [2]
[1]"CNRS - Chimie ParisTech", Paris, France - Paris (France), [2]"Ghent University", Ghent, Belgium - Paris (France)

Intergranular corrosion (IC) is a major degradation problem of polycrystalline materials that has been shown to be intimately related to the local microstructure, type and energy of grain boundaries. For fcc materials such as copper, only coherent twin (∑3 CSL with (111) plan) are reported to have good resistance to IC. Other special grain boundaries (∑5 to ∑29 CSL) as well as random grain boundaries (without a CSL configuration) would not resist intergranular corrosion.



In this work, high purity copper was chosen as a model material to investigate the relationships between microstructure (grain boundary type) and local corrosion properties (dissolution) at the emergences of grains boundaries. Electrochemical scanning tunneling microscopy (ECSTM) coupled to electron backscattered diffraction (EBSD) was applied to observe in situ topographic changes as function of the applied electrochemical potential. A nano-indentation method using the STM tip was developed to combine ECSTM and EBSD analysis on a very same copper local surface (see Figure).

ECSTM data were obtained in situ after a surface preparation producing oxide-free surfaces with emerging grains boundaries. Performing cycles of anodic dissolution in the absence of any surface oxide reveals a grain boundary type-dependent corrosion behavior. Localized attack is initiated at grains boundaries that can be assigned to either random-type boundaries or non-coherent CSL's based on EBSD while, in the same conditions, coherent twin grain boundaries do not corrode. Direct coupling of ECSTM and EBSD, shows that the IC behavior measured at the emergence of the grain boundary at the solid/liquid interface is dependent of the local surface structure along the boundary.



CUL - Cultural heritage

P01.032-CUL191

SURFACE AND MICROSTRUCTURAL ANALYSES OF A ROMAN QUADRANTES DATING BACK TO 1ST CENTURY AD

A. De Ruggiero [1], S. Kaciulis [2], A. Mezzi [2], R. Montanari [1], A. Varone [1], R. Volterri [1]

[1]Department of Industrial Engineering, University of Rome "Tor Vergata" - Rome (Italy), [2]ISMN – CNR, 00015 Monterotondo Stazione - Rome (Italy)

The Roman quadrantes made of a copper alloy belongs to a group of more then 8.000 coins found in the river Tiber during a short time archaeological research in 1987-88 [1]. They were buried in the river bed, six meters from the right bank, near Porta Portese. Most of the recovered ancient coins are low value bronze-copper coinage in poor or very poor state of conservation, but extremely useful to the twofold purpose of revealing the standards of every-day life in town as well as providing a large documentation of samples to deepen the research in this field, where many questions are not solved yet.

The quadrantes coined in the 1st century AD has been examined by means of X-ray diffraction (XRD), Secondary Electron Microscopy (SEM/EDS) and XPS. In particular, the spectra of Cu 2p, Cu LMM and the valence band have been investigated to identify the oxidation state of Cu. Moreover, XPS depth profiling by Ar+ ion sputtering and XPS chemical imaging have been employed for the investigation of micro-chemical composition of the coin surface.

The surface of the coin is covered by a patina of cuprite Cu2O and malachite Cu2CO3(OH)2. Like other ancient coins, it exhibits an anomalous patina that may contain copper sulphides (mainly covellite Cu2S) or copper chlorides and oxychlorides (typically nantokite CuCl).

References

1- F. Gauzzi, R. Montanari, P. Serafin, R. Volterri, "Microchemical and X-ray diffraction (XRD) analyses for the characterization of some monetary specimens of roman imperial age", Proc. of the 2nd Intern. Conf. Archaeometallurgy in Europe, Aquileia, June 2007.

ELC - Micro- and optoelectronics

P02.005-ELC023

INTERFACIAL REACTIONS AND MECHANICAL STRENGTH OF AU-IN AND AG-IN JOINTS DURING TRANSIENT LIQUID PHASE BONDING

J-W. Yoon, B.S. Lee
Korea Institute of Industrial Technology (KITECH) - Incheon (Korea, republic of)

In recent years, the field of power electronics has attracted increasing attention for applications in the automotive sector such as the development of electric vehicles (EVs) and hybrid electric vehicles (HEVs), due to the various environmental regulations imposed worldwide. In power electronics systems, the first-level chip interconnection plays an important role because it directly interfaces with the power devices and the ceramic substrates. The use of high power induces large thermo-mechanical stresses in electronic devices during operation. Therefore, the power modules in the EVs and HEVs require improved high-temperature stability, necessitating the need for highly reliable die bonding materials and methods [1]. Consequently, the reliability requirements for such modules have become highly stringent and new packaging materials and technologies are required to meet the demands of power electronic modules [2]. Some good candidates for high temperature applications include high-temperature solders such as Au-20Sn, Ag or Cu sinter pastes, and transient liquid phase (TLP) bonding materials. In particular, the TLP bonding technology is suitable for use in high temperature environments owing to its relative low bonding temperatures, high re-melting temperatures and simplicity of the bonding process. In this study, Au-In and Ag-In TLP bonding technologies have been investigated as die-attach methods for power electronics packaging. We first evaluated the sequential interfacial reactions and transformation of the In solder to the intermetallic phase during TLP bonding (Fig. 1). In order to determine the effect of interfacial reactions and reaction products on the mechanical properties of the TLP bonded joints, die-shear tests are conducted using a global bond tester. Further, the relationship between the mechanical properties of the TLP bonded joints and interfacial reactions is discussed.

References

[1] Y.H. Byun, C.M. Jeong, J.W. Yoon, C.H. Kim, C.S. Kim, B.W. Lee, S.W. Booh, U.I. Chung, Proc. 8th IEEE Vehicle Power and Propulsion Conference (VPPC 2012), Seoul, (2012) 1070.

[2] B.S. Lee, C.W. Lee, J.W. Yoon, Surf. Interface Anal. 2016, 48, 493.

P02.006-ELC055

SEQUENTIAL INTERFACIAL REACTIONS AND MECHANICAL STRENGTH OF SAC305 SOLDER JOINTS WITH THIN ENEPIG SURFACE FINISHES

J-W. Yoon [1], J.H. Back [1], S.B. Jung [2]
[1]Korea Institute of Industrial Technology (KITECH) - Incheon (Korea, republic of), [2]Sungkyunkwan University - Suwon (Korea, republic of)

In recent years, the surface mount technology and flip chip bonding has increased the importance of solder joint reliability in microelectronic packaging. The solder alloys and surface finish materials should be able to produce a reliable solder joint when assembled in these packages. Among the many PCB surface finishes, electroless nickel-immersion gold (ENIG) and electroless nickel-electroless palladium-immersion gold (ENEPIG) are very versatile, especially for high-end product applications [1]. However, recent studies have shown that the electroless plated Ni(P) layer formed during ENEPIG metallization dramatically increased the electrical impedance of solder joints [2]. Ho et al. studied ENEPIG with thin Ni(P) layer to improve the connection conductivity, and reported that the submicron-thick amorphous Ni(P) layer could be exhausted during the reflow process and the electrical impedance could be effectively reduced [2]. In addition, recent advanced microelectronic packages demand to reduce the bump pitch of the flip chip packages under approximately 30 µm. To meet this requirement, we should reduce the thickness of the electroless Ni(P) layer in ENEPIG surface finish in the near future. In this paper, we evaluated the solderability of thin ENEPIG plating layer for fine-pitch package applications. Firstly, the wetting behavior, interfacial reactions, and mechanical reliability of a Sn-3.0Ag-0.5Cu (SAC305) solder alloy on a thin ENEPIG coated substrate were evaluated. (Fig. 1). In order to determine the effect of interfacial reactions and reaction products on the mechanical properties of the ENEPIG joints, shear tests are conducted using a global bond tester. Further, the relationship between the interfacial reactions and mechanical strength of the joints is discussed.

References

[1] J.W. Yoon, J.H. Bang, C.W. Lee, S.B Jung, J. Alloys Comp. 627 (2015) 276–280.

[2] C.Y. Ho, J.G. Duh, Mater. Chem. Phys. 148 (2014) 21-27.

P02.007-ELC149

MULTIVARIATE DATA ANALYSIS TO SIMPLIFY TOF-SIMS DATA ANALYSIS IN AN INDUSTRIAL CONTEXT

D. Breitenstein [1], D. Heller [1], E. Tallarek [1], W. Brock [1], R. Ter Veen [1], B. Hagenhoff [1], M. Fartmann [1], R. Kersting [1], C. Engelhard [2]

[1]Tascon GmbH - Muenster (Germany), [2]Universität Siegen - Siegen (Germany)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has developed into a popular tool in industry for failure analysis. Often the analyses are performed by a comparison of one 'good' and one 'bad' sample. Usually, not much is known about the chemical composition before the analysis. Therefore, a comprehensive technique, such as ToF-SIMS, is needed enabling a reliable elucidation of the chemical surface composition and thus contributing to the root cause analysis of e.g. the defect formation. However, the high amount of information included in each ToF-SIMS spectrum results in complex and time-consuming data analysis. Over the last decade, multivariate data analysis (MVA) has increasingly been used to simplify the data interpretation.1 However, in root cause analysis, in particular in an industrial context, this is rarely done as for an efficient MVA approach some challenges have to be overcome.

The most used methods in MVA are classification or calibration techniques. In our context the classification of 'good' and 'bad' samples was already observed by their physical behavior, which led to the initial failure. Calibration methods could be used to relate the external variables such as 'good' and 'bad' samples to the chemical surface composition. However, often they cannot be applied due to a very limited amount of samples and a limited amount of measurements per sample (due to e.g. sample size, sample topography, financial and time constraints.).

In addition, an appropriate data preprocessing is crucial for a successfully MVA. However, no general rules exist and, as Graham et al. reported2, the preprocessing always depends on the data set. In addition, the signals in the ToF-SIMS data vary over several orders of magnitude. The significant signals often lie in different intensity ranges. Therefore, an appropriate scaling is extremely difficult.

In this study we show an MVA approach, which takes these challenges into account and has provided solutions for many of our customer's problems. Although the classification is already known, we use classification techniques such as Principal Component Analysis (PCA), but focus on the loadings to investigate the signals (root) inducing this classification. We have developed a procedure for the efficient extraction of significant signals - in different intensity ranges - from these loadings. This strategy will be discussed along several examples.

References

(1) Wagner, M. S.; Graham, D. J.; Castner, D. G. Appl. Surf. Sci. 2006, 252, 6575–6581.
(2) Graham, D. J.; Wagner, M. S.; Castner, D. G. Appl. Surf. Sci. 2006, 252, 6860–6868.

ENV - Environment

P02.009-ENV011

MIGRATION OF NEW BIO-BASED ADDITIVES FROM PLASTICIZED PVC STABILIZED WITH EPOXIDIZED SUNFLOWER OIL

N. Lardjane [1], N. Belhaneche-Bensemra [2], V. Massardier [3]
[1]universite Mouloud Mammeri de Tizi ouzou - Hasnaoua Ii (Algeria), *[2]Laboratoire des Sciences et Techniques de l'Environnement. Département de Génie de l'Environnement, Ecole Nationale Polytechnique - Bp 182 El-Harrach, Alger* (Algeria), *[3]INSA, Université de Lyon - F-69621 Villeurbanne* (France)

Plasticized formulations stabilized with ESO as a new biodegradable stabilizer and epoxidized soya bean oil (ESBO) as a commercial stabiliser for comparison were realized. Two plasticizers were used: dioctyl phthalate (DOP) and di isononyl adipate (DINA). The artificial aging of the PVC samples was investigated under uncontrolled temperature in the laboratory for four months. The morphological changes were followed by scanning electron microscopy (SEM). Furthermore, the evolution of the bacterial growth was considered. The development of bacterial biomass of the samples plasticized by the DINA does not vary in the same way compared to the samples plasticized by the DOP, this difference is related to the structure of the two plasticizers. Indeed, the DOP has an aromatic ring so it persists in the soil, while the DINA has a linear structure; it is easily assimilated by the microorganisms which explains the decrease of the bacterial growth since the first month [1, 2]. Analysis of samples taken after 4 months of soil burial by scanning electron microscopy (Figure 1:) reveals holes at various location in the case of samples containing the DINA and ESO, which is not the case for samples containing DOP and ESO. This is likely to be areas where colonies of microorganisms were strongly attached during biodegradation. These tests allow us to confirm that the samples containing ESO and DINA are more biodegradable compared to the other formulations containing DOP.

Key words: PVC, ESO, artificial aging, plasticizers, DINA.

References

1. Nalli S, Gooper D, Nicelli JA (2006) Metabolites from the biodegradation of di-ester-plasticizers by Rhodococcus rhodochrous. Sci The Tot Environ 366: 294.
2. Nalli S, Gooper D, Nicelli JA (2002) Biodegradation of plasticizers by Rhodococcus rhodochrous. Biodegradation, 13, 352.

P02.010-ENV189

MECHANOCHEMICAL ACTIVATION OF NANOSIZED CATIO3 AND ITS INFLUENCE ON THE STRUCTURE AND PHOTOCATALYTIC ACTIVITY

I. Avramova [1], I. Stambolova [1], V. Blaskov [1], K. Zaharieva [2], K. Milenova [2], D. Stoyanova [1], L. Dimitrov [3], A. Eliyas [2], N. Kaneva [4], K. Papazova[4], A. Bojinova[4]

[1]Institute of General and Inorganic Chemistry, BAS, "Acad. G. Bonchev" St., Bl. 11, 1113 - Sofia (Bulgaria), [2]Institute of Catalysis, BAS, "Acad. G. Bonchev" St., Bl. 11, 1113 - Sofia (Bulgaria), [3]Institute of Mineralogy and Crystallography "Acad. I. Kostov", BAS, "Acad. G. Bonchev" St., Bl.107, 1113 - Sofia (Bulgaria), [4]Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia University „St. Kl. Ohridski", J. Bauchier Blvd., 1164 - Sofia (Bulgaria)

Calcium-titanate, $CaTiO_3$ powders were synthesized by mechanochemically treated hydrothermally prepared powders. The samples were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Diffuse-reflectance spectroscopy (DRS), IR spectroscopy, DTA-TG and BET method. X-ray diffraction analysis revealed a pure well crystallized ortorhombic polycrystalline phase for all samples. The crystallites size decreases with the increasing of time of mechanochemical (MC) activation. The samples, MC activated showed different hysteresis loops comparing with the reference sample. Increasing the time of milling leads to shift of the IR band corresponding to Ti-O streching and Ti-O-Ti bridging stretching modes at 568 cm^{-1} to 577, 581 and 585 cm^{-1} for samples MC activated for 15, 30 and 45 minutes, respectively. The band gap energy of the samples decreases with the MC activation time. The photocatalytic activity of the $CaTiO_3$ samples was evaluated by azo dye (Reactive Black5, RB5) and paracetamol degradation under UV irradiation. This study proved that the $CaTiO_3$ exhibited lower photocatalytic activity for the paracetamol degradation. The photocatalytic activities towards azo dye degradation under UV light are increased with the MC activation time.The highest degradation of RB5 is observed for the sample, MC activated for 45 minutes and reaches about 96,8 % after 1 h irradiation. The samples showed smaller crystallites size and the narrower band gap, which resulted in the high separation efficiency of photoinduced charge, which are the reasons for the enhanced photocatalytic activity.

P02.081-ENV467

SYNTHESIS OF POLYPYRROLE/SBA-15 NANOCOMPOSITE FOR REMOVAL OF CATIONIC AND ANIONIC DYES FROM AQUEOUS SOLUTION

B. Boukoussa [1], A. Hakiki [2], R. Hamacha [2]

[1]Université des Sciences et de la Technologie Mohamed Boudiaf - Oran (Algeria), [2]Laboratoire de Chimie des Matériaux L.C.M, Université d'Oran1 Ahmed Benbella, BP 1524 El-Mnaouer, 31000 Oran, Algeria - Oran (Algeria)

A series of nanocomposite polypyrrole (PPy)/SBA-15 was synthesized using an in situ chemical method. The structural features of the materials were determined by various physico-chemical techniques such as X-ray diffraction (XRD), nitrogen sorption at 77 K, Fourier transform infrared spectroscopy (FTIR), scanning electronic microscopy (SEM) and thermogravimetric analysis ATG. The obtained materials were used as adsorbents for the removal of cationic and anionic dyes. Effective parameters on dyes removal such as pH, the amount of adsorbent and contact time were examined and optimized at temperatures ranging from 20 to 40°C. Optimum values were pH 6, contact time of 15 min and température adsorption 20°C. Moreover, kinetics of the adsorption process was studied by investigating the concentration changes of resorcinol solution with adsorption times. The driving forces for the adsorption process derive from the hydrogen-bond, and acid–base interactions between the adsorbent and adsorbate. The high polymer loading are also advantageous for the adsorption process.

P02.082-ENV472

GREEN NANOTECHNOLOGY" HIGHLIGHTS: SURFACE ANALYSIS OF POWDERED SILICA OBTAINED FROM RICE HUSKS

A. Rashkovskiy [1], A. Smolyanskii [2], N. Muzafayev [3], V. Agakuliev [3]

[1]Systems for microscopy and analysis - Moscow (Russian federation), [2]D.Mendeleev University of Chemical Technology of Russia - Moscow (Russian federation), [3]WATERSMOOTH LTD - Shenzhen (China)

In this study the biosilica surface properties, elemental content, and chemical composition has been investigated by means of various experimental technique: scanning (SEM) and transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), low-temperature sorption of nitrogen, mass-spectrometry with induced-connected plasma (MS-ICP), and etc.

According to XRD data the powdered biosilica is completely amorphous. SEM and TEM study of the concerned powder showed that the biosilica nanoparticles can be agglomerated and form the microstructures. These ones had the mean size from 22 to 31 nm and they contained numerous pores. These observations have been confirmed by sorption analysis: the distribution of the pore sizes had the maximum at 4.887 nm. A conclusion related to considerable surface roughness of the biosilica particles has been made from the fractal analysis of the sorption isotherm. The calculated fractal surface dimension was 2.41±0.01 that corresponds to the case of the extended particle surface.

The powder under study contained a lot of admixtures which are the extremely low concentrations of the different metals, namely: Al (8.2·10-3%), Ti (3.09·10-3%), Ni (2.9·10-4%). The metal concentrations were determined by means of EDAX and MS-IPC techniques. The values of the observed metal concentrations exceeded the detection limit more than order. It was established that the SiO2 content was equal 98%.

According to XPS data, the main elements containing in the biosilica were O(1s), F(1s), and Si(2p) which have the following concentrations (% (at.)/%(wt.)): O(1s) - 64.90/53.00, F(1s) - 5.96/5.78, Si(2p) - 28.13/40.33. It is interesting to note a considerable contribution of the fluorine atoms. Possibly they can be introduced in the SiO2 during the biosilica production. It was concluded that fluorine atoms can exist in the SiO2 matrix in two states: i) the strongly doped SiO2 which contains 6.5% of the F atoms incorporated in the biosilica matrix latitude, ii) the weakly doped SiO2 which contains 1.1% of the adsorbed F atoms, forming strong surface chemical compound.

Thanks/Acknowledgement

The present study has been carried out with the support of Russian Foundation for basic research (Project No. 17-07-00524)

GEO - Geology and geochemistry

P02.011-GEO228

SURFACE CHEMICAL REACTIONS ON PYRROTHITE (FES) THIN FILMS

M. Niño Orti [1], E. Flores [2], C. Sanchez [2], J.M. Rojo [1]
[1]Instituto Madrileño de Estudios Avanzados IMDEA-Nanoscience - Madrid (Spain), [2]Dpto. Física de Materiales, Universidad Autónoma de Madrid, UAM - Madrid (Spain)

Iron sulfides in their different chemical composition (pyrite, pyrrothite, trolite, greigite, etc.) are important materials in a number of different fields like prebiotic chemistry, catalysis, engineering, geochemistry, etc. Among those minerals, FeS_2 and FeS are particularly important because of the strong catalytical properties of their surfaces. Furthermore, they are in the basis of the so-called "Fe-S World" in bio- and geochemistry [1] a theory proposing a route through a series of chemical reactions for the formation of simple inorganic molecules in geological environments in the early history of Earth. An effort to demonstrate the experimental feasibility of the different reactions involved in that hypothesis has led to some, yet inconclusive, results [2]. Most of this experimental work in prebiotic chemistry has been done using chemical reactors: well-sealed glass containers filled with the reactants in a non reactive gas or, often, in aqueous solution, and submitted to a number of processes (varying temperature, pressure, etc.) for periods from minutes to days.

As a different strategy, we carry out ultra high vacuum (UHV) experiments using surface physicochemical techniques to study some of the basic reactions of the Fe-S world hypothesis, on the following grounds: (i) Chemical reactions on surfaces are recognized as key ingredients of the prebiotic world (ii) Surface Science techniques have access not only to the final state but, also, to intermediate reaction products. The chemical reactions that we have studied on those surfaces are

$$H_2S + FeS \rightarrow FeS_2 + H_2$$

$$N_2 + 3FeS + 3H_2S \rightarrow 3FeS_2 + 2\ NH_3$$

We have prepared stoichiometric iron monosulfides (FeS, troilite) thin films by sulfidation of Fe films in a sulfur atmosphere, and characterized these films by x-ray photoemission spectroscopy (XPS) and x-ray diffraction (XRD). Using XPS and thermal desorption spectroscopy (TDS) we study the chemical reactivity of the FeS surface under nitrogen and hydrogen sulfide exposures corresponding to the above basic reactions. Here, we present evidence of these reactions on the FeS surface, under well-defined conditions.

References

[1] For a review, see G. Wächtershäuser "From volcanic origins of chemoautotrophic life to Bacteria, Archaea and Eukarya" *Philos. Trans. Royal Soc*. **361**, (2006) 1787.

[2] E. Dröbner at al. "Pyrite formation linked with hydrogen evolution under anaerobic conditions" Nature 346, (1990) 742. M.Dörr et al. "A posible prebiotic formation of Ammonia from Dinitrogen on Iron Sulfide Surfaces" Angew. Chem. Int. Edit. **42**, (2003) 1540.

P02.012-GLA155

SPUTTER-CLEANING OF AIR-EXPOSED LEAD-SILICATE GLASS SURFACE BY ARGON CLUSTER ION BEAM

P. Jiricek [1], **J. Zemek** [1], **J. Houdkova** [1], **K. Jurek** [1], **O. Romanyuk** [1], **O. Gedeon** [2]

[1]*Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10 - Prague* (Czech republic), [2]*University of Chemistry and Technology, Technicka 5 - Prague* (Czech republic)

Ion beam techniques are currently used in surface science for surface cleaning and concentration depth profiling. The interaction of conventional (monoatomic) ion beams with solid glass surfaces is a rather complex process. It includes the formation of an altered surface layer with modified composition and bonding, structural damage, and high gradients of mechanical stresses. Composition changes originate mainly from preferential sputtering, radiation enhanced diffusion, internal electric field formation and ion implantation of primary ion beam species.

A lot of efforts have been devoted to suppress the formation of the altered surface layers. Now, the most promising method seems to be the application of multi-atomic or molecular ion beams consisting of large aggregates of atoms or molecules, called clusters.

In this contribution we investigate lead-silicate glass surfaces by using high-energy resolved X-ray induced photoelectron spectroscopy before and after argon cluster ion beam sputtering. The emphasis is laid on the possible changes in surface composition and chemical bonding

The dependences of NBO and BO vs. sputtering time are displayed in Fig. 1. The BO percentage abruptly decreased from 25.5 at.% to 12.1 at.% after the first sputtering and then suddenly increased and remained approximately saturated with the value close to 17 at.%, that is 23 mol%. This value is in good agreement with the published experimental BO data for composition close to the orthosilicate [1]. It indicates that sputter-cleaned lead-silicate glass surfaces reflect surface properties similar to the glass surfaces created by fracturing in UHV conditions [1].

Thanks/Acknowledgement

This work has been supported by the Ministry of Education, Youth and Sports of the Czech Republic (Grant LM2015088), GACR project P108/12/G108 and GACR project 15-12580S.

References

[1] K.N. Dalby, H.W. Nesbitt, V.P. Zakaznova-Herzok, P.L. King, Resolution of bridging oxygen signals from O 1s spectra of silicate glasses using XPS: Implication for O and Si speciation, Geoch. Cosmoch. Acta 71 (2007) 4297-4313.

P02.013-GLA261

THE LUMINESCENCE PROPERTIES OF ZINC–SILICATE GLASSES ENRICHED BY HOLMIUM, YTTERBIUM AND SILVER

S. Vytykácová [1], P. Varák [1], B. Švecová [1], J. Oswald [2], P. Nekvindová [1]

[1]*Department of Inorganic Chemistry, University of Chemistry and Technology - Prague* (Czech republic), [2]*Institute of Physics, Czech Academy of Sciences, v.v.i. - Prague* (Czech republic)

Rare-earth doped glasses have been recently investigated mainly for their photoluminescence properties. Their strong photoluminescence in IR region make them promising material in photonics for fabrication of optical components. Holmium as a dopant for this utilization is suitable element especially for its strong emission around 2 µm. This fact is favourable mainly because of occupancy of currently used telecommunication lines. Near infrared region is also safe for human eye. Previous studies on RE doped glasses shown, that it is possible to enhance the intensity of luminescence by presence of silver with various valences and thus increase the efficiency of luminescence in these glasses. Nevertheless, the mechanism is still unknown. This contribution is focused on the luminescence properties of the new holmium-ytterbium-zinc silicate glasses as well as on study of mechanism, how presence of silver influences the resulting optical and luminescence properties. Difference between the effect of silver with various valences, i.e. ions or different size metal nanoparticles, has been investigated.

Silicate glasses with content of holmium and ytterbium were melted, cut and polished to the optical quality. Density of all samples was obtained, refractive index were measured by m-line spectroscopy. Glass transformation temperature was determined by thermogravimetric analysis. Prepared glasses were subsequently doped with silver using ion exchange and annealed around the glass transition temperature to induce the nucleation and growth of silver metal nanoparticles. Concentration profiles of silver and its movement during thermal annealing was measured by electron microprobe analysis. Presence of silver metal nanoparticles was observed by absorption spectroscopy in UV-VIS region. Size of created silver nanoparticles was calculated from absorption spectra using Mie´s theory. The photoluminescence properties were measured in range 1000 – 2500 nm. The transmission electron microscopy together with low temperature measurement of luminescence have been also done in the select samples.

It was shown, that holmium-doped glasses exhibit strong luminescence around 2 µm. Positive influence of silver on the photoluminescence intensity was also confirmed. Results were compared with previous studies on the erbium-ytterbium doped silicate glasses as well as the mechanism of luminescence enhancement was discussed.

Thanks/Acknowledgement

We acknowledge the Czech Science Foundation project P 108/12/G108.

LIF - Life science

P01.035-LIF310

CHARACTERISATION OF COFFEE SAMPLES BY TOF-SIMS

G. Ferraz Trindade [1], L.F.S. Rosa [2], E.M.S. Rosa [2], C.E.L. Dos Santos [3], J.F. Watts [1]
[1]The Surface Analysis Laboratory - University of Surrey - Guildford (United kingdom), *[2]Ion Beam Centre - University of Surrey - Guildford* (United kingdom), *[3]IMEF - Universidade Federal do Rio Grande - Rio Grande Do Sul* (Brazil)

Coffee is the world's most widely traded tropical agricultural commodity with global production for 2016 of over 151 million 60 kg bags, according to the International Coffee Organization. The geographic origin of coffee influences its quality and therefore it is important to develop methods that are able to identify and authenticate coffee samples. There is a number of works that have reported methods of identification of coffee origin based on analytical chemistry techniques [1, 2]. In this work, it is proposed an easy and quick sample preparation method combined with ToF-SIMS analysis in order to differentiate coffee regions as well as obtain extra information about its compounds.

Coffee from four different regions in Brazil was analysed. The samples were dissolved using either water or alcohol and the solution was dropped onto clean pieces of silicon wafer. The ToF-SIMS analysis was carried out using a TOF.SIMS 5 system from ION-TOF GmbH (Münster, Germany) using 25 keV Bi_3^+ ion beam operated in the high current bunched mode delivering 0.3 pA and rastering the beam in regions of 100 x 100 μm^2. The data was processed using principal components analysis and non-negative matrix factorisation. A k-nearest neighbour classification model is also proposed.

Thanks/Acknowledgement

The authors wish to thank the funding agency Coordination for the Improvement of Higher Education Personnel - CAPES (project: 11995-13-0)

References

[1] da Rosa, Jeane Santos, et al. "Mass spectrometry screening of Arabica coffee roasting: A non-target and non-volatile approach by EASI-MS and ESI-MS." Food Research International 89 (2016): 967-975.

[2] Garrett, Rafael, Claudia M. Rezende, and Demian R. Ifa. "Coffee origin discrimination by paper spray mass spectrometry and direct coffee spray analysis." Analytical Methods 5.21 (2013): 5944-5948.

MET - Metals

P01.036-MET035

COMPARISON OF NICKEL-TITANIUM ALLOY SURFACE ANODIZED IN PHOSPHORIC- AND SULFURIC-ACID ELECTROLYTES

N. Ohtsu, Y. Hirano
Kitami Institute of Technology - Kitami (Japan)

A nearly equiatomic NiTi alloy shows the attractive properties of shape memory and superelasticity. Anodic treatment of NiTi alloy has been studied to form a chemically stable oxide on its surface, whereas oxide layer growth does not proceed appropriately because Ni in the alloy becomes an obstacle for the growth. It has been reported that the anion in an electrolyte affects the characteristics of an anodized surface1). Thus, selecting an appropriate electrolyte might improve the layer growth behavior. In this study, surface layer on NiTi alloy formed by anodizing in H_3PO_4 and H_2SO_4 electrolytes were characterized using XPS and SPM, and thereafter, the effect of the electrolyte on anodized surface was discussed.

The NiTi alloy (55.07 at% Ni) used as a substrate was chemically polished using a colloidal silica suspension. The electrolyte used for anodization was an aqueous H_3PO_4 and H_2SO_4 solutions with the concentration ranging from 1 to 1000 mM. The alloy and a Ti electrode were connected to the anode and cathode, respectively, after which a galvanostatic direct current was applied at a constant value of 50 $mA \cdot cm^{-2}$ for 30 min.

Elemental depth profiles of the anodized NiTi surfaces included more O than Ti or Ni. The atomic ratio of O to Ti in this region was approximately 2, and the concentration of Ni was less than 5 at%. Thicknesses of the oxide layer, defined as the depth from the topmost surface to the intersecting point of the O and Ti profiles, are shown in Fig. 1. In the both electrolytes, the layer thickness increased with increasing the concentration until 10 mM, but further increase resulted in the declines of thickness. The result indicated that the oxide growth was related with the anions and its concentration contained in electrolyte. Furthermore, SPM images of the 10-mM H_3PO_4 and H_2SO_4 surfaces (Fig. 1) seemed quite different, indicating that oxide growth behavior occurring on NiTi is different depending on the electrolyte used.

References

1) N. Ohtsu, S. Komiya, K. Kodama, Thin Solid Films 534 (2013) 70-75.

P01.039-MET129

REFLECTED ELECTRON ENERGY LOSS SPECTRA OF ALUMINUM AT GRAZING INCIDENT

A. Sulyok [1], K. Tokési [2]

[1]Institute for Technical Physics and Materials Science, Centre for Energy Research - Budapest (Hungary), [2]Institute for Nuclear Research, ELI-ALPS - Debrecen (Hungary)

Precise knowledge of the energy losses of electrons as they travel within solids is fundamental in electron spectroscopy. The contributions of energy losses in the surface and the bulk region have to be taken into account in the interpretation of the surface sensitive electron spectra. Many authors have studied the combination of surface and bulk losses in various models [1-2]. The absolute intensities of surface and bulk plazmons strongly depend on the primary energy and on the geometrical conditions like angle of incidence of impacting and escaping electrons. Opposite to the bulk losses, the description of surface loss events hasn't been fully solved yet.

In this work the reflected electron energy loss spectra of aluminum are studied both experimentally and theoretically. The backscattered electron energy spectra of aluminum were measured in reflected mode at energy range between 250 eV and 2000 eV and at wide range of incident angle including the very grazing geometry. We obtained a series of single and multiple surface and bulk plazmon losses in the measured spectra as it is shown in the Figure. For the interpretation of our spectra we performed Monte Carlo simulations, which is based on classical transport theory [3,4]. We take into account both elastic and inelastic collisions during the simulation. For the case of the elastic scattering of electrons we use the static field approximation with non-relativistic Schrödinger partial wave analysis. For the case of inelastic scattering we use the dielectric response formalism where we used experimental dielectric function to include all the possible losses.

References

[1] F. Yubero and S. Tougaard, Phys. Rev. B 46 (1992) 2486.

[2]Y.F. Chen, Surf. Sci. 345 (1996) 213.

[3] Z.-J. Ding, R. Shimizu, Surf. Sci. 222 (1989) 313.

[4] K. Tőkési, D. Varga, L. Kover, T. Mukoyama, J. Electron Spectrosc. Relat. Phenom. 76 (1995) 427.

P01.040-MET134

SURFACE PHENOMENA DURING THE EARLY STAGE OF LIQUID PHASE SPS IN BINARY BLEND OF COARSE WC AND NI-ALLOY POWDERS

G. Maizza [1], R. Cagliero [1], A. Iacobone [1], R. Montanari [2], A. Varone [2], A. Mezzi [3], S. Kaciulis [3], P. Soltani [2]

[1]Politecnico di Torino, Dipartimento di Scienza Applicata - Torino (Italy), [2]University of Rome, Department of Industrial Engineering - Roma (Italy), [3]CNR, Institute for the Study of Nanostructured Materials - Roma (Italy)

Spark plasma sintering (SPS) is a non-conventional sintering technique which entails the concurrent application of pulsed DC of high intensity and an uniaxial pressure to achieve a quick densification of metallic and ceramic powders. In the last two decades, SPS has been extensively developed because of its intrinsic peculiarities, as high density currents (up to 2000 A) and high heating rate and shorter sintering time (5 to 20 min) compared to HIP. Joule heating induces intricate electro-thermal phenomena along with relevant sintering mechanisms since the very early stage. Despite the considerable research carried out on SPS phenomena in dense compacts, a little work has been devoted to the initial stage of SPS. In this paper, the effect of pulsed electrical currents has been investigated in the case of electrically conductive binary blend of coarse WC and Ni-alloy (50%wt) powders, under low pressure (16 MPa), in order to assess the kinetics mechanisms in the early stage of sintering. The SPS process has been performed under vacuum in temperature control mode and a heating rate of 100 °C/min.

Upon electrical discharge, the local temperature at the inter-particle gaps and/or their contact points (where ohmic resistance is high) experiences a sharp rise up to about 1,300 °C. Vaporization and melting may take place thereby promoting liquid phase sintering of WC. In particular, for the WC-50%Ni alloy blend, the Ni-alloy powder with a low melting point melted first and homogeneously wet the WC powder. As a result, a distinctive absorption, desorption and multi-species diffusion phenomena originated across a superficial shell of the WC particles (Figure 1). It was observed that upon melting Ni-alloy enveloped the WC particles, uniformized their surface temperature by spreading heat from localized contact points to the whole WC powder surface, thus enhancing a homogeneous atomic interdiffusion of Ni and W.

The samples have been investigated in terms of density, SEM, XRD and XPS analysis. The results of small-area XPS analysis and XPS chemical imaging revealed that WC particles were composed of an outer shell of metallic W, Ni and graphitic carbon, which was probably produced by thermal decomposition of WC.

P01.041-MET181

THE INFLUENCE OF CARBIDES DISTRIBUTION ON CREEP RATE OF THE CREEP RESISTANT STEEL X20CRMOV12.1

D. Skobir Balantic, M. Godec
Institute of Metals and Technology - Ljubljana (Slovenia)

X20CrMoV12.1 is one of the steels that are often used in power plants for steam pipes due to its excellent combination of high-temperature strength, toughness and creep strength. These properties are achieved with heat treatment which consists of austenitizing, quenching and high temperature tempering. The microstructure of such steels consists of highly tempered martensite with finely dispersed carbide particles along boundaries and sub-boundaries of ex-austenitic grains and in their interior. During steel exploitation the working conditions often reach temperatures up to 600 °C or more. Therefore, the particles change their chemical and phase composition as well as their size and distribution.

The aim of this work was to investigate the influence of the tempering time on the change of particles distribution and to determine the effect of particles distribution, spacing and their size on accelerated creep rate.

It was found out that by short tempering of steel (up to 2 h) stringers of cementite particles are formed at great number of ferrite grain boundaries and sub-boundaries.

The number of stringers decreases by longer tempering time parallel to particles coarsening because of grain boundary particles dissolution and lateral diffusion of chromium. By sufficient tempering time, almost all particles stringers are dissolved and the uniform distribution of particles in ferrite matrix is obtained (Figure 1).

Stringers of particles decrease steel creep rate (Figure 2). The steel creep rate increases gradually with decreasing number of stringers. Below a critical number of stringers, it increases much faster by growth of average size and spacing of particles.

P01.042-MET187

CRACK PROPAGATION RESISTANCE IN HYDROCARBON TRANSPORT PIPELINES

O. Ghelloudj, D. Zelmati, D. Berdjane, S. Achouri, A. Gharbi, C.E. Ramoul
Research Center in Industrial Technologies (CRTI), P.O. Box 64, Cheraga 16014 - Algérie (Algeria)

The aim of this paper is to determine the propagation resistance of cracks in grade API 5L X70 steel pipes. These pipes are produced by the Algerian company of manufacture of welded pipes (ALFAPIPE), they are intended for the transport of the hydrocarbons. Mechanical tests such as resilience and tensile strength were carried out on specimens taken from pipe ferrules in the longitudinal and transverse directions. The resilience tests are carried out at different temperatures in order to calculate the stress intensity factor. Tensile tests are used to have the mechanical characteristics of the material. The experimental results are then exploited in the modeling part by the software of calculation of the structures using the method of the finite elements, the calculation code is CASTEM 2016.

Keywords: Tenacity, Fracture, Resilience, Modeling.

References

[1] N. Recho, Rupture par Fissuration des Structures. Edition Hermés, Paris 1995

[2] M.R. KABIRI, Fissuration des aciers à haute température (effet de la géométrie sur la transférabilité des lois de propagation). Thèse de Doctorat. Paris 2003.

[3] B. Barthelemy Notion pratique de la mécanique de rupture. EYROLLES, Paris 1980.

[4] F. Erdogan. International Journal of Solids and Structures 37 (2000) 171-183

[5] S. W Shin, B.Hwang, S. Kim and S. Lee, Fracture toughness analysis in transition temperature region of API X70 pipeline steels. Materials Science and Engineering A 429 (2006) 196–204.

P01.044-MET341

SIMPLIFIED MODELING TO AVOID BREAKAGE OF SHEET METAL DURING TANDEM ROLLING

K. Slimani [1], M. Zaaf [2], S. Tlili [1], C.E. Ramoul [1]

[1]Research Center in Industrial Technologies , Algeria crti.dz - Crti P.o.box 64, Cheraga 16014 Algiers (Algeria), [2]Laboratoire de Mise en forme des materiaux Metalliques (LMF2M) Universit_e Badji Mokhtar, - Annaba, (Algeria)

In the tandem rolling, the simultaneous passage of the sheet between multiple cages poses a control problem of inter-stand tension. Manufacturers tend to ask the equal tension between a cage and another, that is to say between the output of a cage and the input of the next cage. This causes a speed regulation problem. Indeed, this generally gives different speeds between the input and pass out of the previous pass. Which may lead to ripples or excessive tension may cause breakage of the strips.

To illustrate this situation, we propose to take the data from the tandem mill site steel complex Arcelor-Mittal El Hadjar Algeria. It contains five stand tandem mill.

The purpose of this work is to get to determine for each case, the correction to be made to obtain equal speeds and tensions between the output of each cage and the door of the cage that follows.

We first introduced the calculation for three cages [P.MONTMITONET], after the calculations have been developed for five cages and define the relationship between the speed and tension, to derive a generalized formula irrespective of the number of cage .

To our simplified calculation model, two Matlab program was developed;

-the first: Greenhouse to the rolling calculation (speeds, the neutral plane, ...)

-the second: to make corrections tensions in order to obtain equal speed between the output of a cage and the input of the next cage

-The Results show the convergence speed after the correction of tension, like that, to avoid the risk of breakage or undulation of the rolled strip and pre calculated magnitudes we do not stray from reality.

Keys words: Modeling, rolling, tension, speed.

References

[1] P Montmitonnet. Laminage –analyse thermomécanique 2D et application aux produit plats M3066V2, JUIN 2016 .

[2] P Montmitonnet. State of the art in rolling process modeling ,springer-verlag BHM July 2016.

[3] Huy LE DANG .Modélisation simplifiée des processus de laminage 2014 .

[4] A Khalfallah, Identification des lois de comportement élastoplastiques par essais inhomogènes et Simulations numérique, thèse de doctorat soutenue à la faculté des sciences de Tunis, en février 2004.

[5] P Montmitonnet. Lois de frottement et déformation plastique. Matériaux et techniques, N° 1-2-3, p 08-29. 1993.

P01.046-MET385

FABRICATION OF OPEN-PORE TITANIUM SUBSTRATE FOR ELECTRODE BY METAL INJECTION MOLDING

W. Lee, K. Kim, J.M. Jang, S.J. Park, Y.D. Kim
Korea Institute of Industrial Technology - Incheon (Korea, republic of)

Titanium and titanium alloys are materials of great interest due to excellent properties such as high corrosion resistance, mechanical properties and biocompatibility. Due to the excellent stability of titanium against surface and pitting corrosion, titanium is used widely as a substrate of dimensionally stable electrode(DSE) coated by metal oxides such as RuO_2, IrO_2, TiO_2 and Ta_2O_5, resulting to reduce contamination of the electrolysis system, improving the products purity and maintenance costs. Energy consumptions of many electrolysis processes depends on the surface area of anode and the electrode substrates with high specific surface area like mesh and porous material have developed to improve energy efficiency. For example, in our pre-test using open-pore nickel foam with pore size of about 45㎛, energy consumption was dramatically reduced to about 60% compared to a plate typed electrode. However, nickel is not suitable as an electrode due to dissolution into electrolyte. Thus, in this work, fabrication of open celled titanium substrate with the similar structure to nickel foam was attempted using TiH_2 powder injection molding process and polystyrene beads were used to form pores. For injection molding of the mixture of TiH_2 feedstock and polystyrene beads, wax-based binder system was selected. Smooth flow of the electrolyte inside porous electrode is important for a stable electrolysis process and for this, it is necessary to optimize porosity, pore size and strut thickness in open-pore electrode. These structural factors were determined by volume ratio of TiH_2 feedstock and polystyrene beads in the mixture and expansion ratio of polystyrene beads. After injection molding and expansion of polystyrene, binder and polystyrene were removed through solvent extraction and thermal debinding and followed by sintering in high vacuum. During sintering, TiH_2 powder was decomposed to Ti and H_2 gas. As a result, open-pore titanium substrates for electrode were fabricated successfully with various porosities ranging from 60 to 90% through this fabrication process and it was possible to obtain pore size of about 1 mm.

P01.047-MET425

STRESS RELAXATION MECHANISM IN THE SI-SIO2 SYSTEM AND ITS INFLUENCE ON THE INTERFACE PROPERTIES

D. Kropman
Reseacher - Tallinn (Estonia)

It is known that internal mechanical stresses (IMS) due to the differences in the thermal expansion coefficients between films and substrates and lattice mismatch appear in the Si-SiO_2 system during the process of its formation and that point defects (PD) generation and redistribution could be used to reduce partially the surface stress. However, this process on the atomic scale is till not studied. The goal of the present report is to investigate the stress relaxation mechanism in the Si-SiO_2 system using EPR, IR absorption spectroscopy, scanning elektron microscopy (SEM) and samples deflection measurements. PD density and stresses in the Si-SiO_2 system were varied by oxidation condition (temperature, time, cooling rate, ambient) and by Si_3N_4 deposition on SiO_2. Different sign of the thermal expansion coefficient of the SiO_2 and Si_3N_4 on Si allow to modifay the IMS at the interface. It has been found that samples deflection decreases or increases simultaneously with EPR signal intensity depending on the oxidation condition (temperature).

At oxidation temperature 1100^0C the deflection of the samples(h) decreases with the increase of EPR signal intensity (vacancies),while at a oxidation temperature 1200^0C EPR signal (I) and deflection increase simultaneously. Those allows to suggest that at lower oxidation temperature PD (vacancies) reduce the tensil IMS in Si, while at higher oxidation temperature compressive IMS created PD in SiO_2 (E' centers).At an intermediate oxidation temperature tensil stresses in Si and compressive stresses in SiO_2 may bee equal and compensate each others. It has been find that at oxidation temperature 1130^0C IMS at the Si-SiO_2. interface are lower than at 1100^0C and 1200^0C. Lower defect dencity on samples crossection microphotos obtained by SEM and PD dencity diminishing.in samples oxidized at 1130^0C confirmed thise suggestion. EPR signal and IR absorbtion line-width at 1100 cm-1 dependence on the oxidation time (oxide thickness) is nonmonotonous and depended on the cooling rate.

Absent of the cooling rate influence on the PD dencity and Δv dependence on the oxidation time at I(t) and Δv(t) dependence intersection points show, that IMS by an appropriate choice of the SiO_2 film thickness dissapear. The obtained results may bee explained by the PD generation kinetic model in the Si-SiO_2 system proposed by T.U.Tan and U.Gösele [1] and confirmed experimentaly in. [2].

References

[1]..T.Y.Tan, U.Gosele,J.Appl.Phys.A37(1985)1.

[2].D.Kropman,S.Dolgov,T.Kärner.J.Appl.Phys.A62(1996)469.

NAMA - Nanomaterials

P01.048-NAMA010

FRIR SPECTROSCOPY METHOD FOR INVESTIGATION OF THE CO-NI NANOPARTICLE NANOSURFACE PHENOMENA

I. Markova [1], I. Zahariev [1], M. Piskin [2], D. Ivanova [1], L. Fachikov [1]

[1]*University of Chemical Technology and Metallurgy - Sofia* (Bulgaria), [2]*Yldiz Technical University - Istanbul* (Turkey)

The nonosurface phenomena occurred on the Co-Ni nanoparticle interface are investigated by FTIR spectroscopy. Co-Ni nanoparticles are synthesized through a borohydride reduction with $NaBH_4$ in a mixture of water solutions of chloride salts at a different ratio of Co:Ni, including by a template synthesis using graphite as a support in the presence of β-cyclodextrin. Three ratios of Co:Ni = 1:1, 4:1 and 1:4 are experimented. The morphology, elemental and phase composition of the synthesized Co-Ni nanoparticles are study by SEM (Fig.1), EDS and XRD analyses. FRIR spectroscopy investigations are carried out in the mid-Infrared region from 4000 to 400 cm^{-1}. On the basis of the FTIR spectra (Fig.2) of the Co-Ni nanoparticles and their carbon-containing nanocomposites the created chemical bonds in the corresponding atom groups are established. The observed absorption bands at the corresponding wavenumber [cm^{-1}] characterize the mode of vibrations of the created chemical bonds. Both the different shape and position of the bands at the corresponding frequencies have given information about the vibrations of the created chemical bonds such as C-OH, CO-OH, C-H_2, C=O, C=C, BO_3, BO_4, free OH, H-OH, CoO, NiO and respectively information concerning the nanosurface phenomena occurred on the nanoparticle surface.

Thanks/Acknowledgement

The authors acknowledge the financial support for this investigation provided by the National Science Fund at the Ministry of Education and Science – Bulgaria under the Contract DN 07/29–16.12.2016.

References

1. Ivania Markova-Deneva, Investigation via Infrared spectroscopy of metallic nanoparticles based on copper, cobalt, and nickel synthesized through borohydride reduction method, Journal of the University of Chemical Technology and Metallurgy, 45,4, 2010, 351-378.
2. Barbara Stuart, Infrared spectroscopy: fundamentals and applications, John Wiley & Sons, Ltd, 2008, ISBN 13 978-0-470-85427-3 (H/B).
3. Neamtu, N. Verga, Magnetic Nanoparticles for Magneto–Resonance Imaging and Targeted Drug Delivery Digest, Journal of Nanomaterials and Biostructures, 6, 3, 2011, 969-978.

P01.050-NAMA040

DEVELOPMENT OF SELF-ASSEMBLED MONOLAYER ORGANIC ELECTRONICS: A SPECTROSCOPIC STUDY

M. Sauer [1], J. Bintinger [2], A. Foelske-Schmitz [1]

[1]Analytical Instrumentation Center, Vienna University of Technology, Getreidemarkt 9, 1060 - Vienna (Austria), [2]Faculty of Technical Chemistry, Vienna University of Technology, Getreidemarkt 9, 1060 - Vienna (Austria)

Electronics based on organic molecules have attracted great interest both from research and industry due to their versatility from which a manifold of possible applications might emerge. Specifically, monolayers of large molecules that self-assemble on substrate surfaces (self-assembled monolayers/SAM) have been shown to be of use in a wide range of applications like organic photovoltaics [1], thin-film transistors [2] and non-volatile memories [3].

However, for the development of SAM-field effect transistor (SAMFET) several open questions need to be addressed. The coverage of the surface area as well as the alignment of the molecules are crucial parameters in the fabrication of such devices, which can only be assessed precisely using surface sensitive techniques like X-ray photoemission spectroscopy (XPS) and atomic force microscopy (AFM).

In this contribution we show how XPS can aid the improvement of novel organic FETs which should be able to work as highly effective gas sensing devices by using known SAMFET structures as templates. Long linear molecule structures are anchored by reactive groups to HfO_2/Si substrates. The building process of these molecules has been followed step-by step by angle-resolved XPS (as shown in Fig. 1 on the example of C1s XPS spectra).

Thereby, we are able to evidence an “upright” alignment of the molecules in the SAM. Furthermore, the study deals with the question how electronic properties vary due to differences in coverage of the HfO_2 surface with organic molecules. Concomitantly, we aim to establish a parameter for a critical surface coverage which is crucial to achieve a working FET device.

We thereby demonstrate how these analytical methods can aid the development of future electronic devices based on organic materials.

References

[1] H. Ma et al., Adv. Mater., 20 (2010), 1371.

[2] E.C.P. Smits et al., Nature, 455 (2008), 956.

[3] A. Khassanov et al., Adv. Mater. Interfaces, 1 (2014), No. 1400238.

P01.051-NAMA067

THE PHASE COMPOSITION OF BURIED SILICON INTERLAYERS IN THE AMORPHOUS MULTILAYER NANOSTRUCTURES [(CO45FE45ZR10)/A-SI:H]41 AND [(CO45FE45ZR10)35(AL2O3)65/A-SI:H]41

E. Domashevskaya, Y. . Peshkov, V. Logachev, Y. Yurakov, K. Barkov
Voronezh State University - Voronezh (Russian federation)

Multilayer nanostructures (MLNS) from magnetic layers and nonmagnetic interlayers show unique physical properties: giant magnetoresistance, spin-dependent electron tunneling, and an anomalous Hall effect, determined by structure and phenomena at interphase boundaries.

MLNS [(Co45Fe45Zr10)/a-Si:H]41-(I) and [(Co45Fe45Zr10)35(Al2O3)65/a-Si:H]41 -(II) obtained by ion-beam sputering two targets on a rotating pyroceramics substrate , are amorphous. The layers of the alloy Co45Fe45Zr10 and the composite (Co45Fe45Zr10)35(Al2O3)65 were obtained by spraying with argon ions, and interlayers a-Si: H were obtained by spraying silicon target with argon and hydrogen ions. The magnetic layer and silicon interlayer thicknesses for MLNS (I) were 2.2 / 1.6 nm and for MLNS (II) - 3.2 / 2.2 nm

For determination of the phase composition of the buried amorphous silicon interlayers in the MLNS we used a non-destructive the ultrasoft X-ray emission spectroscopy (USXES) method by registering the silicon Si L2,3 -spectra reflecting the density of (s + d)states distribution in the valence band. Varying the X-ray tube accelerating voltage of RSM-500 spectrometer in the range of 1 kV to 6 kV allows to investigate the MLNS samples without destroying increasing the investigated layers thickness from 10 nm at V = 1 kV to 120 nm at V = 6 kV.

Modeling of the fine structure of the MLNS Si L2,3 - spectra was carried out using reference spectra of cobalt and iron silicides, hydrogenated amorphous silicon and silicon oxides. As a result of modeling, Fe3Si was found in MLNS I interlayers and a small amount of SiO2 decreased with deepening in the MLNS. In the interlayers of MLNS II in addition to the silicides Fe3Si, Co2Si and oxides SiO2, SiO1,3, a small amount of a-Si: H is retained. With a deepening in the MLNS, the proportion of silicide cobalt and suboxide SiO1.3 increases. The formation of interfaces containing non-magnetic silicides of 3d metals and silicon oxides leads to a decrease in the magnetic properties of MLNS.

Fig.1 Experimental and simulated (solid line) USXES Si L2,3 –spectra: left- MLNS [(Co45Fe45Zr10)/a-Si:H]41-(I) and on the right- [(Co45Fe45Zr10)35(Al2O3)65/a-Si:H]41 -(II)

P01.052-NAMA070

DAMAGE ACCUMULATION AND STRUCTURAL MODIFICATION IN VARIOUS GAN CRYSTALLOGRAPHIC ORIENTATIONS IMPLANTED BY 400 KEV AND 5 MEV AU+ IONS

A. Mackova [1], P. Malinsky [2], A. Jagerova [1], Z. Sofer [3], D. Sedmidubsky [3], M. Mikulics [4], M. Pristovsek [5], R. Böttger [6]

[1]Nuclear Physics Institute of the Academy of Sciences of the Czech Republic, v. v. i., 250 68 Rez and Department of Physics, Faculty of Science, J.E. Purkinje University, Ceske Mladeze 8, 400 96 Usti nad Labem (Czech republic), [2]Nuclear Physics Institute of the Academy of Sciences of the Czech Republic, v. v. i., 250 68 Rez - Rez (Czech republic), [3]Department of Inorganic Chemistry, Institute of Chemical Technology, 166 28 Prague - Prague (Czech republic), [4]Peter Grünberg Institut (PGI-9), Forschungszentrum Jülich, D-52425 Jülich and Jülich-Aachen Research Alliance, JARA, Fundamentals of Future Information Technology, D-52425 Jülich - Jülich (Germany), [5]Cambridge Centre for Gallium Nitride, Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS - Cambridge (United kingdom), [6]6Institute of Ion Beam Physics and Materials Research, Helmholtz Zentrum Dresden-Rossendorf, 01328 Dresden - Dresden (Germany)

The crystallographic nature of the ion induced damage created in GaN is accompanied by a build-up of point defects clusters, which increases in density and depth versus the ion fluence. The damage accumulation processes in the c-plane of GaN and the understanding of implantation damage formation for non-polar surfaces may also become important to understand ion implantation processes in nanowires where the non-polar facets form the majority of the surface. Simultaneously for ion track formation the interplay of electronic and nuclear stopping of heavy ions is crucible and the track formation in GaN is challenging nowadays. To shed more light on damage accumulation processes under the medium and high energy heavy ion beams, GaN epitaxial layers polar (0001) and non-polar (11-20) orientations were grown by MOVPE on sapphire and subsequently implanted with 400 keV and 5 MeV Au+ ions using fluences of 5x1014, 1x1015 and 5x1015 cm-2. Dopant depth profiling was accomplished by Rutherford Back-Scattering spectrometry (RBS). Structural and optical changes during subsequent annealing were characterized by RBS/C, Raman spectroscopy, and photoluminescence measurements. Post-implantation annealing induced a structural reorganization of GaN structure in the buried layer depending on the introduced disorder level, i.e. depending on the ion implantated fluence and energy; the damage accumulation and recovery differ for the used crystallographic orientations. The crystallographic orientation of the implanted crystal influences the optical properties of the implanted layer, reflecting the rearrangement of the crystal matrix after the implantation and subsequent annealing. The ion implantation fluences used in this experiment were indicated to follow a various defect build up regimes recently observed in GaN, where the differences between the crystallographic orientations are more emphasized.

P01.053-NAMA076

ANALYSIS OF FLUORINE IN TIO2 NANOPLATELETS BY MEANS OF SEM/EDX, AES AND TOF-SIMS

V-D. Hodoroaba [1], S. Rades [1], T. Wirth [1], M. Holzweber [1], F. Pellegrino [2], G. Martra [2]
[1]Federal Institute for Materials Research and Testing (BAM) - Berlin (Germany), [2]Department of Chemistry, University of Torino - Torino (Italy)

The synthesis of TiO_2 nanoplatelets (see Figure 1) with fluorine-containing reactants is carried out using Ti (IV) butoxide as precursor and concentrated HF as shape controller [1], the final product requires a working up in order to eliminate or at least to reduce the amount of residual fluorides, which is realized here by well-defined thermal treatment.

Qualitative investigation of the bulk elemental composition by means of EDX of TiO_2 nanoparticles (NPs) has identified fluorine in case of the as-synthesized samples. EDX spectra of thermally treated products exhibit either a fluorine content close to the limit of detection. The latter holds also true for the reference sample, TiO_2 NPs of bipyramidal shape [2,3] and prepared by a different synthesis route. For differentiation whether fluorine is present in the bulk or at the surface of the TiO_2 nanoplatelets, top-surface sensitive AES and ToF-SIMS has been applied. Secondary ions of fluorine are detected in ToF-SIMS spectra of all samples, but could be roughly quantified by measurement of same reference sample as for EDX, namely TiO_2 nano-bipyramids. This revealed that the amount of fluorine within1 nm depth beneath the surface is reduced in the thermally treated specimen compared to the raw product down to a content about as low as in the reference sample. AES allows analyzing analysis of the first few nanometers from the top-surface of individual NPs by point analysis. An F KLL peak has been detected at the surface of samples of as-prepared TiO_2 nanoplatelets under optimized measurement conditions, but was not detectable after their calcination, which is in agreement with ToF-SIMS results. Moreover, high resolution AES on single TiO_2 nanoplatelets elucidated that the surface atomic layers surrounding the TiO_2 nanopaltelet contain fluorides before thermal treatment of the NPs.

Thanks/Acknowledgement

This work was supported by the SETNanoMetro Seventh Framework Programme project (project number 604577; call identifier FP7-NMP-2013_LARGE-7).

References

[1] H. Xiguang et al., 2009 *J. Am. Chem. Soc.* **131** 3152
[2] C. Deiana et al., 2013 *Phys. Chem. Chem. Phys.* **15** 307
[3] E. Ortel et al., *Surf. Interface Anal.* **48** 664

Fig. 1 High-resolution SEM image of TiO_2 nanoplatelets

P01.079-NAMA078

THE IMPACT OF THE DIAMOND REINFORCING PARTICLES SIZE ON THEIR INTERACTION WITH THE ALUMINIUM MATRIX OF COMPOSITES IN THE COURSE OF HEATING

V. Popov
National University of Science and Technology "MISIS" - Moscow (Russian federation)

Composite materials with aluminium matrix and diamond reinforcing particles can be used in many industries, e.g. in mechanical engineering for wear reduction or to secure high conductivity and durability [1]. However the formation of aluminum carbide is possible during heating on contact of aluminum with carbon materials. Samples of composites with aluminium matrix and various diamond reinforcing particles were prepared to determine the influence of diamond particles size on these processes: (i) diamond microparticles with size from 40 up to 60 micrometers, (ii) from 1 up to 2 micrometers and (iii) nanodiamonds (the size of the initial particles is 4-6 nm).

Composites were obtained via mechanical alloying. It is known that the production of aluminum carbide on contact with carbon macro-objects starts at the temperatures exceeding 1000°C, that’s why the graphite crucibles are used in the aluminum industry. In case of contact with carbon nano- and microparticles, the outcome is different. DSC and XRD have shown that the reaction between the components with the production of aluminum carbide starts at 400-450°C in the composite materials made of aluminum and nanodiamond reinforcing particles with the 4-6 nm size (Fig.1a). The reaction with diamond microparticles starts at the higher temperatures (over 500-550 °C) and carries less intensively (Fig.1b.).

The studies have shown that the temperature range of use of composites with aluminium matrix and diamond reinforcing particles does not exceed 400 °C for nanoparticles and 500 °C for microparticles.

Fig.1. DSC curves obtained from studying the composites "A1+nanodiamonds (size is 4-6 nm)" (a) and “Al+microdiamonds (size is 40-60 micrometers)” (b)

Thanks/Acknowledgement

The author is grateful to A.Prosviryakov, M.Presniakov, B.Senatulin and E.Shelekhov for assistance in determining the structure. The research leading to these results has received funding from the Ministry of Education and Science of Russian Federation under the project with identifier RFMEFI58716X0030.

References

1. V.A.Popov, E.V.Shelekhov, A.S.Prosviryakov, D.V.Matveev, E.V.Vershinina, M.G.Khomutov. Development of Aluminium Matrix Composites with Non-agglomerated Nanodiamond Reinforcements. Int.J Nanotechnology, 2016, vol.13, Nos.8/9, pp.584-590

P01.054-NAMA104

IMPROVED PERFORMANCE OF DYE SENSITIZED SOLAR CELLS THROUGH WELL-ORDERED TIO2 NANOTUBE ARRAYS WITH DIFFERENT LENGTHS

S. Khameneh-Asl, N.S. Peighambardoust, M. Maghsoudi
Department of Mechanics, Materials Science and Engineering group, University of Tabriz, Tabriz, Iran - Tabriz (Iran, islamic republic of)

EIS is one of powerful tools to investigate internal resistances of DSSCs that reflect the charge transfer process. DSSC is a complex system composed of several interfaces. Electron transport and recombination in photoelectrode, charge transfer process at Pt counter electrode, and the diffusion constant of I3- can all studied by EIS. The equivalent model fitting the impedance spectra of DSSCs based on TiO2 nanotube arrays is shown in Fig. 1 [1]. The effects of annealing temperature, anodization time, amount of water and NH4F in the electrolyte could be analyzed by using EIS [2, 3]. In our study, we prepared TiO2 nanotube arrays by anodization process. In order to further improve of the performance and characteristics of DSSC, TiO2 arrays optimized by changing the different anodization time from 2 to 6 hrs and different annealing temperature from 450 to 750 ºC. Then the optimized samples of 6 hrs anodization time and 450 ºC annealing tempreture were doped in NH3 solution and N2 gas atmosphere and were analyzed by EIS. The experiment results demonstrated that the length of the NTs increased by anodization time increasing. Well-ordered TiO2 nanotube array sample with long nanotube length could effectively increase the photoelectron transfer and reduce the recombination of DSSCs. The 450 ºC annealed and N-doped sample showed the lower resistance of EIS test due to the resistance of the electron transport within photoelectrode and electron lifetime will improve by N doping.

References

1. Qi, Lihong, Zhuoxun Yin, Shen Zhang, Qiuyun Ouyang, Chunyan Li, and Yujin Chen. "The increased interface charge transfer in dye-sensitized solar cells based on well-ordered TiO 2 nanotube arrays with different lengths." Journal of Materials Research 29, no. 06 (2014): 745-752.
2. Hu, Jinghua, Shiwu Hu, Yingping Yang, Shengqiang Tong, Jiejie Cheng, Mengwei Chen, Li Zhao, and Jinxia Duan. "Influence of Anodization Time on Photovoltaic Performance of DSSCs Based on TiO2 Nanotube Array." International Journal of Photoenergy 2016 (2016).
3. Li, Yongkun, Hongmei Yu, Changkun Zhang, Wei Song, Guangfu Li, Zhigang Shao, and Baolian Yi. "Effect of water and annealing temperature of anodized TiO 2 nanotubes on hydrogen production in photoelectrochemical cell." Electrochimica Acta 107 (2013): 313-319.

P01.056-NAMA162

GRAPHENE OXIDE LAYERS MODIFIED BY GOLD ENERGETIC IONS

P. Malinsky [1], M. Cutroneo [1], A. Mackova [1], M. Bohacova [2], D. Bousa [2], R. Bötgger [3], Z. Sofer [2]

[1]Nuclear Physics Institute of CAS, v.v.i - Rez (Czech republic), *[2]Department of Inorganic Chemistry, University of Chemistry and Technology Prague - Prague* (Czech republic), *[3]Institute of Ion Beam Physics and Materials Research, Helmholtz Zentrum - Dresden-Rossendorf* (Germany)

In this work, the effect of gold ion irradiation on graphene oxide foils structure, composition and optical properties were studied depending on the increasing ion fluence. Graphene oxide (GO) is one of many allotropes of graphene. Due to its mechanical, electronic and optical properties, it has been extensively studied in the recent years and it is considered a highly promising material with enormous application potential. In particular, (partial) reduction or reductive pattering of GO has attracted attention recently, thus the investigation of graphene oxide structure modification after the irradiation by energetic ions is highly needed. The ion irradiation of graphene oxide (GO) foil was performed using 40 keV Au^+ ions with fluencies in range from $5x10^{14}$ to $5x10^{16}$ cm^2. The elemental composition of the graphene oxide foils before and after the ion irradiation was investigated using Rutherford Backscattering Spectrometry and Elastic Recoil Detection Analysis. The structural modification of gold irradiated GO was further studied by microscopy methods. The chemical composition and structural changes on the GO foil surface were characterized by techniques including XPS, FTIR and Raman spectroscopy. The surface resistivity changes were measured using standard two point resistivity measurement. The used analytical methods revealed about the removing of oxygen functionalities and reduction on the surface of graphene oxide after gold irradiation that leads to the surface resistivity decrease according the increasing ion fluence.

Thanks/Acknowledgement

The research has been carried out at the CANAM (Center of Accelerators and Nuclear Analytical Methods) infrastructure (LM2015056) and has been supported by the project GA No. 16-05167S.

P01.057-NAMA166

APPLICATIONS OF XPS FOR STUDYING THE COORDINATION CHEMISTRY AT THE SURFACE OF POROUS METAL-ORGANIC NANOSTRUCTURES

A. Cano [1], J. Tóth [2], L. Lartundo [3], L. Kövér [2], E. Reguera [1]

[1]Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Unidad Legaria, Instituto Politécnico Nacional - Mexico (Mexico), *[2]Institute for Nuclear Research, Hungary Academy of Sciences (ATOMKI) - Debrecen* (Hungary), *[3]Centro de Nanociencias y Micro-Nanotecnología, Instituto Politécnico Nacional, - Mexico* (Mexico)

The Prussian blue compound, $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ is considered as the first synthetic coordination polymer, which crystallizes in a cubic unit cell with 10.2 Å of cell edge. This solid forms a 3D framework with interconnected pores or cavities of about 9 Å diameter related with the existence of vacancies for the building block, $[Fe^{II}(CN)_6]^{4-}$ [1]. This compound was the base to develop an extensive and fascinating family of coordination polymers where both internal and outer metals can be replaced by other transition metals, $T_a[M(CN)_6]_b$, which results in a wide diversity of solids with different structures and topology of porous frameworks [2-6]. The cyanometallates family has been intensively studied for their potential applications for gas separation and storage [7,8], molecular magnets [9], rechargeable batteries [10], fuel cells [11], biosensors for medicine (glucose, antigen, cholesterol, uric acid, antihypertensive drug, DNA [12, 13-17], and environmental protection [18-20]. The emerging field of the Nano-devices based on porous cyanometallates networks functionalized on nanostructures is closely related to the knowledge on reactivity, interactions and properties at the nanostructure surface. In that way, our study is oriented to use XPS to follow the oxidation/reduction reactions at the nanostructure surface and in the anchored cyanometallates framework. In this study, special attention is given to establish the optimal experimental conditions to record XPS spectra representative for the composite under consideration, with a minimum damage caused by the sample irradiation with the X-ray beam under ultrahigh vacuum. Following such optimized experimental procedures, valuable information on the nanostructures surface and composites interfaces was obtained. This contribution illustrates the relevance of the measurement procedures to obtain reliable XPS data.

Thanks/Acknowledgement

This research was supported by Consejo Nacional de Ciencia y Tecnología (CONACYT) and its program of PhD scholarship. This study was also supported by grant (SIP 20170198) through the Programa de Beca Estimulo Institucional de Formación de Investigadores (BEIFI).

References

W. Griffith, Q. Rev., Chem. Soc., 1962, 16, 188; J. Roque, E. Reguera, J. Balmaseda, J. Rodriguez-Hernandéz, L. Reguera, LF Del Castillo, Microporous and Mesoporous materials, 2002, 103 (1), 57; M. Avila, L. Reguera, J. Rodriguez-Hernandez, J. Balmaseda, E. Reguera, J. Solid State Chem. 2008, 181 (11), 2899; L. Reguera, J. Balmaseda, C.P. Krap, E. Reguera, J. Phys. Chem. 2008, C 112, 10490; Biao Kong, Cordelia Selomulya, Gengfeng Zheng and Dogyuan Zhao, Chem. Soc. Rev., 2015, 44, 7997

P01.059-NAMA247

MODELLING ENTIRE XPS SPECTRA OF CORE-SHELL NANOPARTICLES FOR THE CALCULATION OF SHELL THICKNESSES AND CORE RADII

M. Hronek [1], H. Kalbe [1], J. Pseiner [1], C.J. Powell [2], W.S.M. Werner [1]

[1]*Vienna University of Technology - Vienna* (Austria), [2]*National Institute of Standards and Technology - Gaithersburg* (United States of America)

The investigation of planar layered samples as well as core-shell nanoparticles (CSNP) based on quantitative X-ray photoelectron spectroscopy (XPS) analysis provides valuable information about the chemical and structural properties of a sample. Particularly, the estimation of shell thicknesses of CSNP from XPS data is well-established [1,2,3]. These methods only make use of the intensities of the main XPS peaks, but neglect the information contained in the shape of the inelastic background which usually exhibits a far larger cumulative intensity than the narrow elastic peaks.

As was previously shown [4], it is possible to calculate planar layer thicknesses from the intensity of the background signals in relation to the peak intensities in XPS spectra. A novel approach for CSNP is presented based on the simulation of entire XPS spectra [1] and the comparison with experimental data. The simulation result is fitted to the measured spectrum with the shell thickness and core radius of the CSNP as fit parameters.

XPS spectra are calculated in a Monte-Carlo (MC) simulation of the electron trajectories [1]. The experimental spectrum is deconvoluted into the contributions of the individual XPS lines which are then compared with the corresponding simulated partial spectra in a fitting routine. The background shape is modelled based on the partial loss intensities of inelastically scattered electrons which are computed from the results of the MC simulations.

The electron energy loss is simulated over a wide range. Thereby, the single particle approximation used by all previous methods breaks down and disordered powders of nanoparticles are simulated instead. Furthermore, the change of the inelastic mean free path (IMFP) as a function of the changing electron kinetic energy must be accounted for.

For this study, a series of polymeric CSNP samples consisting of polytetrafluoroethylene (PFTE) cores and poly(methyl methacrylate) (PMMA) shells were investigated by XPS. The experimental results are presented along with fitted spectra from which shell thicknesses and core radii were determined.

Thanks/Acknowledgement

The funding from the 14IND12 Innanopart project by the EU through the EMPIR initiative is gratefully acknowledged.

References

[1] W.S.M. Werner et al., Nist Database for the Simulation of Electron Spectra for Surface Analysis, SRD 100, Version 2.0, National Institute for Standards and Technology (NIST), Gaithersburg, MD, USA, 2014

[2] H. Kalbe et al., J. Electron Spectrosc. Relat. Phenom. 212, 2016, 34-43

[3] A. Shard, J. Phys. Chem. C, 116(31), 2012, 16806-16813

[4] S. Tougaard, J. Vac. Sci. Technol. A 14, 1996, 1415-1423

P01.060-NAMA252

FIBSIMS: SECONDARY ION MASS SPECTROSCOPY CAPABILITY INTEGRATED ON AN FIBSEM INSTRUMENT

L. Pillatsch [1], F. Östlund [2], J. Michler [1]
[1]Empa (Swiss Federal Laboratories for Materials Science and Technology), Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, CH-3602 Thun, Switzerland - Thun (Switzerland), [2]TOFWERK AG, Uttigenstrasse 22, CH-3600, Thun, Switzerland - Thun (Switzerland)

Surface analysis capabilities (SEM, EDS, WDS, EBSD,..) with an electron beam are well known. Secondary ion mass spectrometry (SIMS) using the focussed ion beam (FIB) is an additional analysis technique revealing the elemental composition of a sample with an excellent lateral (<50 nm) and depth resolution (<10 nm).

The sample is sputtered locally with the FIB. Sputtered ions are collected and selected according to their mass by and orthogonal TOFSIMS (Figure 1) [1][2]. The presented mass spectrometer, based on the time of flight principle, allows for parallel mass detection of all elements of the periodic table. With regard to the small volume sputtered, no elemental information gets lost.

FIBSIMS is seen as complement to EDS/WDS. While with EDS an WDS, concentration down to 0.1% can be determined, FIBSIMS detects, but doesn’t determine concentration, down to the ppm level. The direct measurement of masses allows to detect isotopes and to determine isotopic ratios.

In this presentation, the capabilities and the limits of secondary ion mass spectroscopy in combination with a focussed ion beam will be explained by means of typical application examples such as metals (Figure 2), semiconductors, coatings and multilayer samples.

Figure 1: The incoming ion beam is pulsed by an electric field in orthogonal direction to the initial flight ion trajectory. The principle of mass selection is based on the time of flight particles need for the set distance between the pulser and the detector

Figure 2: Ca migration to grain boundaries of a Mg alloy with hard-phase skeleton. Mapping of the elemental composition of a sample is a standard application for SIMS.

References

[1] J.A. Whitby et al, Advances in Materials Science and Engineering, 2012, article ID 180437

[2] D. Alberts et al, Instrumentation Science & Technology 2014 DOI: 10.1080/10739149.2013.878843.

P01.061-NAMA264

THE EFFECT OF ZINC CONTENT ON THE ENHANCEMENT ER-YB LUMINESCENCE PROPERTIES IN THE SILICATE GLASS MATRIX

S. Vytykácová [1], S. Stanek [1], B. Švecová [1], M. Míka [2], J. Oswald [3], A. Macková [4], P. Malinský [4], R. Böttger [5], P. Nekvindová [1]

[1]*Department of Inorganic Chemistry, University of Chemistry and Technology - Prague* (Czech republic), [2]*Department of Glass and Ceramics, University of Chemistry and Technology - Prague* (Czech republic), [3]*Institute of Physics, Czech Academy of Sciences, v.v.i - Prague* (Czech republic), [4]*Nuclear Physics Institute, Czech Academy of Sciences, v. v. i - Rež* (Czech republic), [5]*5Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research - Dresden* (Germany)

Glasses are a perspective material for use in photonics due to many advantages, such as cheap and simple preparation in optical quality, compatibility with silica fibers, high thermal and chemical stability and very low attenuation (tenth dB/km). Glasses doped with Er and Yb show strong luminescence around 1530 nm, which makes them attractive luminophore for preparation of multifunctional optical components. Disadvantage of this kind of glasses is relatively low solubility of RE ions and high phonon quenching of silicate matrix. However, this fact can be improved by addition of Al2O3 or ZnO. Moreover, the easy doping of silicate glasses with silver ions by ion exchange or ion implantation technique allowed us to focus on the study of mechanism of erbium luminescence enhancement by silver ions. This contribution is focused on the influence of ZnO on the optical and luminescence properties of Er-Yb zinc silicate-glasses. The influence of silver doping on resulting luminescence properties of prepared glasses was also investigated.

Three types of silicate glasses with different content of ZnO and rare-earth ions (Er and Yb) were prepared. For all prepared glasses, the density, glass transformation temperature and refractive index were determined. Moreover, these glasses were doped with silver using two methods – ion implantation and ion exchange and subsequently annealed using various conditions. Distribution and movement of silver through the glass matrix was determined by EMA method (for ion exchange) and simulated by SRIM program (for ion implantation). Presence of the silver metal nanoparticles was observed using optical absorption in UV-VIS range. Size of the created metal nanoparticles was calculated from absorption spectra using Mie´s theory. The photoluminescence spectroscopy at room temperature and at 4K in near IR region as well as TEM were used to observe the size and distribution of silver or zinc oxide nanoparticles. The influence of silver or zinc oxide nanoparticle presence on the intensity of luminescence was investigated.

It was determined, that the addition of ZnO significantly affects solubility of rare-earth ions in glass matrix while not affecting transparency or homogeneity of the glass matrix. Increasing of ZnO content also enhances intensity of luminescence around 1530 nm. Presence of Ag+ ions as well as metal silver nanoparticles positively contributes to the enhancement of erbium photoluminescence intensity. The possible mechanism of this phenomenon will be discussed.

Thanks/Acknowledgement

We acknowledge the Czech Science Foundation project GA 15-01602S.

P01.063-NAMA266

STRUCTURAL AND MORPHOLOGICAL STUDIES OF SNO2 NANOPARTICLES ON TIO2(110) SURFACE

<u>O. Leiko</u>, R. Šedivá, I. Khalakhan, K. Mašek
Charles University, Faculty of Mathematics and Physics, Department of Plasma and Surface Science - Prague (Czech republic)

Metal conductive oxides have been attracting a lot of interest during last decades. Tin dioxide due to its physical properties have found usage in a wide range of applications in chemical industry, photocatalysis and electrocatalysis.

Real catalytic systems are not appropriate for fundamental research due to their complex structure. Thus, purpose of our work was preparation of well-defined model system in form of tin dioxide nanoparticles on the stoichiometric rutile surface. Such system is suitable for morphological, structural and reactivity studies by means of surface physics methods.

The SnO_2 nanoparticles were made by means of physical vapor deposition of metallic tin from sapphire crucible at 1043 K under atomic oxygen flux. Rutile surface was previously oxidized under oxygen flux at 723 K.

Obtained $SnO_2/TiO_2(110)$ system morphology was studied by atomic force and scanning electron microscopies. Chemical analysis was made by x-ray photoelectron spectroscopy and structure was investigated by reflection high-energy electron diffraction method.

SnO_2 nanoparticles having rutile structure formed two grain populations described by the following epitaxial relationships:

$SnO_2(110) || TiO_2(110)$

$SnO_2[110] || TiO_2[110]$ 1st population

$SnO_2[100] || TiO_2[110]$ 2nd population

All SnO_2 nanoparticles exhibited round shape and average grain size of 12 nm in diameter and 17 nm height (Fig. 1).

Whole $SnO_2/TiO_2(110)$ system was found to be structurally extremely robust and remained epitaxial after 30-day under atmosphere exposure. X-ray photoelectron spectra taken after the deposition process indicated besides SnO_2 phase also metallic Sn phase. Since no metallic Sn phase was not detected by reflection high-energy electron diffraction, and considering low value of surface free energy of metallic Sn comparing to that one of tin dioxide, we can assume that surplus of non-oxidized Sn segregate on the surface of SnO_2 nanoparticles and/or TiO_2 substrate and form disordered ultra-thin layer.

Presented $SnO_2/TiO_2(110)$ epitaxial system represents model system perspective for further investigation of its adsorption properties and chemical reactivity in the field of heterogeneous catalysis.

P01.064-NAMA285

ORDERED CORE/SHELL PLASMONICS NANOPARTICLES FOR MOLECULAR ELECTRONICS

A. Ouvrard [1], **N. Alyabyeva** [1], **A. Zakaria** [1], **F. Charra** [2], **B. Bourguignon** [1]
[1]ISMO, CNRS, Univ. Paris-Sud, Université Paris-Saclay - Orsay (France), *[2]IRAMIS Institut Rayonnement Matière de Saclay, SPCSI - Gif/yvette* (France)

Long-range ordered systems at nanoscale made of molecules or/and nanoparticles (NPs) has become a hot topic for many applications like: sensors, energy, plasmonics, catalysis and molecular electronics. Very recently, appeared promising surfaces like $Al_2O_3/Ni_3Al(111)$ or Graphene/Ir(111) allowing to grow high density narrow size distributed NPs [1], well adapted to study how reactivity is modified for small clusters and different core/shell structure and composition [2]. They also give opportunity to be used as a template for molecular electronic purposes by linking them with organic molecules.

In this work, a multi-scale investigation combining microscopy, electron diffraction and optical spectroscopies was conducted to: (i) clearly optimize long-range order and density, of core-shell (Pd/Au) NP grown in UHV on ultrathin Al_2O_3 films on $Ni_3Al(111)$ and (ii) extract electronic, plasmonics and structural properties of NPs and their ordering quality.

(i) LEED and STM investigations of the impact of oxide temperature growth on its structural and electronic properties show a clear correlation of oxide changes with NP ordering and density. STM and Differential Reflectance Spectroscopy (DRS) used to probe core/shell NP morphology and plasmonics response for different NP sizes and compositions, show that NP density and plasmonics response are strongly NP size and composition dependent.

(ii) Probing adsorbed CO on NPs using Sum Frequency Generation (SFG) provides an original way to understand size and composition effects on NP electronic and crystalline structure [3]. SFG experiments conducted on CO adsorbed on Pd/Au NPs, reveal different CO adsorption sites and non-reversible adsorption which depends on shell thickness. Pd segregation to Au shell surface is responsible for the appearance of new adsorption sites. Pd/Au alloy formation at the interface is limited to few monolayers (ML).

Using multi-scale multi-probe approach, long range ordered Pd/Au NPs were obtained and optimized. Optical spectroscopies evidence Pd segregation in the Au shell, but limited to few ML. No plasmonic response is found due to Pd segregation until shell thickness is large enough.

Thanks/Acknowledgement

We gratefully acknowledge the French National Agency for Research (Agence Nationale pour la Recherche, ANR) for financial support through the JCJC program (Project LEMON - DS0305).

References

[1] L. Gavioli et al., Prog. in Surf. Sci., vol. 86, pp. 59-81, 2011.

[2] G. Sitja et al., Nano Lett. 13 (2013) 1977

[3] A. Ouvrard et al., J. Phys. Chem. C, 2017, 121 (10), pp 5551–5564

P01.065-NAMA292

NANOLAMINATION OF GRAPHENE AND ZNO IN HETEROSTRUCTURES

M. Baitimirova [1], R. Viter [2], J. Andzane [1], I. Iatsunskiy [3], A. Ramanavicius [4], M. Bechelany [5], D. Erts [1]

[1]Institute of Chemical Physics of University of Latvia - Riga (Latvia), [2]Institute of Atomic Physics and Spectroscopy of University of Latvia - Riga (Latvia), [3]NanoBioMedical Centre of Adam Mickiewicz University - Poznan (Poland), [4]State Research Institute Center for Physical Sciences and Technology - Vilnius (Lithuania), [5]European Institute of Membranes of University of Montpellier - Montpellier (France)

In past few years nanolamination became interesting for the researchers. Because of processes in the surface boundary layers, materials in nanolaminates exibit new physical properties. Zinc oxide (ZnO) is known as a semiconductor with strong luminescence at room temperature. As it was shown in previous investigations of single graphene-ZnO interfaces, where graphene acted as an excellent electron acceptor and transport material of photoinduced in ZnO electrons [1], photosensitivity of ZnO can be improved by its combination with graphene.

In this research Graphene/ZnO nanolaminates with various number of alternating ZnO and graphene layers were fabricated using atomic layer deposition method for ZnO layers synthesis, and chemical vapour deposition method followed by polymer-based tranfer for preparation of graphene monolayers. Structure and optical properties of created nanolaminates were studied.

The number of alternating graphene and ZnO layers influenced the structure and optical properties of fabricated Graphene/ZnO nanolaminates. Graphene layers, used as a substrate for ZnO deposition, stimulated formation of ZnO crystalline structure, thus avoiding formation of amorphous transition layer at the graphene-ZnO interface. With an increase of number of graphene interlayers in the nanolaminate, the band gap of ZnO decreased and the absorption edge position of ZnO were shifted relative to pure ZnO. This could be related to the formation of optically active defects at the graphene-ZnO interface and at ZnO grain boundaries. Increase of number of graphene layers in nanolaminate resulted in decrease of ZnO photoluminescence, indicating formation of depletion layer in ZnO near each graphene surface due to transfer and trapping of photoexicited in ZnO electrons in graphene [2].

Thus, combination of ZnO and graphene in nanolaminates provides possibility to obtain heterostructures with improved crystalline quality and to tune optical properties of ZnO, that may find applications in future micro- and nanodevices.

References

1. Dutta, M., Sarkar, S., Ghosh, T., Basak, D. J. Phys. Chem. C 116, 20127−20131 (2012)
2. Baitimirova M., Viter R., Andzane J. et al. J. Phys. Chem. C 120, 23716−23725 (2016)

P01.066-NAMA293

XRD AND USXES INVESTIGATIONS OF THE MULTILAYER NANOCOMPOSITES BASED ON (CO45FE45ZR10)35(AL2O3)65

E. Domashevskaya, **Y. Yurakov, V. Logachev, K. Barkov**
Voronezh State University - Voronezh (Russian federation)

Currently, the manufacturers of logic components explore 10 nm technological processes, but further size reduction is difficult due to quantum effects. Morphology of the multilayer nanocomposites structures (MLNS) - the possible basis of the spin transistor - are investigated.

MLNS $(Co_{45}Fe_{45}Zr_{10})_{35}(Al_2O_3)_{65}/a\text{-}Si]_{120}$ (I) and $(Co_{45}Fe_{45}Zr_{10})_{35}(Al_2O_3)_{65}/a\text{-}Si{:}H]_{100}$ (II) have been obtained by ion-beam sputtering of two targets: the alloy $Co_{45}Fe_{45}Zr_{10}$ with Al_2O_3 patches placed on its surface and an Si plate in the Ar plasma (in the case of a-Si:H - with the addition of hydrogen) and deposited on Si - (100) substrate. The thickness of the $(Co_{45}Fe_{45}Zr_{10})_{35}(Al_2O_3)_{65}$ and a-Si layers were 3.5 and 3.4 nm respectively.

The phase composition was studied by the XRD analysis with the diffractometer in the Bragg-Brentano geometry.

To refine electronic structure and phase composition of the samples we used ultrasoft X-ray emission spectroscopy (USXES) method by registering Si $L_{2,3}$ -spectra. The investigated layers thickness are varied from 10 to 120 nm without destruction.

According to XRD data, the presence in a sample (I) of metal oxides and silicides (FeSiZr), and, in a sample (II) - zirconium intermetallides, complex cobalt oxides and at interfaces - of silicides (ZrCoSi, etc.) was found.

Modeling of the fine structure of the MLNS Si $L_{2,3}$ - spectra was performed using reference spectra of cobalt and iron silicides, hydrogenated amorphous silicon and silicon oxides. As a result, FeSi (fig. 1) and CoSi (fig. 2) were found in MLNS (I) and (II), respectively.

Thus, it can be concluded that a partial change in the composition and morphology of the initial components of the MLNS was observed due to the formation of oxides, silicides and intermetallides.

Fig. 1. Si $L_{2,3}$ USXES of MLNS (I). Solid line - simulated spectrum.

Fig. 2. Si $L_{2,3}$ USXES of MLNS (II). Solid line - simulated spectrum.

P01.069-NAMA301

ATOMIC AND ELECTRONIC STRUCTURE OF HYBRID NANOMATERIAL BACTERIOFERRITIN DPS AGGREGATED FROM ESCHERICHIA COLI INORGANIC CORES

S. Turishchev [1], S. Antipov [1], N. Novolokina [1], O. Chuvenkova [1], A. Sinelnikov [1], E. Preobrazhenskaya [2], R. Ovsyannikov [3], A. Tarasov [1], D. Koyuda [1], O. Ozoline [2], E. Domashevskaya [1]

[1]Voronezh State University - Voronezh (Russian federation), [2]Institute of Cell Biophysics - Pushchino (Russian federation), [3]Helmholtz Zentrum Berlin - Berlin (Germany)

Dps protein of Escherichia coli (E.coli) belongs to the subfamily of bacterioferritines and represents a nanoscale hybrid particles consisting of an ~ 9 nm organic shell size with an inorganic core of about 5 nm diameters. The protein formation technique includes its gene cloning into a vector, superproduction of protein and chromatographic fractioning techniques. The protein shell consists of 12 identical subunits with the known crystal structure of a dodecamer. The composition and structure of the core have been less studied and usually associated with the oxidation products of $Fe2+$ ions in the ferroxidase centers of the protein. However, the physical properties of iron ions under anaerobic conditions in vitro may indicate a more complicated composition of the core in the native Dps protein. We used ultrahigh vacuum synchrotron experiments by X-ray absorption near edge structure spectroscopy of the iron absorption edge in the soft X-ray region to get the direct experimental information about specificity of iron atoms local surrounding. Supporting experiments were performed with the use of transmission electron microscopy and dynamic light scattering (Figure). The presence of both trivalent and divalent iron ions in the octahedral and tetrahedral environment of oxygen atoms in the prepared samples consisted of ~ 10 nm hybrid particles with 5 nm inorganic cores is revealed. This shows a complex composition of ions in the core even in the native Dps protein, that has been isolated from aerobically grown bacteria.

Figure. a: dynamic light scattering vs vol. indicating particles sizes ~ 9 nm; b and c: TEM images; d: microdiffraction pattern from bacterioferritin Dps inorganic cores.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019 Project N 16.8158.2017/BCh, RFBR according to research projects N 16-02-01167 a, Russian Science Foundation (Grant №14-14-00985b IT, PAS).

P01.070-NAMA312

PHASE COMPOSITION AND STRUCTURE OF THE MOCVD SNO2/SI NANOWIRES COMPOSITE STRUCTURES

S. Turishchev [1], A. Schleusener [2], E. Parinova [1], O. Chuvenkova [1], D. Koyuda [1], D. Marchenko [3], R. Ovsyannikov [3], A. Tarasov [1], V. Sivakov [2]
[1]*Voronezh State University - Voronezh* (Russian federation), [2]*Leibniz Institute of Photonic Technology - Jena* (Germany), [3]*Helmholtz Zentrum Berlin - Berlin* (Germany)

The increasing interest in area such as detection of hazardous gases or monitoring of combustion processes has lent prominence to gas sensing devices. Solid state gas sensors based on SnO2 have become attractive owing to their manufacturing simplicity, portability. A vast body of literature exists on formation, defect structure and electrical, and optical properties of SnO_2 films or nanowires. Especially, for films prepared by CVD or by spraying techniques, the reports on the presence of the Sn(0) and/or Sn(II) phases are quite conflicting. In present study the growth of tin oxide layers on the 1D silicon surfaces [1] has been investigated.

Formed composite structures were characterized by XRD, SEM/EBSD. Synchrotron PhotoEmission Electron Microscopy (PEEM) technique was applied with the use of synchrotron radiation of Helmholtz Zentrum Berlin BESSY II storage ring [2]. X-ray absorption near edge structure (XANES) technique was used as well [3].

The decomposition of SnO_2 up to metallic tin was observed. According to the XRD data we observed the formation of three different tin phases (SnO_2 , SnO and Sn). The ratio between them exhibits a dependence of the length of the nanostructures. The EBSD data confirm the presence of three different phases along the vertical axis of the nanostructures. The presence of metallic tin inclusions over the whole surface area characterized by presence of oxygen vacancies are confirmed by the PEEM/XANES data (Figure) revealing reconstruction of the composites electronic structure.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh and RFBR according to research projects № 16-42-360612 p_a (with government of Voronezh region), 16-32-00860 mol_a. V.S. is gratefully acknowledges the German Federal Ministry of Education and Research (BMBF) in frame of Baltic Sea Network “NanoPhoto” under Grant No. 01DS14017 for the financial support.

References

[1] Sivakov V.A., et. al. Phys. Rev. B., 2010, vol. 82, p. 125446.

[2] Turishchev S.Yu., et. al. Physics of the Solid State., 2014, vol. 56, p. 1916

[3] Chuvenkova O.A., et. al. Physics of the Solid State., 2015, vol. 57, p. 153

P01.071-NAMA313

ELECTRONIC STRUCTURE OF NANOPOWDER PRODUCED FROM SILICON NANOWIRES

E. Parinova [1], A. Schleusener [2], S. Turishchev [1], D. Koyuda [1], O. Chuvenkova [1], V. Sivakov [2]
[1]Voronezh State University - Voronezh (Russian federation), *[2]Leibniz Institute of Photonic Technology - Jena* (Germany)

Hydrogen is regarded to be one of the most promising green energy source in the Industry 4.0. One of the promising approach to produce hydrogen is photocatalytic water splitting. To split water into hydrogen and oxygen, a minimum energy of 1.23 eV is required. Silicon is one of the best studied semiconducting material and the second most abundant element in the earth crust. However, the band gap of bulk silicon is 1.12 eV which is too small to provide electrons and holes with enough energy to split water. Top-down formation of silicon nanowires and further powder formation on its basis with a sufficient large optical band gap may allow to drive the photocatalytic hydrogen production. Here we report first synchrotron experiments results of the electronic structure studies of Si nanopowder produced from silicon nanowires.

X-ray absorption near edge structure (XANES) investigations near the $L_{2,3}$ core level of silicon and K core level of oxygen as well as X-ray photoelectron spectroscopy (XPS) studies were performed at the Helmholtz Zentrum Berlin with the use of BESSY II highly brilliance synchrotron radiation of the Russian-German beamline equipped with the multitask set of UHV chambers and SPECS PHOIBOS 150 hemispherical electron energy analyzer. Used techniques are characterized by high sensitivity to surface and local atomic surrounding.

Si $L_{2,3}$ XANES results allow to assume the ordered atomic structure in studied particles. XRD and TEM measurements confirms particles crystallinity with two main sizes of 7 nm and 40 nm and core-shell structure. Natural SiO_2 surface layer thickness was estimated as less than 1 nm and no suboxides formation was detected. Nanoparticles developed surface lead to electronic structure transformation that is characterized by additional states appearance in the conduction band.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh. V.S. is gratefully acknowledges the German Federal Ministry of Education and Research (BMBF) in frame of Baltic Sea Network “NanoPhoto” under Grant No. 01DS14017 for the financial support.

P01.073-NAMA333

MICRO TO NANOSILVER CYTOTOXICITY: INFLUENCE OF GRAIN SIZE AND SYNTHESIS ROUTE

O. Vasile [1], E. Andronescu [1], B.S. Vasile [1], R. Trusca [1], E. Vasile [1], C. Bleotu [2], A.M. Holban [2], C. Chifiriuc [2], F. Iordache [3]

[1]*University Politehnica from Bucharest, National Research Center for Micro and Nanomaterials - Bucharest* (Romania), [2]*Microbiology Immunology Department, Faculty of Biology, University of Bucharest - Bucharest* (Romania), [3]*Institute of Cellular Biology and Pathology of Romanian Academy, "Nicolae Simionescu", - Bucharest* (Romania)

Although engineered silver nanopowders offer great promise in various fields of biomedical, industrial and ecological applications, little information is known about their cytotoxicity effects. The aim of the current study was the synthesis and cytotoxicity assessment of silver powders using the pyrosol method at temperatures of 600°C, 650°C and 700°C, respectively sol-gel method and heat treatements at 500°C, 600°C, 700°C and 800°C. The synthesized Ag powders were characterized from the structural, compositional and morphological point of view by using XRD, SEM, and TEM coupled with SAED. In order to determine the influence of the synthesis route on Ag particles cytotoxicity, different sizes of micro and nanosilver synthesized powders were evaluated for their potential toxicity. Their cytotoxicity was evaluated based on their influence on cellular morphology and proliferation rate, cell cycle and apoptosis of undifferential stem cells, endothelial cells and tumoral cells, assessed through flow cytometry, cloning and MTT assay. The results showed that the cytotoxicity of the synthesized silver nanoparticles depends on the synthesis route, the pyrosol synthesized nanoparticles exhibiting a higher cytotoxicity as compared to those obtained by the sol-gel method.

Thanks/Acknowledgement

This paper is supported by the Sectorial Operational Program Human Resources Development, financed from the European Social Fund, and by the Romanian Government under the contract number ID 134398 (KNOWLEDGE).

P01.074-NAMA334

EU2O3-DOPED ZNO NANOSTRUCTURED MATERIALS: SYNTHESIS, ADVANCED CHARACTERIZATION AND TOXICITY

B. Vasile, O.R. Vasile, C. Ghitulica, F. Ilie, I. Nicoara, O. Oprea, A. Surdu
University Politehnica from Bucharest, National Research Center for Micro and Nanomaterials - Bucharest (Romania)

In this work ZnO nanostructures (nanopowders and nanostars) have been synthesized via a simple sol-gel method. The used methods used to synthetize the nanostructures involves two steps as follows: (1) precipitation of zinc acetate precursor for the synthesis of ZnO nanopowders and Zinc chloride precursor for the synthesis of ZnO nanostars and (2) addition of Eu2O3 in different concentrations (1%, 3% and 5%) using europium acetate as precursor. Detailed crystalline parameters for each of the species synthetized were analyzed using X-ray diffraction. Structural transitions were also discussed. The structure and morphology of the as-prepared ZnO nanopowders and nanostars were investigated by electron microscopy. TEM investigations have shown an average particle size range from 23 to 29 nm and polyhedral and spherical morphology with tendency to form aggregates for nanopowders. For nanostars structures

Thanks/Acknowledgement

Otilia Ruxandra VASILE's work is supported by the Sectorial Operational Programme Human Resources Development, financed from the European Social Fund, and by the Romanian Government under the contract number ID 134398 (KNOWLEDGE). The present work was also possible due to the EU-funding grant POSCCE-A2-O2.2.1-2013-1/Prioritary axe 2, Project No. 638/12.03.2014, cod SMIS-CSNR 48652 and by the Sectoral Operational Programme Human Resources Development, financed from the European Social Fund and by the Romanian Government under the contract number POSDRU/86/1.2/S/58146 (MASTERMAT).

P01.076-NAMA361

MAGNETIC ORDERING IN TWO-DIMENSIONAL ARRAYS OF MAGNETIC NANOPLATES WITH PERPENDICULAR ANISOTROPY

A. Chumakov [1], O. Konovalov [1], A. Vorobiev [2], A. Eliseev [3], L. Trusov [3], A. Eliseev [3]
[1]European Synchrotron Radiation Facility - Grenoble (France), *[2]Uppsala University; ILL - Grenoble* (France), *[3]Moscow State University - Moscow* (Russian federation)

Recently a new method was developed for production of novel type of stable magnetic colloids based on disc-like hard magnetic hexaferrite ($SrFe_{12}O_{19}$, space group $P6_3/mmc$) particles electrostatically stabilized in aqueous solution [1]. The colloidal single crystalline particles possess a platelet-like shape with the mean lateral size of about 100 nm and the thickness of several nanometers. Each particle carries a large permanent magnetic moment oriented perpendicularly to the pellet surface, along the easy axis of magnetization c [2] and exhibits the highest reported values of the intrinsic coercivity field (of about 5600 Oe) for ferrite particles in stable colloids.

Presented study is aimed at a development of self-assembly-based technology for fabrication of ordered two-dimensional (2D) arrays of charged disk-like magnetic nanoparticles (MNPs) with large permanent magnetic moment and high coercivity for the next study of their non-trivial magnetic properties.

Electrostatic interaction between the positively charged magnetic nanoparticles and the Langmuir layer of negatively charged surfactant (DPPG) spread at the air-liquid interface of hexaferrite aqueous colloid was used to assemble a 2D layer of disk-like MNPs, Fig.1. In-plane and out of plane structure of this layer v.s. surface charge density was characterized with X-ray Reflectivity (XRR) and Grazing Incidence Diffraction (GID) methods at the ESRF beamline ID10-EH1. XRR revealed a 5 nm thick layer of hexaferrite platelet particles formation below the DPPG monolayer after few hours. GID study showed an existence of in-plane diffraction peaks, that correspond to (110) and (200) Bragg reflection of hexaferrite, and one out-of-plane peak (201) [2]. Position of these peaks on GID pattern evidences the 2D organization of MNPs with the orientation of the magnetization axis c perpendicularly to the Langmuir film.

Our study reveals that: 1) indeed a 2D monolayer of magnetic hexaferrite platelet nano-particles forms under the negatively charged Langmuir film; and 2) the magnetic moment of the nanomagnets is oriented perpendicularly to the air-liquid interface.

References

[1] L.A. Trusov, et al. Chem. Comm. (2014) **50**, 1458

[2] M. Stingaciu, et al. Scientific Reports (2015) **5**, 14112

P01.077-NAMA372

DEVELOPMENT OF OXIDE NANOFIBER TIPPED CANTILEVER AS A SUBSTRATE FOR CROSS SECTIONAL TRANSMISSION ELECTRON MICROSCOPY ANALYSIS

M. Shima [1], K. Watanabe [1], M.S. Rosmi [2], S. Sharma [1], G. Kalita [1], M. Kitazawa [3], M. Tanemura [1]

[1]*Nagoya Institute of Technology - Nagoya (Japan),* [2]*Universiti Pendidikan Sultan Idris - Perak (Malaysia),* [3]*Olympus Co. Ltd. - Nagano (Japan)*

Transmission electron microscopy (TEM) is a powerful tool for the material analysis. For TEM analyses, samples should be thin enough. This requirement makes the sample preparation time-consuming in general. For the cross sectional TEM (X-TEM), samples are prepared by ion milling of the mechanically polished material or by thinning the desired region of the material using a focused ion beam. In both methods, thinning process is employed after the synthesis of materials, and hence the damage to the sample induced by ion irradiation is unavoidable. Thus, the development of simple and damage free sample preparation technique is indispensable. Here we propose a silicon oxide nanofiber (SON) grown on a tip of a cantilever as a substrate onto which thin films are deposited for X-TEM analysis.

Ion irradiation onto carbon and carbon coated materials induces the formation of the carbon nanofiber (CNF) tipped cones (conical structures) without any catalyst even at room temperature [1]. By using this technique, batch fabrication of CNF tipped Si cantilevers for atomic force microscope (AFM) is possible [2]. In this ion-induced CNF growth, a variety of elements can be included into CNFs during the CNF growth by a simultaneous supply of metals and semiconductors during ion irradiation [3]. Based on this technique, Si-included CNF was grown on a tip of Si cantilever (AC160TS; Olympus) by supplying Si during the CNF growth. This cantilever was then annealed at 1000°C in atmospheric ambient to form SON tipped cantilever. Figure 1(TEM images of ZnO film deposited onto SON. Inset is the lattice image of a ZnO grain) shows a TEM image of ZnO film deposited onto the SON tipped cantilever thus prepared, disclosing a cross sectional view of the sample. As seen in the inset, the lattice image of ZnO is clearly observable. Thus, it is believed that the SON tipped cantilevers are promising substrates for X-TEM analysis.

References

[1] M. S. Rosmi, et al., Scientific Reports 4 (2014) 7563.

[2] M. Kitazawa, et al., J. Vac. Sci. Technol. B 27 (2009) 975.

[3] M. Z. M. Yusop, et al., ACS Nano 6 (2012) 9567.

P01.080-NAMA397

ONE-DIMENSIONAL ZNO NANOSTRUCTURES AND THEIR OPTOELECTRONIC APPLICATIONS.

R. Yatskiv, J. Grym, J. Vanis, M. Hamplova
Institute of Photonics and Electronic - Prague (Czech republic)

One-dimensional ZnO nanostructures have attracted increasing interest in recent years due to their potential in optoelectronic applications. The lack of p-type ZnO emphasizes the importance of rectifying junctions realized on these materials. Recently, we have demonstrated that colloidal graphite, deposited by a simple drop casting technique, forms a rectifying contact on both nanostructured and bulk ZnO [1-3]. Charge carrier transport of the graphite/bulk ZnO junction is dominated by thermionic emission at and above room temperature [1]. The transport mechanism of the graphite/ZnO nanorods junction can be described by a tunnel-recombination current transport mechanism via interface states [3]. These nanostructured heterojunctions show potential in different applications, such as highly sensitive UV photodetectors [4], or hydrogen sensors operated at room temperature [5].

An alternative way to create rectifying junctions is to use other p-type materials, either inorganic or organic to form heterojunctions with n-type ZnO. GaN is considered the most promising p-type semiconductor. One of the crucial problems in such heterojunctions is to create a contact on ZnO nanorods. Conventionally, a three-step approach is used to prepare a contact: first, the free space between the individual ZnO nanorods is filled with an insulating layer; second oxygen plasma is used to remove the insulating layer from the top of the ZnO nanorods; and finally, a contact is deposited. In addition, in most cases GaN is covered with a ZnO seed layer to grow ZnO nanorods, which results in the formation of interface states. All the listed fabrication approaches strongly affect both electrical and optical properties of as grown ZnO nanorods and current transport in such heterojunctions. In this work we present electrical properties of single ZnO nanorods/GaN heterojunctions, where ZnO nanorods are contacted directly by conductive AFM. We show that transport through a single ZnO nanorod/GaN heterojunction is affected by defect distribution in ZnO nanorods.

Thanks/Acknowledgement

This work was supported by the Czech Science Foundation projects: 17-00546S and 15-17044S.

References

[1] R. Yatskiv and J. Grym, Appl Phys Lett 101 (16), 162106 (2012).

[2] R. Yatskiv, J. Grym, K. Zdansky and K. Piksova, Carbon 50 (10), 3928-3933 (2012).

[3] R. Yatskiv, V. V. Brus, M. Verde, J. Grym and P. Gladkov, Carbon 77, 1011-1019 (2014).

[4] R. Yatskiv, J. Grym and M. Verde, Solid State Electron 105, 70-73 (2015).

[5] R. Yatskiv, J. Grym, P. Gladkov, O. Cernohorsky, J. Vanis, J. Maixner and J. H. Dickerson, Solid State Electron 116, 124-129 (2016).

P01.082-NAMA423

STRUCTURAL AND ELECTRONICS PROPERTIES OF RH-DOPED SNO2(110) SURFACES: AB-INITIO CALCULATIONS

F. Bouamra, A. Boumeddiene
University of Blida 1 - Blida (Algeria)

Actually, tin dioxide SnO_2 thin films present an important material for several applications: spintronics, optic, magnetic support for registration, catalysis, solar cells[1], etc…

In our investigation, we are interested by the (110) plane of SnO_2 , because it's known by the most stable one energetically [2].

Structural and electronics properties has been calculated for different atomic Rh/Sn ratio: 9.09%, 14.28%, 20% and 26.31% using a density functional theory (DFT) at B3LYP level with CRYSTAL09 program[3]. These structures are obtained by substitution of Rh atoms with Sn of the most outer atomic face of SnO_2(110) which contain Sn and O atoms [4]. Band structures, total density of state (DOS) and projected to the atomic orbitales of Rh, Sn and O atoms (PDOS), the differential charge density $\Delta n(r)$ of different plane of the surface are represented and discussed. We present then, the variation of magnetic moment with Rh/Sn ration. Finally, an analysis of Mulliken population has been also done at the surface of SnO_2(110)-doped Rh. The obtained results are compared with those of Sb-doped SnO_2(110) [5]. Values of band energies are calculated from band structure are represented

	E_g(eV)
0%	2.82
9.09%	2.68
14.28%	2.88
20%	2.65
26.31%	2.17

Table 1: gap energy values for different ratio of Rh/Sn 9.09%, 14.28%, 20% and 26.31%.

Thanks/Acknowledgement

This work was supported by the Algerian ministry of higher education and scientific research. We are glad to acknowledge Professor Michel Rérat and Jacques Hertzberg of Chemical-Physics group of IPREM of Pau University, for the benefit physics discussions and technical assistance.

References

[1] R. Fabricio Sensato, Rogerio Custodio, Monica Calatayud, Armando Beltran, Juan Andres, R. Julio, Sambrano, Elson Longo, Periodic study on the structural and electronic properties of bulk, oxidized and reduced SnO2(110) surfaces and the interaction with O2, Surf. Sci. 511 (2002) 408–420.

[2] J. Oviedo, M.J. Gillan, Reconstructions of strongly reduced SnO2(110) studied by first-principles methods, Surf. Sci. 513 (2002) 26–36.

[3] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D'Arco, M. Llunell, CRYSTAL09, University of Torino, 2010.

[4] F. Bouamra, A. Boumeddiene, M. Rérat and H. Belkhir, App. Surf. Sci. (2013) 41-44.

[5] A. Boumeddiene, F. Bouamra, M. Rérat and H. Belkhir, App. Surf. Sci. (2013) 581-587.

P01.083-NAMA442

APPLICATION OF SILICA-TITANIA-TMPTA-ACRYLIC COATINGS ON GLASS SURFACES BY AEROSPRAY TECHNIQUE

S. Pérez García, A.R. Vázquez-Velázquez, M.A. Velasco-Soto, L. Licea-Jiménez
Centro de Investigación en Materiales Avanzados S.C., Unidad Monterrey, Alianza Norte No.202, PIIT, Apodaca, NL., México. CP.66600. - Monterrey (Mexico)

One of the most used devices for renewable energy generation is photovoltaic systems. There are factors that influence the performance and efficiency of the photovoltaic cell based electricity generation energy, one of them is the environmental condition. The solar panels are exposed to the environmental features and interact with the weather condition; the result is a soiled panel, mainly with dust, organic material, etc. Panels can be protected by self-cleaning coatings, most recently, nanoparticles are being exploited for this endeavor. The modification of nanoparticles materials has taken importance recently, mainly in the modification of the material surface, because when modified the surface get different characteristics in comparison to the initial material. Changes are possible through functionalization, this process bring new features and properties to a material by changing the surface chemistry of the material, generating a novel material [1-3]. In this work we describe the functionalization of metallic oxides nanoparticles like titania and silica with a coupling agent, after the functionalization, the nanoparticles were dispersed in a medium of ethanol and acrylic acid, which acted as polymer matrix, later, coatings were casted onto glass substrates by aerospray technique. The nanocomposite was characterized by water contact angle, SEM, XPS and UV-VIS. We found that coatings are superhydrophilic, transparent and potentially useful for self-cleaning coatings.

Keywords: functionalization, nanoparticles, self-cleaning, nanocomposite, aerospray.

Thanks/Acknowledgement

The authors are greatful for the financial support of project CEMIESOL P21.

References

1. Catalina, C., et al., Nanocomposite acrylic paint with self cleaning action. J. Coat. Technol. Res., 2012. 9: p. 687-693.
2. J.Basu, B., et al., Effect of microstructure and surface roughness on the wettability of superhydrophobic sol-gel nanocomposite coatings. J. Sol-Gel Sci Technol, 2010. 56: p. 278-286.
3. Taurino, R., et al., Preparation of scratch resistant superhydrophobic hybrid coatings by sol-gel process. Progress in Organic Coatings, 2014. 77: p. 1635-1641.

P01.106-NAMA474

PHASE TRANSITION FROM THE PHOTONIC GLASS TO THE PHOTONIC CRYSTAL

A. Chumakov [1], A. Chumakova [2], A. Mistonov [3], I. Shishkin [2]
[1]ESRF - European Synchrotron - Grenoble (France), [2]Petersburg Nuclear Physics Institute NRC "Kurchatov Institute" - Gatchina (Russian federation), [3]Saint Petersburg State University - Saint Petersburg (Russian federation)

Today, the main method of photonic crystals formation is colloidal self-assembly, based on self-organization of colloidal particles into periodically ordered systems. To produce the photonic materials we have used for the first time a new method, which prototype is known in ceramic technology as slip casting. It has provided the systems consisting of monodisperse spherical particles with different extent of positional order, ranging from the photonic glass through structures with short-range order to photonic crystal. This order-disorder phase transition is affected by variation of different parameters of colloidal suspension and deposition time.

At the initial precipitation time the colloidal spheres form a disordered array. However, during the decreasing of suction rate of the solvent into gypseous sell, the grains with the close packing of the particles are formed. By scanning electron microscopy it was revealed that the grain consist of hexagonal ordered close packing layers. The average spheres diameter is 203 ± 5 nm. The thickness of the film depending of precipitation time has varied from 1 to 1.8 mm for different series of the samples. Typical diffraction patterns were obtained from the sample structure by the method of small-angle X-ray diffraction (BM26B “DUBBLE” and ID10, ESRF). During the experiment the chip sharp of the opal-like film was scanned along the thickness by the X-ray beam.

It has been found that the strong disorder structure was mainly produced at absorption rate of solvent $>10^{-3}$ ml/sec/cm^2, then as colloidal spheres begin to pack to polycrystall structure at the absorption rate $<10^{-4}$ ml/sec/cm^2. With increase the thickness of photonic crystal the phases of order revolve with each other (photonic glass → polycrystalline structure with short-range order → polycrystalline structure with long-range order). The crystallite size depends on the absorption rate and changes from 1,5 µm to 5,5 µm (depending on series samples). The ratio between the amorphous and the order parts of samples can be discribde in term of the Percus-Yevick model and is 5%.

It was reveled that the structure of the photonic glasses obtained by the new technology depends on the suction rate and changes from the disordered spheres array to polycrystalline structure. Using of proposed technology “slip casting” alloys to synthesize the photonic glass structure up to few millimeter of the thickness by large area and different forms.

Thanks/Acknowledgement

Authors acknowledge ESRF for hospitality and thank for support the Russian Foundation of Basic Research Grant No. 16-32-80107 "mol_ev_a".

NRG - Energy production and storage

P01.084-NRG065

IMPROVED GDOES DEPTH PROFILING OF CIGS SOLAR CELLS BY ADDING NITROGEN TO ARGON SPUTTER GAS

W. Hempel, W. Wischmann
Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg - Stuttgart (Germany)

Glow **D**ischarge **O**ptical **E**mission **S**pectroscopy (**GDOES**) is a practical tool for obtaining fast depth profile measurements. However, analysis of Cu(In,Ga)Se_2 (**CIGS**) films on Mo reveals some problems in depth resolution, especially at the interface between layers.

In this work, GDOES measurements performed with a mixture of 5% nitrogen in argon are compared with those using pure Argon as sputter gas. Addition of nitrogen shifts the sputter conditions to a reactive mode with the effect that the sputter rate of the metallic molybdenum back contact decreases by a factor of 10. Since the sputter rate of the compound semiconductor CIGS stays constant, the transition from the CIGS absorber to the molybdenum back contact can be recorded more smoothly. The intersection of the CIGS absorber to the molybdenum layer is recognizable by a kink in the graphs of composition ratios, so that difference of maximum and minimum of [Ga]/([Ga]+[In]) composition ratio can clearly be determined.

Furthermore, some artefacts, which were created by matrix effect, vanish because of the use of nitrogen in sputter gas. For example, the calculated [Cu]/([Ga]+[In]) composition ratio is constant over entire sample depth, while for regular measurement with argon a non-existant gradient occurs. A commonly present $MoSe_2$ layer can also be detected well in the Se/CIGS graph. Even the distribution of sodium in the Mo back contact can be better described when using this gas mixture.

Left figure: depth profile performed with argon as the sputter gas; Right figure: same sample measured with a mixture of nitrogen and argon.

Thanks/Acknowledgement

Support of the Federal Ministry for Economic Affairs and Energy and the State of Baden-Württemberg is gratefully acknowledged.

P01.085-NRG083

INSIGHT ON ULTRA-FAST LITHIUM ION TRANSPORTATION IN SUB-MICRON LITHIUM COBALT OXIDE SINGLE CRYSTAL-BASED CATHODES

T. Yamada [1], N. Zettsu [2], K. Teshima [2]

[1]Center for Energy and Environmental Science, Shinshu University - Nagano (Japan), [2]Center for Energy and Environmental Science & Faculty of Engineering, Shinshu University - Nagano (Japan)

Development of high-power density battery is one of important issues to manage high-performance energetic applications including electric vehicles, rescue robots, and so on. So far, a variety of studies focusing on active materials have been reported. For example, surface treatments and element dopings are dominant approaches because these techniques improved their conductivities. In addition, morphologic controls should be also effective since it is expected that conductivities of the materials depend on crystal facets. Lithium cobalt oxide, $LiCoO_2$ consists of LiO_2 layers and CoO_2 layers stacking along to *c* axis to crystallize as hexagonal system. For increase of bulk conductions, *ab* planes should be increased, though $LiCoO_2$ prefers to grow 001 face due to its lower surface energy than that of others. Recently, we grew submicron, low-aspect ratio $LiCoO_2$ crystals using flux method (abbreviate as flux grown $LiCoO_2$), which is one of liquid-phase crystal growth techniques, and the flux grown $LiCoO_2$ crystals exhibited good battery capacity even at 10 C rate[1] as active material in a half cell. In this study, we investigated the electrochemical and crystallographic characteristics of the flux grown $LiCoO_2$ crystals for development of high-power density batteries.

The flux grown $LiCoO_2$ crystals were grown as explained in the reference[1]. The electrochemical properties were investigated using half cells. Charge-discharge profiles at 4.2-2.5 V at 10 C rate exhibited capacity of *ca*. 115 $mAh\cdot g^{-1}$ for the flux grown $LiCoO_2$, which was slightly lower than *ca*. 120 $mAh\cdot g^{-1}$ of a reference sample, prepared by solid-state process. Post annealing of the flux grown $LiCoO_2$ crystals led an increase of the capacity up to *ca*. 130 $mAh\cdot g^{-1}$. It is suggested that the post annealing affected to remove inactive phases including Li_2CO_3 on $LiCoO_2$, which should be formed during flux growth process. The cycle performances were also investigated. After 40 cycles, the capacities faded down to *ca*. 25 % for the reference and *ca*. 70 % for the flux grown $LiCoO_2$ crystals of their initial capacities, respectively. These results suggest the use of the flux grown $LiCoO_2$ crystals at high rate is available.

In the presentation, we will discuss the electrochemical stability of the flux grown $LiCoO_2$ crystals in terms of morphologies, structure, and surficial states for further improvements to realize high capacity and high cycle ability.

Thanks/Acknowledgement

This work was supported by JST CREST Grant Number JPMJCR1322, Japan.

References

1. K. Teshima, et al., *Cryst. Growth Des.*, 2010, 10, 4471-4475.

P01.086-NRG084

APPLICATION OF ENERGY STORAGE MATERIALS USING SILICON SLUDGE GENERATED IN WAFER PROCESSING

D.S. Kil, H.D. Jang, H. Chang, J.H. Choi
Korea Institute of Geoscience & Mineral Resources(KIGAM) - Daejeon (Korea, republic of)

A large amount of silicon nanoparticles are generated during the slicing of silicon ingots into thin wafers for the fabrication of integrated-circuit chips and solar cells. This results in a significant loss of valuable materials at about 40% of the mass of ingots. In addition, a hazardous silicon sludge waste is produced containing largely debris of silicon, and silicon carbide, which is a common cutting material on the slicing saw. Efforts in material recovery from the sludge and recycling have been largely directed towards converting silicon or silicon carbide into other chemicals. Here, we report an aerosol-assisted method to extract silicon nanoparticles from such sludge wastes and their use in lithium ion battery applications. Using an ultrasonic spray-drying method, silicon nanoparticles can be directly recovered from the mixture with high efficiency. The yield of the recycled silicon was about 80% and metallic impurities were completely removed by acid treatment. Then, the as-recovered silicon was encapsulated by graphene and applied to anode material for Li ion batteries. The as-fabricated silicon-graphene composites showed very high performance as Li ion battery anodes in terms of capacity, cycling stability, and Coulombic efficiency.

Thanks/Acknowledgement

This work was supported by the R&D Center for Valuable Recycling, funded by the Ministry of Environment(Project No. 2016002220002)

References

1. Lin, Y. C., Wang, T. Y., Lan, C. W. & Tai, C. Y. Recovery of silicon powder from kerf loss slurry by centrifugation. Powder Technol. 200, 216–223 (2010)
2. Drouiche, N. et al. Recovery of solar grade silicon from kerf loss slurry waste. Renew Sust. Energ. Rev. 32, 936–943 (2014)
3. Jang, H. D., Kim, H., Kil, D. S. & Chang, H. A Novel Recovery of Silicon Nanoparticles from a Waste Silicon Sludge. J. Nanosci. Nanotechnol. 13, 2334–2338 (2013)

P01.087-NRG090

ELECTROCHEMICAL PROPERTIES OF SOME IONIC LIQUIDS

I. Bou Malham [1], R. Khalil [1], M. Azar [1], M. Turmine [2]
[1]Université Libanaise, Faculté des Sciences IV. Laboratoire Energétique et Réactivité à l'Echelle Nanométrique, Haouch El-Omara, Zahlé, Liban. - Zahlé (Lebanon), *[2]2. Sorbonne Universités, UPMC, Paris 06, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, 4, place Jussieu, 75005, Paris - Paris* (France)

In the paste several years, ionic liquids have attracted a fast-growing research interst as innovating solvents. This growth is explained in particular by the need of developing respectful processes of the environment [1].

In electrochemistry, ionic liquids are more used since they have, especially sufficient electric conductivity and large electrochemical window. The majority of ionic liquids has a very high viscosity, which strongly influences one of the principle steps of electrochemical processes, matter transport by diffusion of soluble products.

With the aim of using ionic liquids as electrolyte during the electrodeposition of nanostructured thin layers of zinc oxide (ZnO) [2,3], electrochemical studies, in particular the cyclic voltammetry and the electrochemical impedance spectroscopy (EIS), were realized for three hydophobic ionic liquids. Relevant physicochemical properties were studied, such as viscosity, density and diffusion coefficient of ferrocenemethenol (taken as redox probes) [4] in the three ionic liquids considered under various conditions. This work showed the effect of the length of alkyl chain of the cation on the electrochemical behavior of ionic liquids.

The objective of this work is to correlate the properties of the ionic liquids used with the nature of obtained films of zinc oxide.

Thanks/Acknowledgement

This work is partly supported by lebanese university research program. One of us (Rita KHALIL) is supported by a grant from the Lebanese University. All these sources of support are gratefully achnowledged.

References

1. Li,H. et al., Influence of alkyl chain length and ionion species on ionic liquid structure at the graphite interface as a function of applied potentien. J. Phys. Condens. Matter, 2014. 26(28): p. 284115.
2. Azaceta, E. et al., Electrochemical reduction of O_2 in 1-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ionic liquid containing Zn^{2+} cations: deposition of non-polar oriented ZnO nanocrystalline films. Physical Chemistry Physics, 2011. 13(29): p. 13433-13440.
3. Azaceta, E. et al., Electrochemical deposition of ZnO in a room temperature ionic liquid: 1-butyl-2-methypyrrolodinium bis (trifluoromethane sulfonyl) imide. Electrochemistry Communications, 2009. 11(11): p. 2184-2186.
4. Lovelock, K.R. et al., On the diffusion of ferrocenemethanol in room temperature ionic liquids: an electrochemical study. Phys Chem Chem Phys, 2011. 13(21): p. 10155-64

P01.088-NRG165

CORROSION STUDY OF IN-OPERANDO MONITORING SYSTEMS FOR WATER ELECTROLYSIS

I. Biswas, M. Schulze
German Aerospace Centre (DLR) - Stuttgart (Germany)

In the joint R&D project "In-situ Diagnostics in Water Electrolysers (INSIDE)", supported by the EU Fuel Cell and Hydrogen Joint Undertaking, an electrochemical in-situ diagnostics tool for the monitoring of locally resolved current densities in polymer electrolyte membrane fuel cells is adapted to three different water electrolysis technologies: based on proton exchange membranes (PEMWE), on anion exchange membranes (AEMWE), and alkaline water electrolysis (AE). The tools are carried out as modified printed circuit boards (PCB), attached to or replacing the bipolar plate in the electrolyser cell. A prototype for AEM is displayed in Fig. 1. In this work, the stability of the used PCBs under the electrochemical ambience of the three technologies was assessed.

Unsurprisingly, highly concentrated KOH lye used in AE holds the largest challenge to the materials. Copper areas obviously require a protective coating. More interestingly, the epoxy resin based PCB material itself is prone to a corrosion process, which is depending not only on the chemical conditions, but on the underwent potential. The analysis of pristine and aged PCB materials with infrared absorption spectroscopy in attenuated total reflection contact mode and photoemission spectroscopy show predominantly a surfacial hydrolysis of aliphatic ether and epoxy groups. (Fig. 2: 925 cm^{-1} and 1010 cm^{-1}), while aromatic compounds become more exposed to the surface upon aging.

Under the examined conditions, up to 30%wt of KOH at 70°C, the PCB was material showed sufficiently stable up to 2.0 Volts in preliminary corrosion tests.

P01.089-NRG344

NANO COATING OF PT ON THE CARBON BASED CATALYSTS FOR PEM FUEL CELLS

S. Khasl [1], S. Behjat [2], S. Khameneh Asl [3]

[1]University Of Tabriz - Tabriz (Iran, islamic republic of), [2]Oil and Petroleum University - Tehran (Iran, islamic republic of), [3]University of Tabriz - Tabriz (Iran, islamic republic of)

With increasing pollution and decrease in global reservoirs of fossil fuels, a lot of interest has been attracted to fuel cells as efficient and clean energy sources. Polymeric (membrane) fuel cells are special type of fuel cells, which can be built in small dimensions and power. These cells use hydrogen (and oxygen or air) and produce water. In these cells, platinum is used as electrode (and electrocatalyst) both in anode and cathode, due to its low overvoltage for both hydrogen and oxygen. To increase the efficiency of these coatings, it is best to produce platinum particles with maximum area and it automatically leads to nanometric particles. In this thesis, platinum particles are electrodeposited first on Floride doped Tin Oxide (FTO) and then on graphite. Electrodeposition is conducted via DC and pulse methods. Floride doped Tin Oxide (FTO) samples have been examined using voltametry in 0.5M H_2SO_4 and graphite samples have been examined in 0.5 M H_2SO_4 + 0.5 M CH_3OH. Specific area of platinum on Floride doped Tin Oxide (FTO) substrates has been calculated. In graphite substrates, comparative analysis has been performed. Prepared samples have been examined using scanning electron microscope. For Floride doped Tin Oxide (FTO) sample, AFM test has been performed to approve the results of SEM. According to results, Platinum particles with approximate diameter of 30 nanometers have been successfully coated on Floride doped Tin Oxide (FTO) and graphite.

References

S. Srinivasan, R. Mosdale, P. Stevens and C. Yang, "Fuel Cells: Reaching the Era of Clean and Efficient Power Generation in the Twenty-Frist Century," Annual Review of Energy Environment, 1999, pp. 20-25.

EG&G Technical Services Inc., in Fuel Cell Handbook, U.S. Department of Energy Office of Fossil Energy National Energy Technology Laboratory, 2005, pp. 15-45.

J. Larminie and A. Dicks, in Fuel Cell Systems Explaind, 2nd ed., Chichester, John Wiley, 2003, pp. 67-119.

G. Hoogers, in Fuel Cell Technology Handbook, CRC, 2003, pp. 137-160.

P01.090-NRG401

CHEMICO-PHYSICAL CHARACTERIZATION OF GRAPHENIZED POLYIMIDE FILM BY CO2 LASER WRITING FOR SUPERCAPACITOR APPLICATION

M. Fontana, A. Lamberti, F. Perrucci, M. Caprioli, M. Serrapede, S. Bianco, S. Ferrero, L. Scaltrito, E. Tresso

Politecnico di Torino, Department of Applied Science and Technology (DISAT), Corso Duca Degli Abruzzi, 24 - Torino (Italy)

Graphene-based materials have inspired great research interest in the field of supercapacitors for energy storage applications, since they provide high specific surface area coupled with good conductivity [1]. In recent years, laser-induced graphenization of polyimide has been proposed for obtaining graphene-based flexible supercapacitor devices [2] with the possibility of patterning the electrodes at the micrometer scale. Specifically, a CO2 infrared laser is exploited to break bonds between carbon, oxygen and nitrogen through photothermal effects, leading to the formation of a porous 3D structure of few-layer graphene which can be used as binder-free flexible supercapacitor electrode. Laser writing parameters are expected to influence the morphology and the physical-chemical properties of the laser-induced graphene (LIG), which in turn have a direct effect on the electrochemical performance. In this work, a pulsed CO2 laser working at 10.6 µm wavelength is used for the graphenization of commercial polyimide film. The influence of two process parameters (repetition frequency and scanning speed) on the chemico-physical properties of the LIG is investigated. Specifically, the material is characterized by electron microscopy, X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy and electrochemical measurements. At first, it is shown that by varying the process parameters three different characteristic morphologies can be obtained. Further characterization reveals that changes in morphology are accompanied by different chemical composition and quality of the graphenic structure. Great attention is devoted to XPS, since it provides surface-sensitive chemical information and allows for the investigation of the graphenic structure through signature features of the photoelectron spectrum. By coupling XPS with Raman spectroscopy, subtle differences between the three different kinds of LIG are highlighted, alongside interesting features such as nitrogen self-doping phenomenon [3]. Finally, the electrochemical performance of the samples for supercapacitor application is evaluated in test devices with a interdigitated electrode configuration.

References

[1] L.L. Zhang, R. Zhou, X.S. Zhao, J. Mater. Chem. 20 (2010) 5983.

[2] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E.L.G. Samuel, M.J. Yacaman, B.I. Yakobson, J.M. Tour, Nat. Commun. 5 (2014) 1–8.

[3] A. Lamberti, F. Perrucci, M. Caprioli, M. Serrapede, M. Fontana, S. Bianco, S. Ferrero, E. Tresso, Nanotechnology. 28 (2017) 174002.

P01.091-NRG412

SPONTANEOUS GENERATION OF INTERLAYERS IN OPVS WITH SILVER CATHODES USING ADDITIVES IN A P3HT:PCBM LAYER

U. Vogel [1], B. Shamieh [2], G. Frey [2]
[1]Helmholtz-Zentrum für Materialien und Energie - Berlin (Germany), [2]Technion - Israel Institute of Technology - Haifa (Israel)

A significant contribution to the performance improvement of organic photovoltaic (OPV) devices is due to the successful engineering of the metal/organic interface by introducing interlayers. We report a new efficient methodology for processing interlayers by the spontaneous segregation of additives to a silver cathode. The driving force for this special migration is the chemical interaction between the thiol end groups of the additives HEG-DT [Hexa(ethyleneglycol)-dithiol] and BDMT [1,4-Benzenedimethanethiol] and the thermally deposited Ag metal atoms, see Fig 1, 2. The additives were put in a blend of P3HT:PCBM [Poly(3-hexylthiophene-2,5-diyl) : Phenyl-C61-butyric acid methyl ester] onto PEDOT:PSS.

In addition, we report modification of the Ag work function at the interface and effectively increase the device Voc. Here we show that a spontaneously generated HEG-DT interlayer at the P3HT:PCBM/Ag interface increases the Voc by over 0.1 V and enhances the device efficiency by more than 76%, to ~3% PCE. The presence of the interlayer is confirmed by measuring the composition of the blend/Ag interface using XPS [1][2].

Thanks/Acknowledgement

This research was supported by a grant from GIF, the German Israeli Foundation for Scientific Research and Development, and is gratefully appreciated.

References

[1] B.Shamieh, S.Obuchovsky, G.L.Frey, J. Mater. Chem. C, 2016, 4, 1821-1828
[2] I.Deckman, S.Obuchovsky, M.Moshonov, G.L.Frey, Langmuir, 2015, 31, 6721-6728

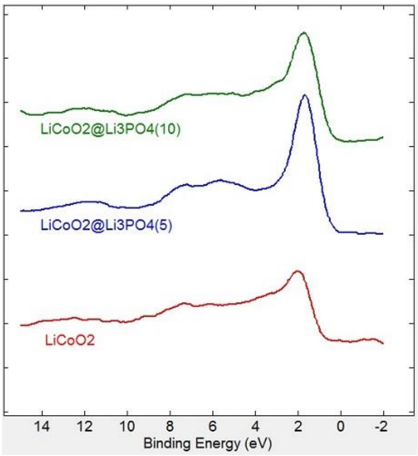
P01.108-NRG471

LI-ION POWDERS SURFACE MODIFICATION FOR CYCLING LIFE EXTENSION. STRUCTURAL AND SURFACE CHEMISTRY STUDY

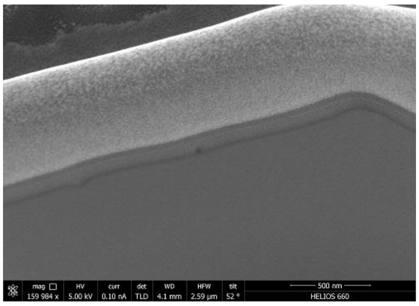
A. Rashkovskiy [1], M. Zakharkin [2], E. Sokolova [2]
[1]Systems for microscopy and analysis - Moscow (Russian federation), [2]Skolkovo Institute for Science and Technology - Moscow (Russian federation)

Lithium-ion batteries are currently prospective devices due to their characteristics of high energy density, light weight and portability. However, during charge-discharge cycles side reactions are observed on the surface of the cathode materials, which reduces the device efficiency. Extension of Li-ion batteries lifetime during several thousand charge-discharge cycles is a significant direction of modern material science for microelectronics. The promising solution is surface modification of cathode materials, as an important method to improve electrochemical characteristics.

In this study the impact of surface modification of several Li-Me-O electrode materials on the kinetics of electrode processes has been investigated in order to develop a standard control techniques of electrochemical characteristics. As an example of modified cathode surfaces, $LiCoO_2$ particles coated with $AlPO_4$ and Li_3PO_4 have been explored by means of various experimental techniques: transmission electron microscopy (TEM), scanning electron microscopy (SEM) with focused ion beam (FIB) and X-ray photoelectron spectroscopy (XPS).



It was shown by Valence Band XPS (Fig.1), that modification of $LiCoO_2$ by Al phosphate leads to increasing of electronic conductivity of mentioned material. Also the results of cycled Li-ion batteries material surface chemistry testing are presented. The influence of cyclyng on surface chemistry and electronic conductivity of anode material in terms of XPS and FIB/SEM (Fig.2) analysis was shown.



Due to the identification of the dependency of the electrochemical parameters on the characteristics of the surface modifications the forecasting technique of novel battery materials life time is discussed.

OXI - Oxides

P02.014-OXI116

CHARGED POINT DEFECTS IN NICKEL-OXYGEN BINARY SYSTEMS FROM REAXFF ATOMISTIC CALCULATIONS

O. Politano [1], K. Payen [2], A. Chartier [2]
[1]*Laboratoire ICB, Université de Bourgogne Franche-Comté - Dijon* (France), [2]*DEN/DPC/SCCME/LM2T, CEA-Saclay - Gif Sur Yvette* (France)

In nuclear plants, the oxidation process of the alloy 690 releases nickel atoms in the primary water circuit. Subsequently, its activation by irradiation produces 58Co, which is a radio-toxic element and constitutes a major industrial issue. It is known that this corrosion process is driven by the ionic/cationic diffusion through a continuous (Ni,Fe)Cr2O4 spinel corrosion layer and controlled by the oxygen partial pressure [1]. However, the Dieckmann diffusion model is still incomplete as it limits itself to cations only in bulk oxides. Therefore, we are developing an atomistic modeling approach to study the cationic diffusion in the (Ni,Fe)Cr2O4 spinel including oxygen contribution and also grain boundary effects. We use the empirical ReaxFF force field developed by A. Van Duin [2]. This force field allows charge transfers between atoms and it reproduces more accurately than non-reactive force fields the bond making and bond breaking. This opens the opportunity to access for example charged point defects and subsequently Brouwer diagrams, i.e. the concentration of point defects as a function of the oxygen partial pressure.

We are presenting herein the first steps of this study on the nickel-oxygen binary system. Firstly, we calculated the physical properties of different nickel oxide compounds (NiO, Ni2O, NiO2, Ni2O3, Ni3O4 …). These oxides were chosen in order to serve as references and also to cover much of the formal oxidation states of nickel that may occur during its oxidation. The evolution of the calculated charges of nickel and oxygen atoms will be commented and then used as references for the charged point defects. Secondly, we calculated the formation energies of vacancies and interstitials in NiO in different charge states in order to draw the Brouwer diagram. Charge polarization and formation energies are analyzed in light of the reference states mentioned above. Results are compared with available theoretical and experimental data.

References

[1] R. Dieckmann, J. Phys. Chem. Solids 59 (1998) 507.

[2] C. Zou, Y. K. Shin, A. C. T. van Duin, H. Fang, Z. Lui, Acta Mater. 83 (2015) 102.

P02.015-OXI126

XPS ANALYSIS OF METAL/OXIDE PILE AND CORRELATION BETWEEN BINDING ENERGY SHIFT AND CORRELATION BETWEEN BINDING ENERGY SHIFT AND ELECTRICAL PROPERTIES

C. Fontaine [1], B. Pelissier [2], T. Chevolleau [2], M. Gros-Jean [3]

[1]Stmicroelectronics, Laboratoire des technologies de la microélectronique (LTM), Université Grenoble Alpes - Crolles (France), *[2]LTM, Univ. Grenoble Alpes - Grenoble* (France), *[3]Stmicroelectronics - Grenoble* (France)

In order to decrease leakage current in gate transistors[1], high permittivity dielectrics associated with metal gates have been introduced. This stack comes however with carriers' mobility degradation and poorer control of the threshold voltage, generally due to vacancies[2], inducing the creation of charges or dipoles. It is though necessary to control, and first characterize, these charges.

This study attempts to solve this problematic using the XPS technique. Actually, by taking into account presence of charges in a HKMG pile, electrostatic potential variations appears, so the kinetic energy of electrons going through these charges is modified. Consequently, a shift in the XPS spectra obtained appears.

In this study, we focus on a stack composed of a 300mm silicium substrate, a thin layer of SiO_2, a HfO_2 high permittivity dielectric layer and a TiN metal gate. If we consider a potential difference in the SiO_2/HfO_2 stack, the Silicium electrons see their binding energy modified whereas the Titanium electrons aren't shifted, because they don't cross the dipole.

Thanks to analysis made in high reproductibility conditions with a clean room "in line" spectrometer, and by comparing samples to a reference, we highlight difference between the binding energy of silicium and titanium, which directly impact transistors' electrical properties.
Furthermore, the TiN reference potential used is highly reliable thanks to the TiN deposition on the whole 300 mm surface, permitting the dilution of parasite electrons.

The effect of different process parameters associated with some reproductibility tests will be shown here, these results will be match with some electrical results obtained by Cocos(Corona oxide characterization of semiconductor), and it will be presented that the physical-chemical effects, such as the regrowth of interfacial oxide, can be uncorrelated from the impact of charges.

References

[1]G.Wilk, Applied Physics Letters, vol.89, 2001.

[2]S.Ferrari, Journal of Applied Physics, vol.96, 2004

P02.016-OXI288

ELECTRONIC STRUCTURE AND PHASE COMPOSITION OF TIN-OXYGEN SYSTEM SURFACES AND INTERFACES BY XANES SN M4,5 SYNCHROTRON SPECTRA AND AB INITIO MODELING

D. Koyuda, M. Manyakin, S. Kurganskii, O. Dubrovskii, O. Chuvenkova, E. Domashevskaya, S. Ryabtsev, S. Turishchev
Voronezh State University - Voronezh (Russian federation)

Tin dioxide is a well-known material wide-spreaded for the modern technologies. Nanotechnology progress resulted in the critical influence of surface composition on properties of many newly synthesized materials. Phase and chemical composition of surface layers can substantially differ from bulk composition of a material, that is why it is necessary to use surface sensitive techniques to study them, e.g. X-ray absorption near-edge structure spectroscopy (XANES), that implies using of highly intensive synchrotron radiation. XANES relative to Sn $M_{4,5}$ edge (density of p- and f-electronic states in the conduction band) for tin metallic foil, bulk SnO and SnO_2 oxides and tin oxide nanolayers have been obtained while same XANES for single crystalline Sn, SnO, SnO_2(O) and SnO_2(T) have been ab-initio calculated [1].

Analysis of the experimental XANES results was performed by linear combination fitting (LCF) of the calculated spectra. According to the LCF, an experimental X-ray absorption spectrum of an object with unknown phase composition can be represented as a linear combination of the known reference spectra of phases this object includes. Contribution of every reference spectrum to resulting model spectrum equals to relative weight of a component in a sample. The results of such linear combination of the calculated SnO and SnO_2(T) spectra with different weight coefficients (with 10% increment) are shown in Figure. These results are of substantial interest both from theoretical and practical points of view, and may be used for diagnostics of the wide range of nanostructured tin oxides.

Figure. The weighted sums of the calculated SnO and SnO_2(T) spectra.

Thanks/Acknowledgement

The study was funded by the Ministry of Education and Science of Russia in frameworks of state task for higher education organizations in science for 2017-2019, Project N 16.8158.2017/BCh and RFBR according to research projects № 16-42-360612 p_a (with government of Voronezh region), 16-32-00860 mol_a.

References

[1] M.D. Manyakin et. al. Computational Materials Science. 2016. V.121. p.119.

P02.017-OXI355

ELUCIDATING THE TARGET VOLTAGE BEHAVIOUR DURING REACTIVE MAGNETRON SPUTTERING: AN IN-VACUUM XPS STUDY OF THE OXIDE FORMATION ON THE TARGET SURFACE

R. Schelfhout, K. Strijckmans, D. Depla
Research group DRAFT, Department of Solid State Sciences, Ghent University - Ghent (Belgium)

Reactive DC magnetron sputtering is a common technique to deposit compound films. Using an elemental metal target, the film composition on the substrate can be changed by controlling the reactive gas flow. The interaction between the metallic atoms of the target and the reactive gas is however not restricted to the substrate, but also on the target surface leading to 'target poisoning'. This reaction results in the well-known hysteresis effect in the target voltage as a function of reactive gas flow. Remarkably, based on this hysteresis behaviour, two groups of metals can be distinguished[1]. In a first group containing aluminium and yttrium, the discharge voltage decreases when the target goes into poisoning. Whereas for the second group containing tantalum and titanium, the opposite occurs.

Up till now, no experimentally vouched explanation was given for this behaviour. In this study, we examined the target surface using in-vacuum X-ray photoelectron spectroscopy (XPS). It was found that the metals of the second group have substoichiometric compound residing on the surface, in contrast to the metals of the first group. Its origin can be explained within the framework of the noted Reactive Sputter Deposition model[2]. Moreover, its consequences on the hysteresis effect are discussed.

Thanks/Acknowledgement

The financial support by the FWO-Flanders is acknowledged.

References

[1] Depla et al. J. of Appl. Phys. 101, 013301 (2007)
[2] Depla et al. J. of Phys. D: Applied Physics 40 (2007)

P02.018-OXI358

DEPTH PROFILING OF TAOX FILM BY USING AR GAS CLUSTER ION BEAM

A. Kim, S. Hong, K.J. Kim
Korea Research Institute of Science and Standards - Daejeon (Korea, republic of)

The use of cluster primary ions in X-ray photoelectron spectroscopy (XPS) has provided a step change in the capability of XPS for depth profiles of metal oxide thin films with reduced preferential sputtering and organic depth profiles without inducing severe surface topography or chemical damage. In particular, the preferential sputtering of oxygen in TaO_x film after monoatomic Ar+ ion beam bombardment has been observed even at 200 eV of the reduced Ar^+ energy[1]. The TaO_x film showed good resistive switching performance due to oxygen vacancy in the film, resulting in the TaO_x-based nonvolatile resistive random access memory (RRAM) device. Therefore, the quantitative analysis of TaO_x film is very important in terms of the verification of resistive switching performance. The preferential sputtering of oxygen in TaO_x film easily occurs during depth profiling of TaO_x film by using monoatomic Ar^+ ion. In order to reduce the preferential sputtering, Grilli et al. utilized Ar^{n+} gas cluster ion beam (GCIB) instead of the monoatomic Ar^+ ion and compared the preferential sputtering of Ta_2O_5 at different energies of Ar GCIB. They found that the preferential sputtering of Ta_2O_5 could be reduced by a half or one third by using the cluster ion beam. However, further development is needed to establish optimum balance between good sputter rate and sputter induced damage. In this study, we investigate the effect of oxygen flooding during the depth profiling of Ta_2O_5 and TaO_x films using Ar GCIB. Furthermore, we present the effect of Ar GCIB energy on the preferential sputtering.

References

[1] R. Grilli, R. Simpson, C.F. Mallinson, M. A. Baker, Surf. Sci. Spectra, 21, p50 (2014)

[2] R. Grilli, R. Simpson, C.F. Mallinson, M. A. Baker, Surf. Sci. Spectra, 21, p68 (2014)

POL - Polymers

P02.019-POL036

SURFACE ANALYSIS USING SILVER DEPOSITION SURFACE-ASSISTED LASER DESORPTION/IONIZATION IMAGING MASS SPECTROMETRY.

T. Satoh [1], M. Shima [1], H. Niimi [1], N. Kikuchi [1], M. Fujii [2], T. Seki [3], J. Matsuo [3]
[1]JEOL Ltd - Akishima (Japan), [2]Yokohama National Univ. - Yokohama (Japan), [3]Kyoto Univ. - Uji (Japan)

The matrix-assisted laser desorption/ionization imaging mass spectrometry (MALDI-IMS) has an advantage in organic compounds analysis due to an ability of analyzing molecular structure. MALDI-IMS has been widely applied to biological studies. MALDI-MS is considered to be a powerful tool for synthetic polymer and additive analyses; however, MALDI-IMS in industrial applications is still limited. There are two issues for applying the MALDI-IMS to surface analytical tools, i) lateral resolution depend on sample preparation methods and ii) the probing depth is rarely discussed. For the surface sensitive analysis, solvent-free sample preparations can be preferred because of not changing the surface composition. These methods can be used to control the sizes of the matrix crystals, and can produce crystal layers that are 1–10 µm thick. Another ionization technique used for IMS is surface-assisted laser/desorption ionization (SALDI). In this study, we investigated the lateral resolution and probing depth using solvent-free silver nanoparticle(Ag-NP) SALDI-IMS. The Ag-NP homogeneously distributed in 10-nm-thick on sample surface will be expected to improve the IMS results.

We constructed a thin film with two layers by coating the IRGANOX^{TM}1010(BASF SE) on a polystyrene (PS) or an IRGANOX^{TM}3114(BASF SE) layer. Ag-NPs were homogenously distributed by vacuum deposition to form a 10-nm-thick layer. The probing depth and lateral resolution of the solvent-free Ag-NP SALDI-IMS was investigated using various thicknesses of IRGANOX1010 layer. Mass spectra were acquired using a high-mass resolution MALDI time-of-flight mass spectrometer (JMS-S3000, JEOL Ltd.) with spiral ion trajectory. The diameter of laser spot was adjusted to 20 µm.

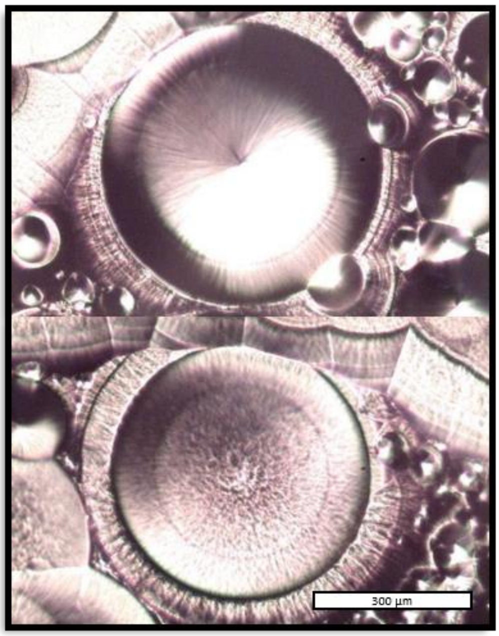
Ag adduct ions of IRGANOX1010, IRGANOX3114 and PS repeating structures appeared in the mass spectrum, which showed that Ag-NPs on the sample surface enhanced the ionization efficiency by functioning as cationization agents. At the lateral resolution of this method (20 µm), complementary grid patterns (55 lines per inch) of IRGANOX1010 on the bottom layer (PS or IRGANOX3114) were observed. The probing depth was investigated with IRGANOX1010 layers of different thicknesses, the detection of silver adduct ions from bottom layer indicated Ag-NP SALDI could ionize the bottom layer beyond the IRGANOX1010 layer. The probing depth was 50–100 nm for 10-nm-thick Ag-NP SALDI.

P02.083-POL464

TEMPLATE INDUCED POLYMER MELT CRYSTALLIZATION OF POLYPROPYLENE INVESTIGATED BY RAMAN MICROSCOPY

T. De Los Arcos, S. Waschke, G. Grundmeier
University of Paderborn - Paderborn (Germany)

The crystallinity of isotactic polypropylene formed from the melt on flat silicon substrates with different surface characteristics has been investigated by confocal Raman spectroscopy. The silicon templates were covered with self-assembled monolayers of three different organosilanes (–CH3, –CF3 and -phenyl terminal group) leading to different surface chemistry and different surface energies. The crystallization of polypropylene could be therefore investigated as function of substrate surface chemistry as the only differentiating parameter. After crystallization, the polymer interface is dominated by the formation of spherulites in two well differentiated size ranges: smaller spherulites with diameters up to 50 µm and larger spherulites within an approximate size range between 300 and 600 µm. From the morphological point of view, two different kind of spherulites were identified in the images: the most common shows a radial structure growing from a central point of crystallization; the second kind does not possess the central crystallization point and have a homogeneous appearance. Raman depth slicing was performed on spherulites of both types as function of the substrate chemical termination. The influence of the surface chemistry in the interface on the crystallization of the polypropylene is discussed with regard to crystallization theories.



Thanks/Acknowledgement

We acknowledge the support of the German Research Foundation (DFG) within the framework of the Transregional Collaborative Research Center TRR 87/1 (SFB-TR 87) “Pulsed high power plasmas for the synthesis of nanostructured functional layers”.

P02.084-POL470

ANALYSIS OF PROTEIN ADSORPTION ON PDMAEMA POLYMER BRUSHES: A TOF-SIMS STUDY

N. Hartmann [1], M. Thomas [2], U. Hagemann [1], S. Franzka [1], M. Ulbricht [2]

[1]Interdisciplinary Center for Analytics on the Nanoscale (ICAN), University of Duisburg-Essen - Duisburg (Germany), *[2]Department of Chemistry, University of Duisburg-Essen - Essen* (Germany)

Stimuli-responsive polymers are used in a wide range of applications, e.g. as self-cleaning coatings, in drug delivery devices, responsive membranes and sensors. Via controlled reaction schemes, i.e. atom transfer radical polymerization (ATRP), ultrathin surface-grafted brushes of stimuli-responsive polymers with thicknesses below 100 nm can be synthesized. The coatings rapidly respond to changes of external stimuli, such as temperature, pH, salt concentrations or proteins [1-2]. Reversible switching takes place on a milli-/microsecond time scale [1]. This establishes a pathway towards miniaturized smart devices with unprecedented functionalities.

Tailoring of stimuli-responsive polymer brushes for bioapplications requires a fundamental knowledge of their interaction with proteins and other relevant biomolecules. In this study TOF-SIMS has been employed in order to i) determine the relative density of initiator groups of silane monolayers which serve as reactive platforms for the subsequent growth of PDMAEMA (Poly(N,N-dimethylaminoethyl methacrylate)) brushes via ATRP, ii) characterize PDMAEMA brushes with varying grafting density (polymer chains per unit area) and iii) reveal the adsorption of bovine serum albumin (BSA) on and in such brush layers. This approach takes advantage of the inherent high sensitivity of TOF-SIMS for monolayer-, protein- and polymer-specific molecular fragments. An argon gas cluster ion source is used for controlled depth profiling of the organic coating. The experiments are complemented by measurements using XPS, AFM and fluorescence spectroscopy.

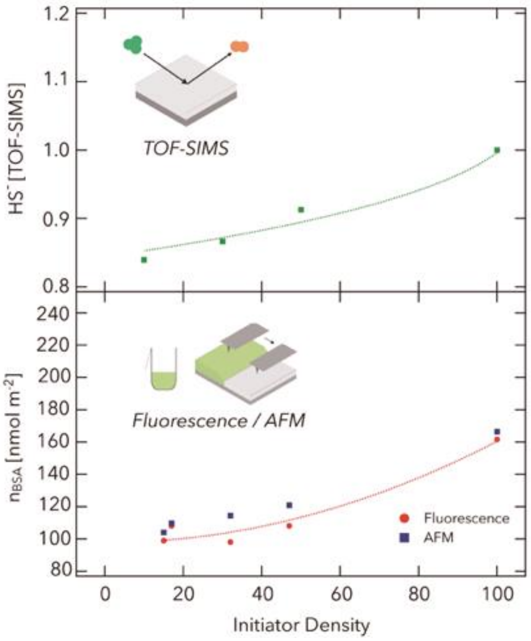


Figure 1 displays the relative and absolute protein uptake depending on the initiator group density as determined by TOF-SIMS, AFM and flourescence spectroscopy. The results shed light on the dependence of the penetration and adsorption of proteins in polymer brushes with varying grafting density.

Thanks/Acknowledgement

We gratefully acknowledge financial support by the German Science Foundation (Grant HA 2769/7-1) and the Professor Werdelmann foundation.

References

[1] Amiri Naini, C.; Franzka, S.; Frost, S.; Ulbricht, M.; Hartmann, N. Probing the Intrinsic Switching Kinetics of Ultrathin Thermoresponsive Polymer Brushes. Angew. Chem. Int. Ed. 2011, 50, 4513–4516

[2] Thomas, M.; Gajda, M.; Amiri Naini, C.; Franzka, S.; Ulbricht, M.; Hartmann, N.; Poly(N,N-dimethylaminoethyl methacrylate) Brushes: pH-dependent switching kinetics of a surface-grafted thermoresponsive polyelectrolyte, Langmuir 2015, 31, 13426–13432.

SLI - Solid-liquid interface

P02.025-SLI057

A NEW DIMENSION ADDED TO XPS SYSTEM TO BETTER CHARACTERIZE LIQUID METAL-SOLID-GAS INTERACTIONS.

M-J. Cornu, A. Koltsov, J. Scheid
ArcelorMittal Research - Maizières-Lès-Metz (France)

The understanding of high temperature reactions between solids, liquid metal and gas environment is limited by the lack of a suitable experimental set-up coupled to surface characterization equipment. Ex-situ transfers at low temperature between annealing furnace, wettability device and analytical tools induce noticeable changes of surface composition distinct from the reality of phenomena. So, our X-Ray Photoelectron Spectroscopy (XPS) tool is directly connected to a High Temperature Wettability Device (HTWD) in order to characterize chemical reaction without air contact to avoid any contamination and especially oxidation of samples surfaces.

This device was designed in order to allow measurements of previously inaccessible gas/steel surface and liquid metal/steel surface reactions at high temperature (up to 1000°C).

This device consists of two connected reactors (see figure below) respectively dedicated to the annealing treatments (infra-red lamp furnace) and wettability measurements (sessile or dispensed drop configurations with different kinetic energies). The spreading of drops is followed by high speed CCD video-camera at 500-1000 frames/s in order to reach information at very low contact time.

This experimental set-up works in a well-controlled atmosphere mainly designed to reproduce wettability phenomena occurring on steel surface after the recrystallization annealing and highlights the contact of the solid surface with liquid metal.

It will be particularly useful to understand and to improve the coatability of Advanced High Strength Steels (AHSS), as well as for development of new zinc coatings.

First trials simulating the galvanization of polished pure Fe sample will be presented and as well as drop spreading kinetics and surface characterization of the interfacial layer formed after reaction.

Figure 1: General view of the High Temperature Wetting Device (HTWD) with the wetting chamber (yellow), heating part (pink) and the connection at the XPS prep-chamber (left).

P02.026-SLI089

IN-SITU STUDY OF THE FIRST STEP'S OF COPPER OXIDE FORMATION ON CU (110) ELECTRODE SURFACE

R. Sharif [1], J. Duchoslav [2], S. Vazquez Miranda [3], K. Hingerl [1], C. Cobet [1]

[1]Center for Surface- and Nanoanalytics (ZONA), Johannes Kepler University - Linz (Austria), *[2]Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH (CEST) - Wiener Neustadt* (Austria), *[3]Instituto de Investigación en Comunicación Óptica, Universidad Autónoma de San Luis Potosí (UASLP) - San Luis Potosí* (Mexico)

Copper corrosion and oxidation as well as oxygen adsorption process on single crystal copper surface in UHV have been studied systematically [1]. Recently the electrochemical behavior of copper and the oxide development in alkaline media have been extensively studied [2]. However, due to the complexity of the solid-liquid interface [3], the mechanism of the first steps of copper oxide formation in acidic solution electrochemical environment are not completely understood.

In this work, we study the anodic oxidation of Cu (110) single crystal in $HClO_4$, with the pH series of 1, 1.5, 2.5, 3 and 4 acidic solutions under condition of Oxygen Reduction Reaction (ORR) with Cyclic Voltammetry (CV), in which the integrated charge and ion-exchange is measured. Additionally, we used highly surface-sensitive in-situ Reflection Anisotropy Spectroscopy (RAS) to monitor the reaction processes based on the specific optical respond of the oxide adlayer. The composition of the layers has also been studied qualitatively and quantitatively with chemical and surface analytical methods such as X-ray Photoelectron Spectroscopy (XPS) at the emersed sample. As shown in the CV for pH 2.5 (Fig.1), oxide adsorption/desorption peaks are present around -550mv/-600mv. The oxidation was then investigated by comparing the XPS measurement at two defined potentials: one before -550mv and another after -550mv, referring to the pristine Cu metal and copper surface after first oxidation step, respectively. The transition of Cu metal to Cu(I) as a Cu_2O formation is confirmed as a stable sub-monolayer, with the absence of Cu(II). Our first series results provide already additional insight into the oxidation of Cu(110) in the acidic electrochemical environment.

Keywords: Cu (110), XPS, RAS, CV, oxidation, electrochemistry

References

[1] L.D. Sun, P. Zeppenfeld. et al., Surface Science 602 (2008) L1–L4.

[2] J. Kunze et al., Journal of Electroanalytical Chemistry (2003) 554–555.

[3] G. Barati, C. Cobet, et al., Langmuir 30 (2014) 14486–14493.

P02.027-SLI101

EXTERNAL RBS ANALYSIS SETUP AT UNIVERSITY OF GÖTTINGEN : RBS ANALYSIS FOR LIQUID SAMPLES

M. Saito [1], K. Holm [2], H. Hofsäss [2]

[1]Toray Research Center Inc. - Shiga (Japan), [2]Georg-August-Universität Göttingen - Göttingen (Germany)

Rutherford Backscattering Spectrometry (RBS) is widely used to acquire compositional depth information of surface with high accuracy. Thanks to the high energy of the incident beam, the probe can be extracted to air. However, RBS is usually performed in vacuum condition, because of the energy straggling produced by the exit window and the ion path in air. With this difficulty, only a few groups have published so far about in-air RBS analysis [1, 2]. In this work, we report a recent development of external RBS analysis at University of Göttingen.

2.6 MeV H^+ beam is extracted to air though 200 nm SiN film, which is commercially available for transmission electron microscopy. The ions are irradiated to the sample surface, and backscattered ions are detected by a surface barrier detector, whose scattering angle is set to be 155°. The detector is placed in a vacuum housing with 100 nm SiN window. The irradiation is conducted under He flow atmosphere, to minimize the energy loss, energy straggling and angular straggling.

Figure 1 shows a RBS spectrum of TiON film on a glass substrate, acquired with external beam. The experimental data was fitted with SIMNRA code [3]. The energy resolution evaluated from the analysis is 17 keV, which is equivalent with that of a spectrum obtained in vacuum, considering the energy resolution of the detector and the energy loss of H^+ in the material.

With this instrument of external RBS analysis we can acquire a spectrum of volatile liquid samples. Since RBS can give us depth information, it will open a way to characterize compositional depth profile around solid / liquid interface. The challenge to analyze solid / liquid interface will be presented at the conference.

References

[1] F. Mathis, B. Moignard, L. Pichon, O. Dubreuil, J. Salomon, Nucl. Instr. and Meth. B 240 (2005) 532.

[2] T. F. Silva, N. Added, M. V. Moro, G. F. Trindade, H. C. Santos, C. L. Rodrigues, M. A. Rizzutto, M. H. Tabacniks, AIP Conf. Proc. 1625 (2014) 120.

[3] M. Mayer, SIMNRA User's Guide, ed. R.I. 9/113, 1997, Garshing, Germany: Max-Planck-Institut für Plasmaphysik.

P02.028-SLI164

WETTABILITY CHARACTERIZATIONS OF ELECTRONIC CARDS

A. Le Roy [1], M. Makarov [2], C. Plouzeau [2], M. Turmine [3], V. Vivier [3]

[1]Sorbonne Universités, UPMC Univ Paris 6 - LISE - Groupe Renault-Nissan, Technocentre Renault - Paris (France), [2]Groupe Renault-Nissan, Technocentre Renault - Guyancourt (France), [3]Sorbonne Universités, UPMC Univ Paris 6 - LISE - Paris (France)

One of the critical issue in the automotive industry is the electronic reliability of Printed Circuit Board (PCB). For these materials, three parameters are responsible for an accelerate aging: the electric bias, the ionic release and the dew formation[1]. To understand the formation of the water layer, it is critical to characterize the substrate surface, in terms of structure and chemical composition of the surface and in particular the wettability respect to water. The PCB composition may differ from one provider to the other, however it is always made of a multi-layer material that consisted in epoxy resin, fiber glass and finally a layer of copper whom are laminate together[2]. Copper current collectors are then engraving and the whole surface shows a non-negligible porosity.

In this study, we performed the characterization of different PCB substrates by measuring the contact angle of a glycerol drop. This nonvolatile solvent permits to reach the equilibrium avoiding the solvent evaporation. We set down 56 glycerol drops of 2 µL in order to make a statistic studies. These measures allow distinguishing different nature of PCB's substrates as shown in Figure 1, representing the dispersion of the number of measures in an interval I (of 5°) per the total number of measures in % against the contact angle values given for this interval. It highlights a difference in surface state that are ascribed to structure and/or chemical composition changes. Comparing contact angle measurements to SEM analyses, we can conclude that these changes in wettability were mainly due to the chemical composition of the PCB.

[1] U. Rathinavelu, M.S. Jellesen, P. Møller, R. Ambat, Effect of no-clean flux residues on the performance of acrylic conformal coating in aggressive environments. IEEE transactions on components, packaging and manufacturing technology, 2, (2012). 719-728

[2] R.S. Khandpur, Printed circuit boards design fabrication assembly and testing. The McGraw-Hill Companies, (2006). 1.4.3 33-34

P02.030-SLI335

SURFACE WETTABILITY AND HYDROLYTIC AGEING PROPERTIES OF SILICATES TREATED WITH 3-AMINOPROPYLSILANE COUPLING AGENT AND PHENOL-UREA-FORMALDEHYDE BINDER

D. Okhrimenko [1], A. Budi [1], M. Ceccato [1], D. Johansson [2], D. Lybye [2], K. Bechgaard [1], S. Stipp [1]

[1]*Nano-Science Center, Department of Chemistry, University of Copenhagen - Copenhagen* (Denmark), [2]*ROCKWOOL International A/S - Hedehusene* (Denmark)

Phenol-urea-formaldehyde (PUF) binder and 3-aminopropylsilane (APS) are widely used simultaneously for creating mechanical strength in silica or silicate based materials, such as glass or mineral fiber composites. When such materials are subjected to high humidity and temperature, their mechanical strength suffers from PUF and APS detachment from the material surface caused by temperature accelerated hydrolysis. Therefore, better understanding of the hydrolytic stability of APS and PUF layers is needed to prevent material properties degradation.

The ability of water to adsorb and react with the surface is controlled by the surface energy of the solid and its wettability. In this work, we investigated the solid surface energy, γ_S, and the wettability of pure and APS treated silica wafers and the complex silicate surfaces used in industry (mineral fibers and fiber melt wafers), using contact angle and vapour adsorption techniques. We also compared their wettability properties with similar industrial mineral fiber samples containing hydrophobization agent (mineral oil) and PUF binder. The hydrolytic stability of APS and PUF was studied during ageing in a wide range of relative humidity (RH) and temperature, reflecting industry tests and storage conditions.

Wafer and mineral fiber material ageing was monitored with X-ray photoelectron spectroscopy (XPS) and streaming potential. Results from ab initio molecular dynamics simulations helped to clarify the effect of temperature and humidity on the ageing process. Our results demonstrated that APS and PUF, deposited on the silicate surface, significantly decrease surface energy but water adsorption is still high enough to facilitate ageing. APS layers are unstable at temperature >50 °C and RH >75%. PUF binder degrades at humidity >55% RH. Adsorption of water and surface energy are lower and material stability is higher when a hydrophobization agent is applied to the APS treated surface. There is a direct correlation between wettability and stability of APS and PUF treated materials. This information is useful for hydrophobization optimization of composite mineral fiber materials.

P02.031-SLI389

THE ROLE OF ADVENTITIOUS ORGANIC MATERIAL AND SOLUTION SALINITY IN THE WETTABILITY PROPERTIES OF ALUMINOSILICATES (K-FELDSPAR)

M. Ceccato [1], B. Lorenz [1], M. P. Andersson [1], S. Dobberschütz [1], J.D. Rodriguez-Blanco [2], K.N. Dalby [1], T. Hassenkam [1], S.L.S. Stipp [1]

[1]Department of Chemistry, University of Copenhagen - Copenhagen (Denmark), [2]Department of Geology, Trinity College Dublin - Dublin (Ireland)

Among the many factors that are thought to control the oil recovery rates during low salinity flooding of sandstone reservoirs, the wettability of the minerals that make the pore surfaces is reported to control the low salinity (LS) effect. In contrast to quartz and clays, surface composition and wettability of feldspar has not yet been systematically investigated, even though feldspar is a major component of sedimentary rocks. In this study, we determined how the wettability and surface charge of K-feldspar, namely perthitic microcline, respond to various salinity solutions, with respect to its interaction with oil model components, in order to predict its reservoir behavior.

We investigated the K-feldspar surfaces with X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The AFM force mapping was made with tips functionalized with acidic and nonpolar components, so as to cover the polarity spectrum of oil components present in reservoirs. We discovered a reproducible and reversible change in adhesion when sea water is replaced with low salinity solutions. This translates directly into wettability modification of the mineral surface, where both oil-like acidic and aliphatic components stick less to the feldspar surfaces in low salinity solutions. The results can be explained using density functional theory (DFT) calculations, through an increase of electric double layer repulsion and a minor contribution of ion bridging. We also observed a thin layer of adventitious organic carbon on the mineral surface after exposure to air, which can affect the interaction characteristics of the surface. The molecular structure and distribution of the organic layer were monitored with angle resolved XPS (ARXPS), which showed that the main component of the C1s peak is C-H/C-C bonds. However, the presence of carboxylate groups at the interface of the mineral surface, demonstrated that oxygen-bearing organic molecules are located in the innermost part of the adsorbed organic layer, nearest the mineral surface.

These results provide insight into the interaction between any organic compound and K-feldspar, where wettability characteristics change as a function of solution composition, the type of oil and the properties of the pore surface, and where the presence of adventitious organic material must be considered.

P02.085-SLI462

WATER ADSORPTION ON A SURFACE OF POLAR DIELECTRICS

E. Yakushkin

Institute of Cristallography RAS, 119333, Moscow, Russia - Moscow (Russian federation)

Adsorption of water on a surface of ferroelectrics is caused by an electric relief of its domain structure. Such adsorption was directly observed by AFM technique [1,2]. It is known, that water adsorption essentially influences electric properties of ferroelectrics (see, for example, [3]). Last circumstance is important for corresponding ferroelectric devices.

In the present work the influence of the adsorbed water on electric and thermal properties of well-known ferroelectrics is investigated. In particular, the thermal behavior of a well-known ferroelectric barium titanate with the adsorbed water on its surface is investigated. The so-called method of modulation "ac-calorimetry" was used. This sensitive method allows investigating thermal properties of very thin samples and samples of very small weight. This gives a chance to observe the different fine effects, for example the surface effects, sorption-desorption effects etc. Very important that in this precise technique it is possible to realize the thermal cycling synchronous with heat capacity measurements. This particularly gives the possibility to consider the sample prehistory.

In particular, it was revealed, that the adsorbed water essentially changes thermal behavior of a barium titanate single crystal, such as heat capacity anomalies at phase transition. Also the simultaneously observed thermal anomalies of the adsorbed water layer differ from thermal anomalies of volumetric water. These anomalies particularly depend from a surrounding atmosphere, because the sorption-desorption process depends on the ratio between partial pressure PH2O of the water vapor in the atmosphere and pressure PS of the saturated vapor at the sample surface. These pressures increases differently with temperature: PH2O~T and PS~exp[–1/T]; i.e., the pressure of the saturated vapor grows faster. Accordingly, some anomalies peculiarities are observed depending on the temperature, state of the atmosphere and the corresponding ratio PS/PH2O.

Nevertheless there are fundamental questions - how is water adsorbed, what are chemical and electrostatic forces that form the adsorbed layer, etc.

References

1. B.Jiang,Y.Bai, Jiang-Li Cao,Y. Su, San-Qiang Shi, W.Chu, and L.Qiao, J. Applied Physics 103, 116102 (2008)
2. D.Y.He, L.J.Qiao, Alex A.Volinsky, Y.Bai, M.Wu, and W.Y.Chu, Applied Physics Letters 98, 062905 (2011)
3. J. Wang, G.Song Thin Solid Films 515, 8776 (2007)

SPEC - In situ spectroscopy

P01.092-SPEC060

NEAR AMBIENT PRESSURE XPS STUDY OF THE GAS DETECTION MECHANISM OF NANOSTRUCTURED SNO2 SENSITIVE LAYERS

M. Vorokhta [1], I. Khalakhan [1], B. Smid [1], M. Novotný [2], M. Vondrácek [2], P. Fitl [3], M. Vrnata [3], J. Lancok [2], V. Matolin [1]

[1]Department of Surface and Plasma Science, Charles University - Prague (Czech republic), [2]Institute of Physics, Academy of Sciences of the Czech Republic - Prague (Czech republic), [3]Department of Physics and Measurements, Institute of Chemical Technology - Prague (Czech republic)

It is known that morphology of the sensitive layer seriously affects the sensetivity of a gas sensor. The nanostructured layers exhibit large surface-to-volume ratio with high concentration of active surface sites for chemisorption. In this work we studied the influence of SnO_2 sensitive layer morphology and nature of detected gas on operation of chemiresistors. The SnO_2 nanostructured layers of several different morphologies prepared by magnetron sputtering and pulsed laser deposition were in-situ studied by means of NAP-XPS in presence of organic Lewis bases (methanol, ethanol, acetone) with different concentrations in synthetic air and pressures (up to 1 mbar). It was also possible to follow the resistivity of the oxide nanostructured films simultaneously with NAP-XPS measurements during analytes adsorption. It made the spectrometer especially powerful in studying gas sensing mechanisms and materials.

P01.093-SPEC094

X-RAY PHOTOELECTRON SPECTROSCOPY OF COOPER COMPLEXES WITH NON-INNOCENT LIGANDS

T. Ivanova [1], A. Sidorov [1], K. Maslakov [2], S. Nikolaevskii [1], M. Kiskin [1], S. Savilov [2], V. Lunin [2], R. Linko [3], V. Novotortsev [1], I. Eremenko [1]

[1]Institute Ganeral&Inorganic Chemistryt, RAS - Moscow (Russian federation), *[2]Department of Chemistry, M. V. Lomonosov Moscow State University - Moscow* (Russian federation), *[3]Peoples' Friendship Universty - Moscow* (Russian federation)

X-ray Photoelectron Spectroscopy (XPS) was first used to study the electronic structure, the nature of the spin density redistribution and the magnetic state in mono- CuLN=N (**I**) and binuclear $[Cu_2(Piv)_4LCH_3]_n$ (**II**) copper complexes with non-innocent ligands. Non-innocent - property of complex as a whole, not just of the ligand as the central metal atom can strongly influence the electronic structure of the ligand, if there is strong mixing of the ligand and metal orbitals.

The spectra Cu2p, Cu3s, N1s and electron structure of **I**, **II** complexes were investigated. The dependence of the satellite structure of the spectra on the nature of the ligand was found. The values of the spin-orbit splitting, the presence of the satellite structure and the energy binding of $Cu2p_{3/2}$ line correspond to the paramagnetic state of atoms Cu^{II}. From the difference values of the spin-spin splitting for **I** and **II** complexes of copper it follows that the spin density is localized in the copper ion in **I** complexes less than such in **II** complexes. It was found that the data XPS for **I** complex obtained at room temperature (*RT*) are different for those at the temperature of liquid nitrogen (LN_2). The XP-spectrum of the $Cu2p_{3/2}$ line at *RT* is a doublet with Cu^{II} and Cu^{I} respectively. Singlet line copper $Cu2p_{3/2}$ obtained at LN_2 corresponds to the degree of copper oxidation Cu^{II}. This may indicate the possibility of thermally activated equilibrium intramolecular electron transfer in complex **I** at *RT* [1]. The XPS data for the Cu2p, Cu3s lines, obtained at *RT* suggest the existence of valence tautomerism for **I** complex. From [2] it follows that hard nitrogen donor ligands increase valence orbital energy of the metal resulting in a shift in charge distribution to the redox isomer.

XP-spectra of the samples both at *RT* and LN_2 were registered with Axis Ultra DLD spectrometer non-monochromatic under AlK_α radiation, 150 W. A neutralizer was used to eliminate the charging effect during measurements of the spectra. The spectra were calibrated using C1s-line energy which refers to the C-C/C-H bonds; it was take equal to 285.0 eV. Measurements were done at least two times at a pressure of $\sim10^{-9}$ Torr. Spectral fitting was accomplished using the Kratos Analytical package.

Thanks/Acknowledgement

This work was supported by the RFBR (16-03-00047) and Russian Scientific Foundation (14-23-00176).

References

[1] K.P. Bytin, E.K. Beloglazkina, N.V. Zuk, Russian Chem. Rev., 2005, 74(6)531-553

[2] Cortlandt G. Pierpont, Coord.Chem. Rev., 216-217(2001)99-125

P01.094-SPEC287

IN SITU X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF IRON MOLYBDATE BASED CATALYSTS FOR SELECTIVE OXIDATION

P. Simon [1], A.S. Mamede [1], M. Trentesaux [1], A. Borowiec [1], M. Capron [1], J.J. Gallet [2], F. Bournel [2], J.F. Paul [1]

[1]UCCS - Université de Lille - Villeneuve D'ascq (France), *[2]LCPMR - Université Pierre et Marie Curie - Paris* (France)

Nowadays because of decreasing amount of fuel, alternative ways of several compounds production are actively researched. Therefore, products obtained from biomass become more popular and their valorization is now examined. Bioethanol is one of the most largely produced biosourced compound which finds many industrial applications thanks to its easy conversion to high value products. Its mixture with methanol can lead to the formation of acrolein using the *ad-hoc* catalyst.

Catalysts surface modifications can be monitored by in situ/operando surface spectroscopies such as near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). This technique provides direct access to the oxidation state of the active phase at millibar pressures. We applied this approach to the study of an industrial bulk catalyst composed of Iron Molybdate phase ($Fe_2(MoO_4)_3$). This catalyst is used for selective oxidation reactions as it exhibits both the redox and aicido-basic characters required to realize the oxidation/aldolisation reactions. In this study, the conversion of a methanol/ethanol mixture to acrolein was followed[1,2].

The XPS spectra of the catalyst were recorded on the SOLEIL synchrotron TEMPO B beamline. The whole redox processes involving the surface metal centers (Fe and Mo) have been monitored under a mixture of methanol and ethanol at millibar pressures. This allowed us to identify intermediate species formed at the surface as a function of time and temperature. The gas-phase reactants and products were also analyzed simultaneously by mass spectrometry.

The use of NAP-XPS enabled us to demonstrate that molybdenum sites appear to be the active sites responsible for the reaction. Indeed, Mo^{VI} initially present at the surface is reduced at 320 °C under the alcohols mixture (at 1 mbar) into Mo^{V} and Mo^{IV} (the Mo^{IV} species being the main species) (Figure 1). Under reaction mixture (alcohols + oxygen) Mo^{VI} is the main species whereas Mo^{V} and Mo^{IV} species are detected in less quantity.

This *in situ* study demonstrates high potential of NAP-XPS to investigate the behavior of a bulk catalyst under working conditions.

References

1. PCT Patent WO2014068213, assigned to Arkema France, Priority date Oct 17, 2013.
2. Liu L. et al. ChemSusChem 2012, 5, 1162-1180.

P01.095-SPEC319

XPS STUDY OF STRUCTURAL TRANSFORMATIONS IN SOME NI COMPLEXES

T. Ivanova [1], A. Naumkin [2], A. Sidorov [1], K. Maslakov [3], M. Kiskin [1], S. Savilov [3], V. Lunin [3], V. Novotortsev [1], I. Eremenko [1]

[1]*Kurnakov Institute of General and Inorganic Chemistry of RAS - Moscow* (Russian federation), [2]*Nesmeyanov Institute of Organoelement Compounds of RAS - Moscow* (Russian federation), [3]*Department of Chemistry, M. V. Lomonosov Moscow State University - Moscow* (Russian federation)

X-ray Photoelectron Spectroscopy (XPS) investigations of $Ni(L^{CH}{}_3)_3(Piv)_2$ (**1**), $[Ni(L^{CH}{}_3)_2]_2(Piv)_2)$ (**2**) and $[Ni(L^{CH}{}_3)_2]_2(CH_3COO)_2]$ (**3**) complexes, where L_{CH3} - k^2-1,2-diamino-4,5-dimethylbenzene-bis(k^1-diamino-4,5-dimethylbenzene) and Piv - $(CH_3)_3CCOO$, are reported and discussed. Ni atoms are in octahedral coordination in complex **1** and they are in distorted plane-quadratic ones in complexes **2** and **3**. The XPS spectra were excited by monochromatic Al K_a radiation and recorded at *RT* and LN_2 temperature. Quantification data of complexes **1** and **2** based on atomic sensitivity factors (ASFs) are different at *RT* and LN_2 temperature. The compositions of **1** are $C_{17.9}N_{2.5}NiO_{2.5}$ and $C_{28}N_5NiO_{3.4}$, respectively. The similar compositions of **2** are $C_{51.8}N_{7.5}Ni_2O_{2.7}$ and $C_{65}N_8Ni_2O_8$. It should be noted that the composition of **3** with chemical structure closed to that of **2** is $C_{39.7}N_{7.1}Ni_2O_{2.2}$. The corresponding theoretical compositions are $C_{34}N_6NiO_4$, $C42N_8Ni_2O_4$ and $C_{36}N_8Ni_2O_4$. It was proposed that the complexes **1** and **2** are decomposed under X-ray irradiation during recording the spectra. However, a detailed analysis of the high resolution photoelectron spectra and quantification data based on the lineshape analysis do not show any evidence of decomposition. The difference in the results of the quantitative analysis based on the ASFs and fitting the C 1s spectra is due to the fact that in the first case the dependence of the inelastic mean free path (λ) of photoelectrons on the composition of the sample is not taken into account, whereas in the second case λ does not depend on the selected state. In the case of the complex **1** spectroscopic analysis has indicated the dependence of both the position and line shape of the N 1s and O 1s peaks on temperature. Since only the N 1s and O 1s spectra show such dependence, it will be reasonable to assign it to the change in the mutual arrangement of oxygen and nitrogen atoms. As follows from the structural formula of **1**, two states of equal intensity should be observed in the O 1s and N 1s spectra which should be symmetrical. Nevertheless, they have an asymmetrical profiles depended on temperature. A possible reason for this behavior is the redistribution of the electron density on a part of the oxygen and nitrogen atoms unbounded to the nickel atoms.

Thanks/Acknowledgement

This work was supported by the RFBR (16-03-00047) and Russian Scientific Foundation (14-23-00176).

P01.097-SPEC373

TOOL FOR AMBIENT PRESSURE XPS – DEVELOPMENT OF A HIGH PRESSURE ANALYSER

L. Nittler, M. Dzierzega, C. Kirschfeld, L. Walczak
Research & Development Department, PREVAC Sp. z o.o. - Rogów (Poland)

Most of today's researches on catalysis, corrosion, semiconductors, photoelectrochemical energy conversion, battery technology, or energy-saving technologies investigate the chemical composition and properties of surfaces [1-3]. For a long time now, X-ray Photoelectron Spectroscopy (XPS) is considered as a powerful and versatile tool for surface characterization which is able to provide quantitative information about the elemental and chemical composition of surfaces.

However, most of the surface processes of interest in actual researches do not take place under UHV conditions, which is required for standard XPS instruments, but in ambient conditions, high pressures or liquid environments. Hence, results obtained under UHV conditions might be controversial for studying surface processes normally occurring at a different pressure. In the last years major efforts have been undertaken to close this pressure gap and to allow XPS measurements at more realistic process pressures.

Here, we present a new near-ambient pressure XPS/UPS system consisting of, inter alia, an enhanced energy analyser and modified X-ray sources making this system an analytical tool which is perfectly suitable for performing analysis at higher pressure. The electron analyser, which is an evolution of our EA15 analyser, is able to be operated at pressure up to 1mbar. The energy and angle resolved hemispherical analyser with a mean radius of 150mm is equipped with a modern 2-D low noise CCD-MCP assembly and can be operated in different lens modes (transmission or angular resolution).

Our new monochromatic source RMC50, which is able to work at elevated pressure, has a Rowland circle of 500mm diameter and is based on a single ellipsoidal quartz crystal. This monochromator can be used with an Al and Ag twin anode, which can be operated either in high power or small spot mode.

We will present the energy, angular and lateral capabilities of this analyser and the monochromatic source on standard samples for different pressures. Furthermore, we will report the first results using this XPS/UPS system on an actual research topic.

References

[1] C. S. Gopinath et al. Chem. Cat. Chem. 7 (2015) 588
[2] D. Silber et al., Nature Comm. 7 (2016) 12888
[3] S. Axnanda et al., Sci. Rep. 5 (2015) 9788

P01.098-SPEC380

B07: VERSATILE SOFT X-RAY BEAMLINE (VERSOX) AT DIAMOND LIGHT SOURCE

D. Grinter, F. Venturini, R. Arrigo, P. Ferrer Escorihuela, G. Held
Diamond Light Source - Didcot (United kingdom)

VERSOX will provide dipole synchrotron radiation of soft X-rays for studying atomic structures and the electronic/chemical properties of surfaces and interfaces by X-ray Photoelectron Spectroscopy (XPS) and Near-Edge X-ray Absorption Spectroscopy (NEXAFS) under wide-ranging pressures and temperatures. The beamline layout is shown in Figure 1. It has separate sources and optical components to allow independent and parallel operation of two branches: B07-C (Ambient Pressure) and B07-B (High Throughput). Branch C will begin science commissioning experiments in May 2017.

The ambient pressure endstation on branch C is a modular system that allows maximum flexibility with respect to sample environments. The concept includes an interface flange which combines the entrance nozzle of the electron energy analyser and the beamline interface, both of which are differentially pumped, and exchangeable reaction/experiment cells, as illustrated in Figure 2. The maximum pressures that the beamline interface/analyser assembly are expected to maintain are ~100 mbar for H_2 and ~30 mbar for H_2O. Different reaction cells can be fitted depending on users' needs and the nature of the sample. The optics of branch C are optimised for X-rays in the range 250 – 2800 eV.

Branch B (in the construction phase) will consist of a high-throughput endstation (b1) and an extra focus for novel techniques and user-built endstations (b2). It will be optimised for X-rays in the range 50 – 1500 eV, and will focus on samples that do not require as high ambient pressures as in branch C, and also those that are incompatible with UHV requirements due to outgassing. The b1 endstation will have automated sample manipulation to enable automatic screening of large numbers of samples. An additional focus (b2) will be provided in order to facilitate the development of new detection techniques for XAS in combination with scanning probe microscopy techniques.

References

[1] http://www.diamond.ac.uk/Beamlines/Surfaces-and-Interfaces/B07.html

P01.099-SPEC387

EFFECT OF THE STRUCTURE OF COMPLEXES OF LEAD (II) WITH NITRILOTRISMETHYLENEPHOSPHONIC ACID ON THE FORMATION AND THERMOCHEMICAL BEHAVIOR OF THEIR CHEMISORBED LAYERS ON THE CARBON STEEL SURFACE

G. Sapozhnikov [1], F. Chausov [2], N. Lomova [1], I. Shabanova [1]
[1]2Physicotechnical Institute of the Ural Branch of the Russian Academy of Sciences - Izhevsk (Russian federation), *[2]1Udmurt State University - Izhevsk* (Russian federation)

The complexes of lead (II) with nitrilotrismethylenephosphonic acid (NTP) with the different structure (I and II) are synthesized, and the comparative study of the thermochemical behavior of I and II in the free state and their chemisorbed layers on the carbon steel surface by XPS in situ is carried out.

The X-ray diffraction investigation of single crystals with I and II structure shows that in I, PbII atom is surrounded with oxygen atoms, which leads to the strong asymmetric localization of Pb6s lone pair. In structure II, in the PbII environment one of atoms O is replaced with a less electronegative atom N, and the asymmetry of a PbII coordination environment significantly decreases. A priori, in contrast to complex I, a higher stability of complex II should be expected.

However, the study of thermochemical behavior of I and II by XPS in situ has shown that at heating, metal lead is removed at 200 °C in complex II, and in complex I, the Pb–O bonds remain at heating up to 360 °C.

At the interaction of I and II with the carbon steel surface, the pattern is diametrically opposite. Complex II has a higher anticorrosive efficiency and ability to form a protective layer on the steel surface and in the temperature range of 50-350° C it forms a protective layer containing a strong covalently bonded (Pb,Fe)–O–P complex. Complex I doesn't form a strong protective layer because Pb and N are already completely lost below 200 °C with the formation of a layer of iron phosphates FePOx.

P01.100-SPEC415

IN SITU DIFFUSE REFLECTANCE SPECTROSCOPY FOR STUDY OF PHOTO- AND THERMOSTIMULATED PROCESSES IN TIO2 AT 90–720 K

N. Glazkova [1], V. Kuznetsov [2], R. Mikhaylov [1], K. Nikitin [1], N. Serpone [3]

[1]Laboratory "Photoactive Nanocomposite Materials", Saint Petersburg State University - Saint Petersburg (Russian federation), [2]Department of Photonics, Saint Petersburg State University - Saint Petersburg (Russian federation), [3]PhotoGreen Laboratory, Dipartimento di Chimica, Università di Pavia - Pavia (Italy)

UV–Vis–NIR diffuse reflectance (DR) spectroscopy is a valuable tool for study photostimulated processes in solids occurring with participation of light absorbing electronic point defects (color centers) if these centers act as electron or hole traps. Research capabilities of DR spectroscopy are significantly enhanced when spectrophotometer is equipped by an accessory allowing to operate *in situ* in a wide temperature range, in a vacuum or in a selected gaseous atmosphere and to carry out kinetic real time measurements. Kinetic measurements of reflectance/absorbance change at wavelength corresponding to the absorption band/bands of the color centers provide *in situ* monitoring of color centers appearance and decay under light irradiation, thermostimulated annealing and reductive or oxidative treatment.

In present work a construction of a novel cryostat-type "sample in vacuum" accessory developed for DR spectrophotometer Cary 5000 equipped with an integrating sphere and some results of spectral and kinetic DR study of photoinduced color centers in photochromic titania [1] are reported. Specifically examined were the (i) photostimulated formation of Ti^{3+} centers (color centers) and trapped holes under both UV and visible light irradiation, (ii) decay of trapped holes into the valence band and their recombination with Ti^{3+} centers upon temperature programmed heating, (iii) formation of Ti^{3+} centers during high temperature (> 600 K) reduction of TiO_2 in vacuum, (iv) disappearance of reduction-induced Ti^{3+} centers through oxidation at $T > 450$ K in oxygen, (v) pronounced response of the family of hole traps on the reductive/oxidative treatment, and (vi) the reversible temperature-dependent behaviour of Ti^{3+} centers at $T > 200$ K in the dark [2].

Such *in situ* DR spectral and kinetic measurements have opened up a good opportunity to examine systematically the response of color centers to oxidative/reductive treatments, the photoinduced charge carrier separation at traps, the thermostimulated carrier recombination, and a new rather unusual, heretofore not observed, temperature-induced optical phenomenon in TiO_2.

Thanks/Acknowledgement

The work was supported by Grant from the Russian Foundation for Basic Research (№ 16-33-00495). R. Mikhaylov is also grateful to the Project Establishment of the Laboratory "Photoactive Nanocomposite Materials" N 14.Z50.31.0016 supported by a Mega-grant from the Government of the Russian Federation. We are also grateful to the "Nanophotonics" Resource Center of SPbSU.

References

[1] V.N. Kuznetsov, V.K. Ryabchuk, A.V. Emeline, R.V. Mikhaylov, A.V. Rudakova, N. Serpone, Chem. Mater. 25, 170 (2013).

[2] V.N. Kuznetsov, N.I. Glazkova, R.V. Mikhaylov, N. Serpone, Photochem. Photobiol. Sci., 15, 1289 (2016).

P01.101-SPEC427

IN SITU XPS ANALYSIS OF KINETICS AND OXIDE STRUCTURE AT EARLY OXIDATION STAGES OF AUSTENITIC STAINLESS STEEL SINGLE CRYSTAL SURFACES

L. Ma, F. Wiame, V. Maurice, P. Marcus
PSL Research University, CNRS - Chimie ParisTech, Institut de Recherche de Chimie Paris (IRCP), Research Group of Physical Chemistry of Surfaces, F-75005 Paris, France - Paris (France)

Stainless steels have a wide range of applications in various sectors, such as construction, energy industry, transportation, etc. They owe their high technical importance as engineering materials to the formation of a continuous and protective surface oxide layer, the passive film, which provides a high corrosion in chemically aggressive aqueous environment.

In order to better understand the oxidation and corrosion behavior, it is necessary to investigate the early stages of corrosion, in particular, the composition and structure of the Cr-rich oxide and its possible non-uniformity which could be at the origin of localized corrosion phenomena.

The very early stages of oxidation of a Fe-18Cr-13Ni(100) single crystal at RT, 150°C and 250°C has been investigated by *in situ* X-ray photoelectron spectroscopy (XPS). Surface segregation of nitrogen contaminant, oxidation kinetics, chemical states and compounds composition as well as the oxide films stratification were determined by thorough quantitative XPS analysis.

We found that nitrogen starts to segregate to the clean surface at 400°C and reaches its saturation (about 8%at. on surface) when the annealing temperature exceeds 680°C. CrN precipitate in the bulk, CrN located at the outer surface and interstitial nitrogen atom species were identified as the products of Cr-N co-segregation.

Our kinetic results show that the oxidation rate is strongly influenced by the temperature and exposure. For exposure lower than 10 L, the oxidation rate is controlled by adsorption; otherwise, the mobility in the oxide is the main limiting factor.

Fe^{2+}, Fe^{3+} and Cr^{3+} species were identified in oxide films but no Ni oxide was detected. The competition between Cr and Fe oxidation reveals the change from thermodynamic to kinetic controlled steps. Cr oxidizes faster at the very beginning of oxidation (exposure < 10 L) and this causes a Cr-depleted region below the oxide layer. A longer exposure and a higher temperature as well favor the formation of Fe^{3+} species after the depletion of Cr metal. Higher oxidation temperature can promote the diffusion of metallic Cr and Fe from the bulk to the metal-oxide interface and can increase their atomic mobility in oxides. The consumption of Cr and Fe at higher exposure leads to a Ni-rich region located below the oxide film.

Further XPS studies combined STM analysis of oxidation at the very beginning stages will complete the investigation of the growth mechanism of oxides, which will bring new data for the understanding of the localized corrosion initiation mechanisms.

SPECIAL SESSIONS

P02.032-SS113

RELATIVE SENSITIVITY FACTORS IN HARD X-RAY PHOTOELECTRON SPECTROSCOPY

S. Yasuno [1], **S. Ishimaru** [2]
[1]Japan Synchrotron Radiation Research Institute - Sayo (Japan), [2]SPring-8 Service Co., Ltd. - Sayo (Japan)

Hard X-ray photoelectron spectroscopy (HAXPES) has been attracting considerable attention since it can probe the chemical and electronic states of the bulk and buried interface lying at depths of several tens of nm due to its large probing depth.[1] In the last decade, HAXPES have been applied to various research fields, such as electronic devices, organic materials, and rechargeable batteries. However, the quantitative analysis of the HAXPES measurement related to the relative sensitivity factors(RSFs), standard materials and theoretical calculations in hard X-ray region, have not previously been reported in detail. Therefore, in this study, we investigated the procedures of quantitative analysis for HAXPES and development of the RSFs database in the hard X-ray region. Here, we focused the database of the RSFs of compounds provided by Wagner.[2] According to Wagner's RSFs principle, the absolute value of the sensitivity factor will vary with the matrix because of the variability of the mean free path λ, by contrast the relative sensitivity factor will hardly vary because the ratio λ_1/λ_2 for element 1 and 2, is only slightly with matrix dependence. Therefore, with the RSFs of compounds, the corrections related to the mean free path which largely influenced the number of photoelectron (signal intensity) are not needed for the quantitative analysis. In HAXPES, the core level peaks can be measured in a wide kinetic energy. Thus, it is suggested that the Wagner's RSFs obtained by the compound is suitable for HAXPES measurement. Figure 1 shows the empirical sensitivity factors and theoretical sensitivity factors of 2p core level peaks relative to O1s obtained by the photon energy of 7.94 keV. It was found that the RSFs increase with the kinetic energy. Also, the theoretical vales are slightly higher than the empirical values.

Thanks/Acknowledgement

The synchrotron radiation experiments were performed at the BL46XU of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2016A1762, 2016B1555, 2016B1870, 2017A1562).

References

1. K. Kobayashi, Nucl. Instrum. Methods Phys. Res. **A601**, 32 (2009).
2. C.D.Wagner, et al., Surf. Interface Anal. **3**, 211 (1981)

P02.033-SS163

MEASUREMENTS OF ELECTRONIC STRUCTURE OF INSULATORS

V. Astasauskas [1], W. S. M. Werner [1], P. Kuksa [1], J. Pseiner [1], H. Kalbe [1], A. Bellissimo [2]
[1]*Vienna University of Technology - Vienna (Austria),* [2]*Università Roma Tre - Rome (Italy)*

It has been previously shown that it is possible to determine the band parameters of insulators using a combination of single-electron and two-electron spectroscopy. [1]

A number of insulators [Calf Thymus ssDNA, CaF_2, IRGANOX, SiO_2, PMMA, Kapton, PE, HfO_2] has been measured with Reflection Electron Energy Loss Spectroscopy (REELS) and Secondary Electron-Electron Energy Loss Coincidence Spectroscopy (SE2ELCS).

SE2ELCS spectroscopy allows one to observe secondary electron spectra in coincidence with the energy loss of the primary electron. The onset of coincidences (i.e. the energy loss for which correlated electron pairs start to appear) determines the minimum energy required to promote an electron from the top of the valence band to the vacuum level. Since the energy gap (i.e. the energy difference between the valence band maximum and the conduction band minimum) can be measured with electron energy loss spectroscopy, the combination of these methods allows to determine the electron affinity. The onset of coincidences is equivalent to the maximum energy of a correlated electron pair.

The band gap and electron affinity of the above mentioned insulators have been measured. A deconvolution algorithm has been applied to the REELS spectra to acquire the optical constants of the materials. [2] It was found that the optical constants of organic insulators are very similar. Inelastic mean free path of the materials were calculated from the optical constants.

Thanks/Acknowledgement

Financial support by the FP7 People: Marie-Curie Actions Initial Training Network (ITN) SIMDALEE2 (Grant No. PITN 606988) is greatfully acknowledged

References

1. S. Samarin, O.M. Artamonov, A.A. Suvorova, A.D. Sergeant, J.F. Williams, Measurements of insulator band parameters using combination of single-electron and two-electron spectroscopy, Solid State Communications, Volume 129, Issue 6, February 2004, Pages 389-393, ISSN 0038-1098, http://dx.doi.org/10.1016/j.ssc.2003.11.008.
2. Wolfgang S.M. Werner, Simple algorithm for quantitative analysis of reflection electron energy loss spectra (REELS), Surface Science, Volume 604, Issues 3–4, 15 February 2010, Pages 290-299, ISSN 0039-6028, http://dx.doi.org/10.1016/j.susc.2009.11.019.

P02.034-SS322

XPS MULTIQUANT: MULTIMODEL XPS QUANTIFICATION SOFTWARE

M. Mohai
Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences - Budapest (Hungary)

Quantitative evaluation of XP spectra is a major issue in surface characterisation. Numerous methods were published although only the simplest ones are usually built into the commercial data systems used in the routine work. The aim of developing the XPS MultiQuant program was to give a practical tool to the surface chemist, and producing the correct analytical results in most of the cases. The program uses the 'classic' approach of quantification, requiring the input of the integral intensities of the measured XPS lines.

The program [1] has a built-in library with all basic data for the quantification. All of the usual factors and correction methods, including cross section, asymmetry parameter, analyser transmission, IMFP, contamination by the adventitious carbon can be applied.

Simple but useful features make the work very efficient: e.g., calculation of several experimental data sets can be performed simultaneously. Chemical compositions can be presented in several ways, like Atomic %, Atomic ratio or Oxide %, etc. Elements being present in different chemical states can be calculated separately but can be summed up easily.

Several sample geometry models are available in the program: beside the usually applied "infinitely thick homogeneous sample", other ones for layered structures on flat and curved surfaces are also offered. XPS MultiQuant includes these special models to calculate layer structures on powders, fibres [3] and even on randomly stacked cylindrical shape nanotubes [4]. The layer thickness from an angle dependent experiment sets ('ARXPS') can be calculated together.

The layer thickness calculations can transform the surface composition results into another dimension. Thickness data, even it is not absolutely precise, give more information on the studied system. Setting up of a layer model by the program is easy and can be applied routinely [3,4].

The program can also be used for simulations: the integrated photoelectron intensity can be calculated for a defined composition and model layout.

The software made to be ready to communicate with other XPS related applications through XPS Reduced Data Exchange Files [2].

XPS MultiQuant is freeware for non-commercial use (http://aki.ttk.mta.hu/XMQpages/XMQhome.htm).

During the conference the program will be demonstrated and can be examined in the practice.

References

1. M. Mohai, Surf. Interface Anal. 36, 828 (2004); doi:10.1002/sia.1775.
2. M. Mohai, Surf. Interface Anal. 38, 640 (2006); doi:10.1002/sia.2198.
3. M. Mohai, I. Bertóti, Surf. Interface Anal. 36, 805 (2004); doi:10.1002/sia.1769.

4. M. Mohai, I. Bertóti, Surf. Interface Anal. 44, 1130 (2012); doi:10.1002/sia.4864.

P02.086-SS465

LOW ENERGY (1-50 EV) INELASTIC MEAN FREE PATH (IMFP) VALUES ESTIMATED FROM EXPERIMENTAL RESULTS USING MONTE CARLO CALCULATIONS

O. Ridzel, W. Werner, V. Astašauskas
Vienna University of Technology - Vienna (Austria)

An extensive database of secondary electron yield (SEY) values (in the energy range between 10 eV and 10 MeV) has been created from a literature search. As it is well-known SEY values at any energy depend sensitively on the inelastic mean free path (IMFP) values, in particular below 50 eV. A Monte Carlo (MC) code has been developed to simulate the SEY values based on Mott cross sections for elastic scattering, linear response theory (based on empirical optical constants) to describe inelastic scattering and the commonly employed model for the surface barrier in terms of the inner potential and the work function of the solid. References [1] and [2] represent upper and lower extreme IMFP-values. Variation of the IMFP in between these extreme values during the MC simulation and a comparison with the literature data [1,2] give us a realistic estimate for the IMFP values at energies below 50 eV. The presentation will contain first results of this study.

References

1. Tanuma, S., Powell, C. J. and Penn, D. R., Calculations of electron inelastic mean free paths. V. Data for 14 organic compounds over the 50–2000 eV range. Surf. Interface Anal., 1994 21, 165–176.
2. C. T. Chantler and J. D. Bourke, The Journal of Physical Chemistry A, 2014 118 (5), 909-914.

P02.036-SS072

UNIFIT 2018 - THE IMPROVED SPECTRUM PROCESSING, ANALYSIS AND PRESENTATION SOFTWARE FOR XPS, AES, XAS AND RAMAN SPECTROSCOPY

R. Hesse, **R. Denecke**
University Leipzig - Leipzig (Germany)

UNIFIT is a well established specialized software for data analysis and presentation of photoelectron spectroscopy, Auger electron spectroscopy and X-ray absorption spectroscopy data. Now new additions and improvements are presented.

In order to have more linking options for the fit parameters the fit procedures were improved (e.g. to be able to describe multiplet structures from intermediate-coupling Eu $3d_{5/2}$ and Eu $3d_{3/2}$ spin-orbits components for the divalent Eu^{2+} compounds). The selection of the master peaks of the peak fit with relative fit parameters was extended. Now every peak-fit component can be defined as master peak. The parameters of slave peaks with a succeeding component numbers can be linked to the parameters of the corresponding master peak.

The main-memory used by UNIFIT was strongly reduced. The UNIFIT 2018 software needs more than 30% less main-memory with respect to UNIFIT 2017. The large parameter arrays were redefined.

The peak identification for XP spectra was expanded by an automatic option. The peak-finding procedure can be approached by defining of ΔE (energy separation), ΔI (peak height) as well as a check with a data set of main lines. The annotation list may be shown directly.

A fourth spectroscopic method was implemented in the new software. The improved software offers the data analysis of photoelectron spectra (XPS), Auger electron spectra (AES), X-ray absorption spectra (XAS) and RAMAN spectra. The peak fit of RAMAN spectra gives a considerably better analysis of the studied sample with respect to the traditional analysis of untreated data.

Two new 3D plots 'XY 3D 45° Colour Profile' and 'XY 3D -45° Colour Profile' were implemented in the batch processing subroutines.

The selectable processing results for the generation of XY-3D presentations were enhanced. Now, all fit parameters, the position of the maximum and minimum can be selected additionally.

Three new options for the selection of standard windows for easier handling of large data sets were implemented: i) all windows with a defined X position, ii) all windows with a defined Y position, iii) all windows with a χ^{2*} greater than a defined χ^{2*} (after a peak fit to detect incomplete fit results). Additionally, the number of the selected windows is displayed.

We will demonstrate the additional feature using typical applications.

P02.037-SS073

UNIFIT 2017 - THE NEW SPECTRUM PROCESSING, ANALYSIS AND PRESENTATION SOFTWARE FOR XPS, AES AND XAS

R. Hesse, R. Denecke
University Leipzig - Leipzig (Germany)

Auger electron spectroscopy (AES) can provide information which is either complementary to such obtained by x-ray photoelectron spectroscopy (XPS) or opens additional experimental options. Therefore, possibilities for analysing AES data are implemented in the data analysis software UNIFIT 2017. Now measurements of photoelectron spectra (XPS), Auger electron spectra (AES) and X-ray absorption spectra (XAS) can be analysed. To that end the input routine was extended for loading Auger spectra saved in different data formats (e.g. PHI formats: *.spe, *.map, *.pro, *.lin). The identification of the Auger lines is supported by new implemented data banks. A special calculation tool allows the estimation of AES sensitivity factors. The quantification can be carried out using integral or differential Auger spectra. Additionally, empirical sensitivity factors of different spectrometer types were implemented. Examples of such analysis are demonstrated.

In addition, other aspects have been improved to expand the possible applications of the software package. E.g., the calculation of the transmission function T(E) was improved, now allowing T(E) determination using variable kinetic energies, intensity ratios and atomic ratios of the used peaks (e.g., as used in synchrotron radiation excited spectra). The energy range of T(E) was increased to cover from 200 to 5100 eV.

Optimization of data handling and extension of the number of parameters and windows allows the application to large data sets (256x256 spectra), as e.g. obtained in time-dependent or multipoint experiments (e.g. SAM). The generation and display of windows video sequences enhances the presentation of sputter depth profile multipoint measurements.

The total full width at half maximum (FWHM) of original and processed spectra can be estimated separately using a new developed routine. The FWHM is displayed additionally in the fit-parameter table using the convolution routine at the peak fit.

We will show the new features in typical applications and verify their quality.

SUF - Surface functionalization

P02.038-SUF029

OPTICAL, CHEMICAL AND STRUCTURAL ANALYSIS OF POLYMER AND METAL SURFACES TREATED WITH PLASMA FROM LIQUID MEDIA

M. Cobet [1], M. Kehrer [1], T. Stehrer [2], A. Mehic [2], D. Stifter [1]
[1]Center for Surface- and Nanoanalytics, Johannes Kepler University - Linz (Austria), *[2]Fronius International GmbH - Wels* (Austria)

A comprehensive study of the plasma modification of metals and polymers by non-linear and linear optical techniques in combination with X-ray photoemission (XPS) and X-ray diffraction (XRD) as complementary sources of information is presented. The used plasma is of a novel type, where also liquids can be ignited into the ionized state.

Surface activation by plasma treatment happens mainly by inducing functional groups and polar adsorbates on the very surface and is a common procedure in order to increase the surface energy for bonding or coating of otherwise inert or non-polar materials. Atmospheric plasma (cold plasma) modification by the use of air is already established in industry because it is environmental friendly, cost effective and can be integrated into in-line processing. Here, we used in a first step a jet plasma from water in different mixtures with air on polypropylen and AlMg3, two materials relevant in industry.

For a detailed understanding of the chemical microscopic processes induced by this special conditioning we used Sum-Frequency-Generation (SFG), Raman, and Ellipsometry in addition to XPS and XRD. While SFG is probing vibrational spectral resonances of molecular adsorbates which are not readily accessible by other optical methods, linear optics like Raman and ellipsometry provide valuable information about the oxidation of metals, i.e. the formation of amorphous transparent layers on the surface and the degree of crystallinity in polymers. Structural information especially with respect to the question of amorphisation of polymers during the treatment (by thermal effects) is crosschecked with XRD, where it is found that the isotactic crystal structure is only broken at the very surface but does not affect deeper layers. HR-XPS-spectra and valence-band scans show a high level of functionalization with hydroxyl-, carboxyl-, and carbonyl-groups as well as amino- and nitro-groups. The N-content could be raised to 4-5%. The absolute content of hydrogen is increased when adding water to the plasma and the integration of nitrogen can be completely prevented, if exclusively water is used as a medium, which is of advantage for certain types of adhesives.

In conlusion we show, that the use of water in addition to air has many advantages compared to conventional air atmospheric pressure plasmas, like a much higher content of polar groups in case of metal-surfaces. We point out the ability of the system to select their chemical composition (with respect to N, O, and H) by the choice of mixing in a wide parameter space.

P02.039-SUF098

SPECTROSCOPIC STUDIES OF TETRAHYDROXYBENZENE ADSORPTION ON METAL SURFACES

A. Nefedov, F. Bebensee, C. Woell
Karlsruhe Institute of Technology - Karlsruhe (Germany)

The chemical state of molecular blocks used to build a supramolecular structure on the surface is crucial to structure rationalization, because dehydrogenation reaction may obstruct self-assembly. However, in some cases, such reaction may actually be desired, as it opens new possibilities for hydrogen bonding. While previous STM results on the adsorption of tetrahydroxybenzene (THB) on Cu(111) provide a clear picture on the spatial arrangement of the molecules, the electronic structure is not understood yet. These relevant questions were suitably addressed by high-resolution XPS and especially NEXAFS owing to its extremely high chemical sensitivity. As the dehydrogenation is currently considered to proceed differently on Ni(111) compared to Cu(111), we studied the impact of annealing temperature for both substrates in more detail. Once the transition temperatures were determined from XPS experiments we elucidated the electronic structure of the various phases with NEXAFS spectroscopy. Cu/Ni(111) single crystals were previously cleaned by repeated sputtering/annealing cycles. THB molecules were deposited at 340 K keeping the substrate at room temperature.

Figure presents NEXAFS spectra obtained directly after THB deposition and after annealing up to 625K. From angle dependences of π*-resonances the flat orientation of the THB molecules on the Cu(111) surface was determined. The black curve is very similar to the spectrum observed before for dihydroxybenzene [1]. However after annealing at 625 K the change in the electronic structure was clearly determined by XPS and NEXAFS. The presence of reasonable contribution at E=284.5 eV in the NEXAFS spectrum which is a benchmark of p-benzoquinone, allows us to assign this spectrum as dihydroxybenzene/p-benzoquinone mixture [1] according to the previous model of dehydrogenation of THB in dihydroxybenzoquinone.

In a case of Ni(111) substrate the dehydrogenation takes place already at RT confirming the previous observation about higher activity of nickel.

References

1 D. Solomon et al. SSSAJ, 2009, 73(6), 1817.

P02.040-SUF102

FUNCTIONALIZATION OF SUPPORTS FOR ASSEMBLY OF TITANIA NANOPARTICLES WITH DEFINED SIZE AND SHAPE

S. Rades [1], E. Ortel [1], T. Wirth [1], M. Blanco [2], E. Gomez [2], A. Martinez [2], G. Martra [3], P. Borghetti [4], J. Jupille [4], V.D. Hodoroaba [1]

[1]Federal Institute for Materials Research and Testing (BAM) - Berlin (Germany), [2]IK4-TEKNIKER - Eibar (Spain), [3]University of Torino - Torino (Italy), [4]Universite Pierre et Marie Curie (UPMC) - Paris (France)

The physico-chemical characteristics of TiO_2 coatings can greatly influence their final performance. In EU/FP7 SETNanoMetro project different deposition procedures have been set for applying films of TiO_2 nanoparticles with defined and homogeneous thickness on supports of interest for the applications studied in the project [1]. The selected substrates are: (i) silica glasses for photocatalytic measurements, (ii) Ti-alloys for orthopedic and/or dental prostheses, for cell cultures, and (iii) conductive glasses (e.g. FTO) for dye-sensitized solar cells. The film deposition procedure applied here is the self-assembly of TiO_2 nanoparticles in multiple layers. For this, the layer-by-layer deposition method has been employed. This technique of thin film fabrication consists of the deposition of alternating layers of oppositely functionalized materials with wash steps in between. However, the controlled assembly of TiO_2 nanoparticles on the surface of the selected supports requires a proper functionalization of the supports in order to promote the adhesion of the film to the substrates [2]. The current study collects the procedure followed for the functionalization of silica glasses, conductive glasses and titanium alloys. The three types of supports have been analyzed after functionalization procedures with SEM, ToF-SIMS, AES (see Fig. 1), XPS and AFM. Elemental and chemical composition of surfaces of substrates show differences in the degree and manner of modification in dependence on the type of substrate. Further results regarding prepared controlled assembling films will be presented.

Thanks/Acknowledgement

This project has received funding from the European Union's Seventh Framework Programme under grant agreement no. 604577 (SETNanoMetro).

References

[1] E. Ortel, I. Häusler, W. Österle, S. Narbey, F. Oswald, I. Andersen, M. Holzweber, W.E.S. Unger, V.-D. Hodoroaba, *Surf. Interface Anal.* **48** (2016) 664-669.

[2] A.K. Singh, A.W. Flounders, J.V. Volponi, C.S. Ashley, K. Wally, J.S. Schoeniger, *Biosensors & Bioelectronics* **14** (1999) 703-713.

P02.041-SUF138

INFLUENCE OF THE SURFACE PROPERTIES OF BUILDING MATERIALS ON THE COLONIZATION BY PATHOGENIC MICROBES

M. Horgnies [1], **V. Morin** [1], **I. Dubois-Brugger** [1], **F. Serre** [1], **S. Vacher** [2]
[1]*LafargeHolcim R&D - Saint Quentin-Fallavier* (France), [2]*Conidia - Quincieux* (France)

Certain microbial species degrade indoor air quality and lead to the proliferation of diseases in public spaces, food industries and hospitals [1,2]. New solutions about building materials ought to be found to limit the colonization by moulds and bacteria on the surfaces of our close environment [3-5]. Several methods were used in this work to study how the surface properties (composition, pH, roughness, etc.) of several building materials (gypsum plasterboard, fired clay brick, wood, ordinary concrete, ultra-high performances concrete) could influence the colonization of different microbial species affecting the indoor air quality or responsible for some health diseases. The results highlighted that roughness (and surface porosity) were the main parameters governing the probability of settlement of mould spores. Indeed, an absence of colonization was detected on very smooth surfaces made of ultra-high performances concrete (characterized by a very dense particles-packing and an average roughness below the common diameter of mould spores). Moreover, the test of viability of bacteria demonstrated that pH acted as one of the main parameters to reduce the proliferation of such microbes. Indeed, even a carbonated surface of concrete, characterized by low alkaline pH (< 9), was able to reduce drastically the amount of bacteria detected after 48h. However, the deposition of a siloxane-based water-repellent coating on such building materials promoted the colonization by fungi and was not able to remove all the bacteria.

Thanks/Acknowledgement

The authors would like to thank F. Legrand (LafargeHolcim R&D) for her help during the analyses by profilometry.

References

[1] World Health Organization. WHO guidelines for indoor air quality: dampness and mould. WHO: Geneva, Switzerland; 2009.

[2] Verdier T., Coutand M., Bertron A., Roques C., A review of indoor microbial growth across building materials and sampling and analysis methods, Building and Environment, 80 (2014) 136-149.

[3] Vacher S., Hernandez C., Bärtschi C., Poussereau N., Impact of paint and wall-paper on mould growth on plasterboards and aluminium, Building and Environment, 45 (2010) 916-921.

[4] De Muynck W., De Belie N., Verstraete W., Antimicrobial mortar surfaces for the improvement of hygienic conditions, Journal of Applied Microbiology, 108 (2010) 62-72.

[5] Urzi C., De Leo F., Evaluation of the efficiency of water-repellant and biocide compounds against microbial colonization of mortars, International Biodeterioration and Biodegradation, 60 (2007) 25-34.

P02.042-SUF145

XPS CHEMICAL STATE IMAGING OF STRUCTURED SURFACES: FROM METAL OXIDE GAS SENSORS TO POLYMER AND DNA MODIFIED SUBSTRATES

V. Trouillet [1], F. Behboodi-Sadabad [2], P.A. Levkin [2], M. Hirtz [3], M. Bruns [1]

[1]IAM-ESS and KNMF, Karlsruhe Institute of Technology (KIT) - Eggenstein-Leopoldshafen (Germany), [2]ITG and IOC, Karlsruhe Institute of Technology (KIT) - Eggenstein-Leopoldshafen (Germany), [3]INT and KNMF, Karlsruhe Institute of Technology (KIT) - Eggenstein-Leopoldshafen (Germany)

Usually X-ray photoelectron spectroscopy (XPS) doesn't represent the method of choice to chemically image structured surfaces in comparison to analysis techniques like time-of-flight secondary ion mass spectrometry (ToF-SIMS) or Auger electron spectroscopy (AES). This is mainly due to the multiple of acquisition time needed for serial or even parallel XPS imaging. However, with the recent introduction of rapid mapping modes this drawback can be overcome. As a test structure shown we firstly used a gas sensor micro array based on a 4x8 mm^2 SnO_2 layer subdivided into 38 detectors by parallel 50 µm platinum strip electrodes [1]. The images in fig.1 chemically prove the sharpness of structures and can be achieved within 1 hour acquisition time which is comparable to ToF-SIMS measurements.

The short acquisition time opens-up the possibility to image structured bio/polymer surface modifications which often is hampered by the X-ray sensitivity of the organic materials. We therefore focus here on the characterization of structured surfaces prepared by means of e.g. light triggered reactions combined with shadow masking techniques or µ-contact printing approaches.

Recently, we showed that UV irradiation can be used to create 2D gradients and patterns of plant phenolic compounds on both polar and non-polar substrates [2]. In order to visualize the phenolic patterns, secondary modification of phenolic nanocoating with silver particles or Rhodamine dye can be employed. However, our goal is to obtain such lateral information directly without any pretreatment of the samples. Therefore, we report XPS results obtained directly from C 1s components of the polymer.

Moreover, this option enables us to rapidly locate optically non-visible structures of ultra-thin top-layers, e.g. of µ-contact printed DNA areas on Au-substrates. This renders possible the subsequent in-depth analysis of precise areas of interest using high energy resolution XPS.

References

[1] V. Trouillet, H. Tröße, M. Bruns, E. Nold, R. G. White, Journal of Vacuum Science and Technology A, 25 (2007) 927.

[2] F. Behboodi-Sadabad, H. Zhang, V. Trouillet, A. Welle, N. Plumeré, P. A. Levkin, Adv. Funct. Mater. (2017), in press.

P02.043-SUF216

CHEMICAL MODIFICATION INDUCED BY MICROSCOPIC LOW ENERGY ELECTRON BEAM ON SELF-ASSEMBLED MONOLAYERS

Q. Wu [1], L. Sala [2], L. Amiaud [2], A. Lafosse [2], C. Mathieu [1], C. Lubin [1], N. Barrett [1]
[1]SPCS, CEA, CNRS, Université Paris-Saclay, CEA Saclay, - 91191 Gif-Sur-Yvette Cedex (France), *[2]Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Univ Paris-Sud, Université Paris-Saclay, - F-91405 Orsay,* (France)

Crosslinked aromatic self-assembled monolayers (SAMs) were shown to be robust anchors and templates for biomolecules, precursors for building carbon nanosheets and nanomembranes as well as negative resists for lithography [1]. Terphenylthiol (TPT) SAMs anchored on gold substrates are good models to demonstrate the effects of low-energy electron irradiation on aromatic SAMs. Remarkable chemical modifications as consequences of different electron-induced processes from 6 up to 50 eV have been observed through high resolution electron energy loss spectroscopy [2, 3]. Thus, low energy electrons provide chemical control in surface modifications. However, the electron beam spread for low energy irradiation is usually in millimeter scale. Concentrating the irradiation on a microscopic scale for lithographic/sensing applications is necessary. Complementary studies on electronic structure changes in irradiated SAMs are also needed.

Here we demonstrate that chemical modifications induced by low-energy electrons can be restricted in micrometer scale on TPT layer using low energy electron microscope (LEEM). Spots with sizes about 3 µm irradiated by 10 eV electrons and exposure times from 3 to 30 minutes are shown in the LEEM image at 0.35 eV (Fig.1). Work function changes in TPT films as a consequence of chemical modification are observed by measuring the energy shifts of MEM-LEEM transition for different irradiated areas. The MEM-LEEM transition curves corresponding to irradiated areas presented in Fig.1 show a global decrease in work function with increased irradiation dose (Fig. 2). Imaging in photoemission electron microscope (PEEM) with a He-I (21 eV) source reveals the same changes in work function in irradiated areas, whereas valence band maximum position of the molecule layer stays constant during the electron irradiation.

References

[1] Turchanin, A. & Gölzhauser, A., *Prog. Surf. Sci.*, 2012, **87**, 108-162.

[2] Houplin, J., et al., *Langmuir*, 2015, **31**, 13528−13534.

[3] Amiaud, L., et al., *Phys. Chem. Chem. Phys.*, 2014, **16**, 1050-1059.

P02.044-SUF236

ATMOSPHERIC PRESSURE PLASMA DEPOSITION OF ANTIBACTERIAL QUATERNARY AMMONIUM SILANE ON PP SURFACE FOR ADVANCED WOUND DRESSINGS

J. Kovac [1], G. Jakša [1], A. Zabret [2], M. Kralj Kuncic [2], B. Verheyde [3], D. Vangeneugden [3]
[1]Jozef Stefan Institute - Ljubljana (Slovenia), *[2]Tosama - Domžale* (Slovenia), *[3]Flemish Institute for Technological Research (VITO) - Mol* (Belgium)

A new atmospheric plasma technology was applied for deposition of antibacterial quaternary ammonium silane on non-woven materials for advanced wound dressings. A new remote plasma configuration was used in which a plasma polymerization process can be carried out by introduction of chemical precursors in a plasma afterglow. The plasma reactor was implemented in an existing production process for wound dressings. In this study Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride solution (DMO or Si-QAS) was used for antimicrobial coatings on polypropylene (PP) nonwoven substrate. Quaternary ammonium silane was deposited using two different deposition techniques: wet-chemical deposition (dip coating) and atmospheric pressure plasma assisted chemical vapor deposition (AP-PA-CVD). X-ray photoelectron spectroscopy (XPS) and Time-of-flight secondary ion mass spectrometry (ToF SIMS) were used to characterize the composition, the chemical structure and homogeneity of deposited silane layers. Comparison between different deposition techniques, durability, water stability of deposited coatings as well as antibacterial activities were investigated and discussed. The results show that silane coatings could be deposited by both deposition techniques. Silane layers deposited by plasma process are thicker than wet-chemically deposited ones. However, plasma deposited coatings shows better antibacterial activities.

Thanks/Acknowledgement

The research was funded from the EU Programme FP7 under the grant agreement NMP3-SE-2013-604048 within the project with acronym “IP4Plasma”, http://ip4plasma.eu/en/home

P02.045-SUF321

REDUCTION AND COVALENT MODIFICATION OF GRAPHENE-OXIDE BY NITROGEN IN GLOW DISCHARGE PLASMA

M. Mohai [1], K. László [2], I. Bertóti [1]

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences - Budapest (Hungary), [2]Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics - Budapest (Hungary)

Reduction and simultaneous nitrogen introduction into graphene oxide (GO) can be conveniently performed in nitrogen glow discharge plasma [1]. The resulting modified surface can be further functionalized altering its properties to be beneficial for different applications.

In this work we performed glow discharge plasma treatment of thin layers of GO samples in various nitrogen containing gases (mainly N2 and NH3). Experiments were performed in the preparation chamber the X-ray photoelectron spectrometer, allowing ‘in situ’ characterization of the treated surface. Introduction of nitrogen into the top surface was intensified by applying negative voltage on the sample between 0-300 V accelerating the positive plasma ions towards the sample.

Significant amount of nitrogen (≈10 atomic %) was built into the top few atomic layers of the GO samples at application of all types of plasma gases for 10 min reaction time. When comparing the N2 and NH3 plasma treatments, more complete reduction and closely similar amount of nitrogen was found in NH3 plasma.

When increasing the bias, the N-content increased, together with the decrease of the O content. The high resolution C1s, O1s and N1s spectra are broad, representing different chemical states. The peak envelopes of the O1s and N1s lines could be decomposed essentially to three, while the C1s spectrum to five different, well separated peaks, being identical for all samples.

The component peaks were assigned to specific chemical bonding states (N1s: 398.3 eV sp2 pyridine N, 399.8 eV sp2 pyrrole, diazine or triazine N, 401.0 eV N in graphite plane; O1s: 531.0 eV carbonyl, 532.3 eV ether, epoxy, alcohol, ester C=O, 533.7 eV ester C–O–C, carboxyl OH). The relative amounts of C–O and C–N bonding states changed significantly with advancement of the treatment performed at increasing biases. After the reaction with ammonia plasma, amine groups could be also detected by reflection FT-IR measurements thus part of the identified nitrogen-carbon bonds at 399-400 eV binding energy can be assigned to C–NH type bonds.

We attempted to establish interrelations among the different C–O and C–N states. The reasonable agreement found among the amounts of interconnected bonding states supported the validity of the suggested assignments.

Thanks/Acknowledgement

This work was partly sponsored by the National Scientific Research Fund (OTKA) No. K-109558.

References

1. I. Bertóti, M. Mohai, K. László, Surface modification of graphene and HOPG by nitrogen plasma: Quantitative XPS analysis of chemical state alterations, Carbon 84: 185–196, 2015.

P02.088-SUF466

TOWARDS TUNING THE PHYSICAL PROPERTIES IN TWO-DIMENSIONAL POROUS ORGANIC NETWORKS

N. Kalashnyk [1], L. Sosa-Vargas [1], I. Arfaoui [2], F. Charra [3], E. Kim [4], A.J. Attias [1]

[1]Institut Parisien de Chimie Moléculaire (IPCM), Sorbonne Universite´s – UPMC Université Paris 06, UMR 8232 CNRS - Paris (France), [2]MONARIS, Sorbonne Universite´s – UPMC Université Paris 06, UMR 8233 CNRS - Paris (France), [3]SPEC, CEA, CNRS, Université Paris Saclay, CEA-Saclay - Gif-Sur-Yvette (France), [4]Department of Chemical and Biomolecular Engineering, Yonsei University - Seoul (Korea, republic of)

The fabrication of two-dimensional (2D) functional systems with an atomic precision is one of the main challenges in all fields of science and technology. Self-assembly is recognized as a versatile bottom-up method for the formation of these extended 2D structures with long range order on surfaces. In particular, supramolecular chemistry approaches have been successfully applied to design a vast variety of close-packed multicomponent architectures with finely-tuned patterns and physico-chemical properties. It was recently demonstrated that a careful control of geometry, symmetry and dimension of the molecular building blocks can also lead to the creation of surface-supported nanoporous networks. As evidenced from scanning tunneling microscopy (STM) studies a subtle interplay between molecule–substrate and molecule–molecule interactions can further tailor the growth of porous hexagonal, honeycomb or Kagomé assemblies. Such supramolecular architectures with periodic skeletons and ordered nanopores attracted great attention due to their possible applications as storage materials or nanotemplates. In the later case the nanopores can host guest molecules that might be rigidly anchored or rotate inside pores as well as translate between them.

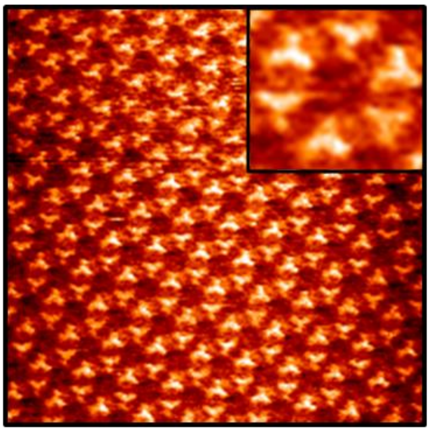


Fig. 1 STM image of honeycomb structure formed by TSB35 on HOPG (30x30 nm^2)

In this work, we report on the fabrication of two-dimensional nanomesh structure that consists of (1,3,5-tris[(*E*)-2-(3,5-didecyloxyphenyl)-ethenyl]benzene (TSB35) molecules self-assembled on highly oriented pyrolytic graphite (HOPG) at the liquid/solid interface. STM images indicate that the interdigitation of alkyl chains in these molecules (typically visualized as three-arm star-shaped features) results in the formation of a highly-ordered honeycomb network on the surface (see Fig. 1). To further functionalize this organic layer metal phthalocyanines (MPc) were selected as guest molecular systems to be trapped in the pore sites (see Fig. 2). This choice was motivated by an ideal pore-phthalocyanine size fit, and by the ability to tune the physical properties of this supramolecular architecture via exchange of central metal or hydrogen atoms at the rim of the phthalocyanines.

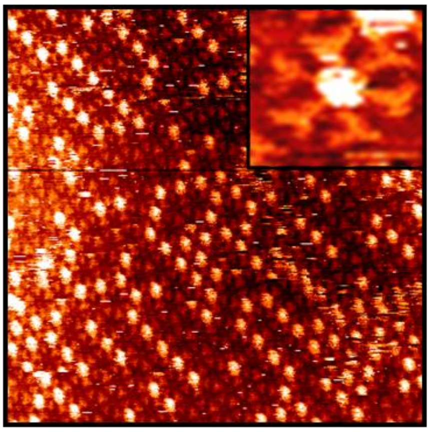


Fig. 2 STM image of ZnPcs anchored in the cavities of host network (60x60 nm^2)

TFC - Thin films and coatings

P02.047-TFC020

STUDY OF PD/Y BASED MULTILAYERS WITH B4C BARRIER LAYERS USING HIGH ENERGY PHOTOEMISSION SPECTROSCOPY COMBINED WITH X-RAY STANDING WAVES

M. Wu [1], V. Ilakovac [1], J.M. André [1], K. Le Guen [1], A. Giglia [2], J.P. Rueff [1], Q. Huang [3], Z. Wang [3], P. Jonnard [1]

[1]Sorbonne Universités, UPMC Univ Paris 06, Laboratoire de Chimie Physique - Matière et Rayonnement, 4 place Jussieu, F-75252 Paris cedex 05, France - Paris (France), [2]CNR, Istituto Officina Materiali 34149 Trieste, Italy - Trieste (Italy), [3]Key Laboratory of Advanced Micro-Structured Materials MOE, Institute of Precision Optical Engineering, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China - Shanghai (China)

We use hard x-ray photoemission spectroscopy (HAXPES) combined with x-ray standing waves to characterize a series of Pd/Y based periodic multilayers designed to work in the 7.5-11 nm range. The samples are prepared by magnetron sputtering. For different samples thin B4C barrier layers are inserted at different locations within the stack: at the Pd-on- B4C interfaces, at the B4C-on-Pd interfaces or at both interfaces. These barrier layers are expected to improve the reflecting performance of the multilayers [1,2]. The aimed period of the samples is 4 nm. The experiments consist in obtaining the core level photoemission spectra of the various elements for a series of grazing angles. The angular scan is made in the range given by the Bragg law, considering the multilayer period and the incident photon energy, in order to generate to strong standing wave in the stack. Owing to the period of the multilayer and the presence of a 2.5 nm-thick capping layer, the photon energy is chosen to be 10 keV in order to probe the first 5-6 periods of the stack. Thus the Bragg angle is a little less than 1°. Rotating the sample enables putting the nodes of the electric field at some particular location of the stack, thus to make the excitation depth-selective, coming from one interface or another or from the center of one given layer. The changes of the chemical shift of the Pd 2p and 3d, Y 2p and 3d, N 1s, C 1s and B 1s core level peaks as a function of the angle, that is to say as a function of the location in the stack will give information about the possible interfacial processes taking place in the multilayers.

References

[1] P. Jonnard et al. Surf. Sci. 604 (2010) 1015.

[2] M. Prasciolu et al. Appl. Opt. 53 (2014) 2126.

P02.049-TFC028

LOCAL ATOMIC STRUCTURE ANALYSIS OF SIO2/SIC INTERFACE USING EXTENDED X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY

N. Isomura [1], T. Murai [2], H. Oji [3], T. Nomoto [2], Y. Watanabe [1], Y. Kimoto [1]
[1]Toyota Central R&D Laboratories, Inc. - Nagakute (Japan), [2]Aichi Synchrotron Radiation Center - Seto (Japan), [3]Nagoya University Synchrotron Radiation Research Center - Nagoya (Japan)

Material interfaces are common in semiconductor devices and their exact structure is a key parameter for device performance. However, it is not straightforward to analyze the exact composition of interfacial structures layer by layer. Here, a local atomic structure analysis of the interface between chemical vapor-deposited SiO_2 and SiC (4H, m-face) is achieved via a combination of chemical-state-selective extended X-ray absorption fine structure (EXAFS) spectroscopy and the use of a sample with a very thin oxide film (~3 nm) [1]. This method provides the spectrum for a specific layer by detecting its Auger electrons using an electron spectrometer, with an analysis depth of a few nanometers. The experiments were performed at the soft X-ray absorption spectroscopy beamline BL6N1 of the Aichi Synchrotron Radiation Center. The Si K-edge EXAFS spectrum, which monitors the SiC-assigned Si KLL Auger peak of the SiO_2/SiC interface, is similar to the total electron yield spectrum of the SiC bulk and differs from that of the SiO_2 bulk. This means that the SiC side of the SiO_2/SiC interface can be measured nondestructively through the SiO_2 film. By using Fourier transforms of the spectrum oscillation, we estimate the coordination number of the first nearest neighbor (1.3 Å) to be reduced by 17% with respect to the SiC bulk, as shown in Fig. 1 (without considering phase shifts). This suggests that carbon vacancy defects exist at the SiC side of the chemical vapor-deposited SiO_2/SiC interface. Thus, our results demonstrate that quantitative analyses of interface structures are possible using the chemical-state-selective EXAFS method, which will enable SiC interfaces to be optimized. Our work will therefore have a large impact on the future of power-electronic devices made of SiC.

References

[1] N. Isomura et al., *Appl. Phys. Express* **9**, 101301 (2016).

P02.050-TFC038

ELECTROPOLYMERIZATION OF ACRYLIC ACID ON CARBON FIBERS FOR IMPROVED EPOXY/FIBER ADHESION

D. Meinderink [1], **A. Bauer** [2], **I. Giner** [1], **H. Steger** [2], **J. Weitl** [2], **G. Grundmeier** [1]

[1]University of Paderborn, Department for Technical and Macromolecular Chemistry - Paderborn (Germany), [2]BMW AG, Department for Chemical Analytics and Process Material - Regensburg (Germany)

1. Introduction

The surface treatment of especially carbon fiber reinforced plastics (CFRP) has reached a high level of interest in the lightweight construction and industry in the recent years. The electropolymerization is a simple technique for several monomers and substrates to get a polymer film or an adhesion promotor. [1-3]

This work illustrates the characterization of electropolymerization of Poly(acrylic acid) (PAA) films on carbon fiber reinforced plastics as a possible adhesion promoter.

2. Experimental section

A typical three-electrode design with polished CFRP as working electrode was used for the electropolymerization of acrylic acid barred from the atmosphere. The electrolyte consisted of: 2.0 M acrylic acid (monomer) with methoxyphenone (inhibitor), 0.2 M zinc chloride (initiator) and 0.04 M *N,N'*-methylenebiacrylamide (crosslinking reagent).

The surface characterization of the electrodeposited films was performed by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Fourier transformation infrared reflection absorption spectroscopy (FT-IRRAS). In addition, the interfacial stability of the electrodeposited polymer was investigated by means of a peel force test.

3. Results

The optimized electropolymerization of acrylic acid on C-fiber based substrates was performed by applying a cathodic potential (-1.0 V vs Ag/AgCl) to the working electrode. XPS and FTIR based studies showed that the chemical nature of the monomer is preserved during the electropolymerization process. Our results show that the thickness of the polymer film can be adjusted by varying the deposition time from 60 sec to 960 sec (Figure 1). The analysis of the wet adhesion revealed a higher interfacial stability when the PAA is applied as an adhesion promoter. A possible deposition mechanism for the PAA with the role of the Zn^{2+} and the inhibitor in the electrolyte could be proposed.

Thanks/Acknowledgement

The authors, Dennis Meinderink, Ignacio Giner and Guido Grundmeier, acknowledge the partial funding of the project by the German Science Foundation (SPP 1640, 1709 / 16-2).

References

[1] K.-B. Hung, J. Li, Q. Fan and Z.-H. Chen, *Composites: Part A*, 39 (2008), 1133-1140.

[2] C. Decker, R. Vataj, and A. Louati, *Progress in Organic Coatings*, 50 (2004), 263-268.

[3] S. Dujardin, R. Lazzaroni, et. al., *J. Mater. Sci.*, 21 (1986), 4342-4346.

P02.051-TFC041

UTILIZATION OF EFFECTIVE MEDIUM APPROXIMATION, RAYLEIGH-RICE THEORY AND SCALAR DIFFRACTION THEORY AT THE OPTICAL CHARACTERIZATION OF RANDOMLY ROUGH SILICON SURFACES COVERED WITH NATIVE OXIDE LAYERS

I. Ohlidal, J. Vohanka, M. Cermak, D. Franta
Department of Physical Electronics, Faculty of Science, Masaryk University - Brno (Czech republic)

Surface roughness is defect occurring very frequently in practice. Many surfaces of solids and boundaries of thin films prepared by various technological procedures exhibit this defect that mostly influences their physical properties in a substantial way. In particular the optical properties of surfaces and thin films together with their optical characterization are influenced by random roughness. Therefore, it is necessary to have methods incorporating this defect into the optical characterization of these objects.

In this contribution the method for the optical characterization of randomly rough surfaces of silicon single crystal covered with very thin native oxide layers (NOL) will be described. This method is based on variable angle spectroscopic ellipsometry and near-normal reflectometry. Ellipsometric data consist of spectral dependencies of three associated ellipsometric parameters measured for several incidence angles and the reflectometric data contain spectral dependencies of reflectance measured at near-normal incidence. Both the data were measured within the spectral range 1.24-6.5 eV (190-1000 nm).

Randomly rough silicon surfaces were prepared by anodic oxidation and following dissolution of grown oxide films. By means of the selecting of the technological conditions of anodic oxidation the silicon surfaces exhibiting slight and moderate roughness with the rms values of the heights of roughness from several nanometers to tens of nanometers were prepared. This implies that the different theoretical approaches must be employed for characterizing individual samples in this method.

A comparison of the effective medium approximation (EMA) approaches and the Rayleigh-Rice theory (RRT) for slightly rough silicon samples is carried out. It is shown that the RRT provides better results than the EMA approaches. For the moderately rough samples the RRT and scalar diffraction theory (SDT) are compared. It is shown that the magnitude of the autocorrelation length T influences whether the RRT is the better method than the SDT for characterizing these surfaces. For larger values of T the SDT is better while the RRT is better for smaller values of T. It is also presented that for rougher silicon surfaces it is reasonable to combine the SDT and RRT. Moreover, it is proved that the NOL thickness and NOL refractive index can be determined with a satisfactory precision within all the approaches.

Thanks/Acknowledgement

This work was supported by the project LO1411 (NPU I) funded by Ministry of Education Youth and Sports of the Czech Republic. The authors also thank to Dr. P. Klapetek from the Czech Metrology Institute for preparing the samples.

P02.052-TFC075

MORPHOLOGICAL AND CHEMICAL COMPOSITION OF CH3NH3PBI3/TIO2 SOLAR CELL LAYERED SYSTEM

V-D. Hodoroaba [1], S. Rades [1], S. Narbey [2], F. Oswald [2], J. Radnik [1]
[1]Federal Institute for Materials Research and Testing (BAM) - Berlin (Germany), *[2]Solaronix SA - Aubonne* (Switzerland)

The motivation behind this work is to produce thin films perovskite solar cells with constant high light conversion efficiency over time [1]. Loss of efficiency may be caused by structural and/or chemical alterations of the complex layered system. As these changes might take place either in the bulk and/or on the surface of the stratified material, analytical tools addressing both key issues are selected and combined. SEM/EDX combined with XPS were chosen as appropriate methodical approach to characterize perovskite laboratory cells in depth and at surface, before and after light exposure. The layered perovskite system investigated here is based on glass covered with fluorine doped tin oxide (FTO), followed by three porous thin films of TiO_2, ZrO_2 and a thick monolithic carbon (Fig. 1 top). TiO_2 film is subdivided into a dense layer covered by porous one constituted of nanoparticles (NPs) of truncated bipyramidal shape [2]. This layered system serves as the matrix for the perovskite. After infiltration of perovskite solution and annealing, EDX spectral maps on cross-sections of specimen have been taken. Distribution of elements Si, Sn, Ti, Zr and C correlate conclusively with layers visible in SEM images. Pb and I are distributed throughout the porous layers C, ZrO_2 and TiO_2, see Fig. 1 bottom. Specimens were exposed to ambient daylight for 7 weeks. SEM/EDX data have been acquired under the same measurement conditions as before the illumination. It was found that several weeks of ambient daylight did not change significantly the qualitative elemental composition of Pb and I throughout the solar cell system. It was confirmed with EDX that NPs identified in high-resolution SEM micrographs contain mainly Pb and I, indicating these to be the perovskite crystals. However, a time-dependent compositional and chemical altering was observed with XPS for the near-surface region of the outermost ~10 nm after 2 months of illumination.

References

[1] L. Etgar et al., 2012 *J. Am. Chem. Soc.* **134** 17396-17399

[2] E. Ortel et al., 2015 *Microsc. Microanal.* **21** (Suppl 3), 1707-1708

Fig. 1 top: layout of solar cell layered system and bottom: 10 kV EDX linescan

P02.053-TFC080

DEPTH ANALYSIS OF AL/ZRC INTERFACES USING SIMS AND X-RAY REFLECTIVITY TECHNIQUES

M.H. Modi [1], M. Sinha [1], A. Bose [2], A. Singh [3], P. Jonnard [4]

[1]*Soft X-ray Applications Lab, Raja Ramanna Centre for Advanced Technology - Indore* (India), [2]*Superconducting Proton Linac Section, Raja Ramanna Centre for Advanced Technology - Indore* (India), [3]*3National Synchrotron Radiation Research Center - Hsinchu* (Taiwan, republic of china), [4]*LCPMR / UPMC/ CNRS - Paris* (France)

X-ray waveguide is analogous to optical fibre where the beam is guided through a core sandwiched between a cladding materials. This concept is used to generate nanosize beams in x-ray regime. In x-ray waveguides, the electric field of incident beam is confined inside a layer through the generation of x-ray standing waves. The guiding layer is generally made of a light material surrounded by two layers made of heavy materials. In the literature very few attempts have been made to understand the role of materials combination, film roughness, interface width, etc. on the performances of waveguides. The main challenge in x-ray waveguide optics is to overcome fabrication difficulties to make smooth interfaces and prevent intermixing between the guiding and cladding layers.

In the present study time of flight secondary ion mass spectroscopy (ToF-SIMS) and soft x-ray reflectivity (XRR) measurements, carried out to analyse interfaces in a C/Al/ZrC/Al/W waveguide structure. The scheme of the sample is shown in Figure 1 where indicated thicknesses are the aimed oens during the design. The Carbon layer was coated to protect the top Al layer from the ambient. The sample was prepared in an ion beam sputtering setup using Ar ion beam in a 3CM dc ion source. ToF-SIMS analysis was done using 30 keV Bi^{1+} ion beam. XRR measurements were carried out using the Indus reflectivity beamline. ToF-SIMS depth profiles of C, Al, Zr and W are shown in Figure 1. They suggest that interdiffusion is taking place at all the interfaces. Details of XRR analysis and SIMS data will be presented and a correlation between optical performances and elemental profiles will be given.

Fig. 1: (top) design of the sample; (bottom) ToF-SIMS depth profiles of the as-deposited C/Al/ZrC/Al/W on silicon substrate.

P02.055-TFC095

STRUCTURAL AND CHEMICAL CHARACTERIZATION OF NANOSTRUCTURED SNO2 AND PD-SNO2 FILMS PREPARED BY GLANCING ANGLE MAGNETRON SPUTTERING

I. Khalakhan [1], M. Chundak [2], T. Duchon [1], P. Kúš [1], V. Potin [3], A. Cacucci [3], K. Veltruská [1], V. Matolín [1]

[1]Charles University - Prague (Czech republic), [2]National Institute for Materials Science - Tsukuba (Japan), [3]Université de Bourgogne - Dijon (France)

Tin oxide is a material which attracts attention of researchers due to its wide varieties of technological applications. The main parameters that can influence its valuable properties are morphology, crystalline structure and stoichiometry. By tuning these parameters it is possible to fabricate nanostructured tin oxide that conforms to its specific technological application. Herein, we present structural and chemical characterization of SnO2 and Pd-doped SnO2 nanoporous films prepared by magnetron sputtering with integrated glancing angle deposition (GLAD) technique. Simultaneous use of these techniques enables controllable deposition of different nanostructured surfaces, such as slanted columns, vertically aligned columns, spiral columns, zig-zag structure etc.

Morphology of SnO2 and Pd-SnO2 nanostructures was investigated by scanning electron microscopy (SEM) and it was shown that slanted columns possess the highest surface area among different types of nanostructures. Characterizations of slanted type of the films were then performed by means of transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and synchrotron radiation photoelectron spectroscopy (SRPES). The influence of substrate annealing and Pd doping on the morphology, crystalline structure and stoichiometry of SnO2 films was investigated. The obtained TEM data showed that annealing of the substrate during the deposition allows changing crystallinity of the deposited nanostructures. Photoelectron spectroscopy measurements revealed 4+ as the main oxidation state of Sn and also confirmed formation of the PdSn alloy in the case of Pd-doped samples.

P02.056-TFC122

MECHANISM OF TRANSBOUNDARY HEAT TRANSFER IN PLANAR MIM METAMATERIAL ON BASE OF TIALN/AG BY EXCITATION OF ELECTRONIC HOT CARRIERS AND PHONONS.

A. Kovalev [1], D. Wainstein [1], V. Vakhrushev [2], R. Gago [3], F. Soldera [4], J.L.L. Endrino [5]

[1]*Surface Phenomena Researches Group, I.P. Bardin Central Research Institute for Ferrous Metallurgy - Moscow* (Russian federation), [2]*Surface Phenomena Researches Group, I.P. Bardin Central Research Institute for Ferrous Metallurgy;Moscow Technological University "MIREA", "MGUPI", - Moscow* (Russian federation), [3]*Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas - Madrid* (Spain), [4]*Department of Materials Science and Engineering, Saarland University - Saarbruecken* (Germany), [5]*Surface Engineering and Nanotechnology Institute, School of Aerospace, Transport and Manufacturing (SATM), Cranfield University - Cranfield* (United kingdom)

Plasmon resonance heterogeneities were identified and studied in Ag and TiAlN layers within a multilayer stack in nanolaminate TiAlN/Ag coatings. For this purpose, a method of high resolution plasmon microscopy was used (Fig. 1). The plasmons intensity, energy, and depth of interface plasmon-polariton penetration were studied by scanning reflected electron energy loss spectroscopy. Phonon spectra were investigated by HREEL spectroscopy. The heat conductivity of such metal-insulator-metal (MIM) nanolaminate coatings was measured by laser reflexometry. Dependences of thermal conductivity coefficient of coatings, MIM interfaces, and resistivity of Ag layers vs. Ag layer thicknesses were calculated on the basis of experimental data. The contribution of phonon propagation and plasmon resonance confinement to the abnormal lower thermal conductivity in the MIM metamaterial with Ag layer thickness below 23 nm is discussed. The thermal conductivity of the multi-layer MIM nanomaterial depends on the combination of several factors. Spatial splitting of plasmons together with quantum phenomena in silver nanolayers suppress the depth of the plasmon-polariton excitations near the metal-dielectric interface and significantly affect the thermal conductivity of TiAlN/Ag MIM coatings. Injection of free silver electrons into TiAlN conduction band is the basis of transboundary SPP electronic mechanism of heat transfer. These results evidence some of the features of the heat transfer mechanism of MIM multilayers and open a new prospective for plasmon physics and engineering of plasmonic metamaterials. The anisotropy of LA and TA phonons interface propagation in nanogeterostrucrures dramatically decreases the heat transfer in multilayer MIM coating. It was found that the distribution of the plasmon resonance within the Ag nanolayers and plasmon-polariton penetration depends on the Ag layer thickness. This is clearly demonstrated by detailed structural investigations using plasmon microscopy. This type of design of MIM planar metamaterial has the property to strongly adjust the heat propagating.

Thanks/Acknowledgement

The research was partially supported by RSF grant #14-12-00170 and RFBR project # 16-08-00527, grant P2013/MIT-2775 (Comunidad Autónoma de Madrid, Spain) and Marie Skłodowska-Curie grant agreement No 645725 (Friends2).

P02.057-TFC152

INFLUENCE OF THE PRELIMINARY ANODIZATION OF AA2024-T3 ON THE CERIUM-BASED CONVERSION COATINGS MORPHOLOGY AND PROPERTIES

I. Avramova [1], S. Kozhukharov [2], C. Girginov [2], G. Avdeev [3]

[1]Institute of General and Inorganic Chemistry, Bulgarian Academy of Science, 11 "Acad. Georgi Bonchev" Str., 1113 - Sofia (Bulgaria), [2]University of Chemical Technology and Metallurgy, 8 "Kliment Ohridski" Blvd., 1756 - Sofia (Bulgaria), [3]Institute of Physical Chemistry, Bulgarian Academy of Science, 11 "Acad. Georgi Bonchev" Str., 1113 - Sofia (Bulgaria)

Cerium-based conversion coatings (CeCCs) on high strength aluminum alloys such as AA20224-T3 can significantly improve their corrosion resistance [1]. Furthermore, the CeCC performance can be additionally improved by appropriate substrate surface conditioning by chemical [2] or electrochemical treatment [3]. In this sense, the anodization appears a promising approach for preliminary surface modification. Considering the above mentioned statements, preliminary anodization of the AA2024-T3 alloy, followed by chemical deposition of cerium oxide layer is proposed, as an approach for further CeCC protective capability extension. The anodization was performed under galvanostatic (15 $mAcm^{-2}$) and isothermal (20 °C) regime in H_2SO_4 (15 wt.%) aqueous solution for different durations (12, 24 and 48 min.). The subsequent dip-coating CeCC deposition was carried out for 4 min. at 60 °C in 0.03 M $(NH_4)_2Ce(NO_3)_5$ solution with NaCl and H_2O_2 as deposition activators. The influences of anodization time on the formation of alumina intermediate layer, as well as its role on the properties of combined alumina/ceria oxide have been studied. The morphologies of the coatings were observed by scanning electron microscopy (SEM). Energy-dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS) were used to analyze the chemical composition and the oxidation states of the elements in the coatings. The XPS shows that the coatings consist of mixed cerium oxides. The Ce^{3+} states increases versus time of advance anodization of the alloy, due to the formation of additional $CeAlO_3$-like phase. The X-ray diffraction (XRD) analysis was performed for evaluation of coatings phase composition. The corrosion behavior of the coatings in conventional model NaCl media was described by regular measurements (for 168 and 672 hours) using Electrochemical Impedance Spectroscopy (EIS), combined with linear voltammetry (LVA). The obtained results are discussed in detail.

Thanks/Acknowledgement

The present research work has been performed with the financial support of the Bulgarian National Scientific Fund, Ministry of Education and Science, under Project DFNI T02/27-2014.

References

[1] T G Harvey, Cerium-based conversion coatings on aluminium alloys: a process review, 48, (4), (2013) 248 – 269.

[2] S. V. Kozhukharov, (2016) Deposition of Environmentally Compliant Cerium-Containing Coatings and Primers on Copper-Containing Aluminium Aircraft Alloys, PUBLISHED IN: Biobased and Environmental Benign Coatings (eds A. Tiwari, A. Galanis and M. D. Soucek), John Wiley & Sons, Inc., Hoboken, NJ, USA. doi: 10.1002/9781119185055.ch2.

[3] S. Kozhukharov, Ch. Girginov, I. Avramova, M. Machkova, Anodic galvanostatic polarization of AA2024-T3 aircraft alloy in conventional mineral acids, Materials Chemistry and Physics, 180 (2016) 301 – 313.

P02.058-TFC180

INTERFACIAL MORPHOLOGY OF ZNO NANORODS ARRAY GROWTH ON CONDUCTIVE AND TRANSPARENT GIZO

F. Martin Jimenez [1], D. Solis Cortes [2], E. Navarrete Astorga [2], M.C. Lopez Escalante [1], E.A. Dalchiele Lueiro [3], D. Leinen [2], J.R. Ramos Barrado [2]

[1]Departamento de Ingenieria Quimica, Universidad de Málaga - Málaga (Spain), [2]Departamento de Fisica Aplicada I, Universidad de Málaga - Málaga (Spain), [3]Instituto de Física, Facultad de Ingeniería, Universidad de la Republica - Montevideo (Uruguay)

ZnO is a wide bandgap semiconductor that has attracted increasing interest due to a direct bandgap of about 3.37 eV and high exciton binding energy (60 meV) at room temperature. It has also has attracted increasing interest due to its ability to form a variety of nanostructures such as nanowires, nanorods, nanobelts, nanocombs and nanospheres. Among them, nanorods when forming arrays (NRAs) are the most interesting, and specifically when NRs are vertically arranged with respect to the substrate. The ZnO nanorods exhibit fewer defects than ZnO thin-film structures present, and present a pseudo-one dimensional structure with an enhanced surface-to-volume ratio and confinement effects. ZnO nanorods, it is, therefore, a promising material for optoelectronic applications. The growth of high quality well-aligned ZnO NRAs is required in practical applications. Moreover, it is important to grow well-aligned ZnO NRAs onto transparent conducting oxides (TOC) electrodes for better light management in optoelectronic devices. ITO and FTO are usually used as TOC. On the other hand, the physical properties of ZnO NRAs are strongly affected by their morphology in terms of shape. In order to grow ZnO NRAs controllably and reproducibly, different works reported the electrochemical growth of ZnO nanorods onto a previously deposited ZnO seed layer. The ZnO seed layers has been reported as grown by different techniques such as: electrodeposition, sol-gel, spray-pyrolysis, atomic layer deposition and sputtering. Indium Gallium Zinc Oxide (IGZO) has emerged as a high quality transparent conductive oxide (TCO) due to its high transmittance, conductivity, mobility, low temperature growth and suitability for many types of substrate materials being more economical than Indium Tin Oxide (ITO). IGZO thin-film transistors. The crystallinity and composition of the GIZO has influence on its electrical conductivity. Crystalline and amorphous IGZO thin films have been obtained by magnetron sputtering on glass by co-deposition from In2O3 (99.99%) and 2% Ga-doped ZnO (99.9%) targets. Chemical characterization of the IGZO films was carried up by XRD, EDS and XPS. Mechanical profilometry and FE-SEM images demonstrate that the surface morphology of the IGZO films were very smooth. ZnO NRAs were growth by electrochemical techniques on the obtained IGZO films without using any ZnO seed layers. HRTEM has been used to study the interface between ZnO NRA/GIZO and comparatively the ZnO NRA/ITO interface too.

Thanks/Acknowledgement

The authors want to thank to the Ministry of Economy and Competitiveness and Regional Andalucía Government for their financial support, project TEC2014-23906 and RNM-1399.

P02.060-TFC224

XPS COMPOSITION STUDY OF HF-AL-OXIDES FOR MIM CAPACITORS

S. Spadoni [1], E. Ravizza [1], S. Grasso [1], R. Piagge [1], B.W. Schmidt [2]
[1]STMicroelectronics - Agrate Brianza (Italy), [2]Physical Electronics (PHI) - Chanhassen, Minnesota (United States of America)

Mixed Hf-Al-oxides are promising high-k dielectrics for Metal-Insulator-Metal (MIM) advanced capacitor [1] since the dielectric constant can be modulated by its composition.

To identify the best film composition versus the required electrical performances the Hf:Al ratio is determined by XPS at high take-off angle (ToA) in order to reduce the adventitious C contribution. This provides an accurate measure if Hf and Al distribution is homogenous in the layer.

Ar^+ sputtering is a common approach to clean surfaces prior investigation or to obtain information from deeper regions. However, severe damage of the materials can affect the validity of the analysis. Monoatomic Ar+ even at low energy causes changes to the chemical states.(Fig.1).

On the contrary, depth profile of near-surface region by C_{60}^+ sputter gun produces a negligible damage (no chemical state reduction observed-Fig.2) therefore allowing an accurate evaluation of film composition.

Different Hf-Al oxides compositions have been explored in the Hf range of 10-30 at%.

C_{60}^+ cleaning gives no visible sign of oxide reduction while, deep etching the film, Hf carbide appears, suggesting that the ion beam damage is reduced but still present.

References

[1] International Technology Roadmap for Semiconductors (ITRS), On-Chip Passives Technology Requirements, Semiconductor Industry Association, Washington, DC, USA, 2013.

P02.061-TFC230

MICRO-ENCAPSULATION OF ISOPHORONE DIISOCYANATE DROPLETS WITH SILICA-ORGANO HYBRIDE SHELL AND APPLICATION TO SELF-HEAING COATING

Y.H. Kim, E.H. Cho, G. Jeoung
Hankyong National University - Ansung (Korea, republic of)

In this research, a self-healing composites, microcapsules were synthesized with an organo-inorgano hybrid shell containing IPDI(Isophorone diisocyanate) through interfacial polymerization method.

The core material was first encapsulated in a soft and thin layer of silica-organo-polymer hybrid material by precipitation from supersaturated with adjusted pH and temperature. Subsequently, controlled growth of this shell was achieved by the drop-wise addition of tetraethoxysilane, at lower ethanol concentrations and higher ammonia concentrations.To confirm the capsule wall thickness and surface morphology, the microcapsules were investigated by optical microscope and SEM(Scanning electron microscopy). SEM showed that the microcapsule particles were typically about 3-5 um in diameter, with silica shells of thickness about 100-500 nm.Finally, the self-healing coating layer were prepared on a test pieces. It was observed that when the scratch was take place, the core material (IPDI) was flows and fills out the cracks, and then it was polymerized with moisture of the atmosphere.

Thanks/Acknowledgement

This research was suppoted from Research Village Project(2016) by a grant of the Korea Small and Medium Business Afministration.

References

1. C.I.Zoldesi at. al. J. Colloid and Interface Sci. 308, 121-129 (2007)
2. S. J. Garcia, et. al., Progree in Org. Coating, 72, 211-221 (2011)
3. S. Yang., et. al., Composites Sci. and Tech., 136, 133-144 (2016)

P02.062-TFC233

HARD X-RAY PHOTOELECTRON SPECTROSCOPY FOR MULTI-LAYER SEMICONDUCTOR SAMPLES

C. Deeks, P. Mack, T.S. Nunney
Thermo Fisher Scientific (United kingdom)

Over the past decade improved instrument reliability and automation has led to the broader use of X-ray Photoelectron Spectroscopy (XPS); changing from a specialist technique only performed by dedicated practitioners to a routine analysis tool that is widespread throughout academia and industry.

In typical operation, with the use of a monochromated aluminium anode, XPS has an inherent information depth of ~10nm. The most common methodology for elucidating the chemical composition further within the bulk is to destructively sputter away layers of material, exposing the underlying substrate, allowing a profile of the chemical composition with substrate depth to be generated through iterative cycles of sputtering and spectra reacquisition.

An alternative, non-destructive approach is to use incident radiation of a higher energy, ‘hard’ x-rays, than that which is typically used in laboratory instruments to perform XPS (HAXPS). Whilst this approach has been used with great success at synchrotron facilities it has not yet found widespread use in laboratory XPS instruments.

The monochromated silver anode is a becoming an increasingly popular option but this has one major drawback as its flux is much lower than a monochromated aluminium anode, and so count rates are much lower and acquisition times are longer.

The alternative to using a monochromated anode is to use a non-monochromated source. These provide much higher count rates, so the acquisition times are much shorter, improving throughput. Hard X-ray sources such as titanium are readily available, but again these have a drawback in that there is the occurrence of satellite features due to other X-ray emission lines.

Here we shall discuss the implementation of HAXPS in laboratory instrumentation, made possible using a hemispherical analyser capable of detecting photoelectrons of high kinetic energy and a twin anode X-ray source. By using a twin anode, qualitative depth profiles can be performed through comparison of analysis using a variety photon energies.

More importantly, we will demonstrate the use of a satellite subtraction feature within the software to remove the effect of these satellite features which cause difficultly in identification and quantification of X-ray peaks. We will present the benefits of using HAXPS on a range of samples, showing the benefits of high energies in depth, as well as the use of Auger shifting and the benefits of software manipulation of the acquired data.

P02.063-TFC246

STRUCTURAL DAMAGE ON SINGLE-CRYSTAL SI LAYER BY HEAVY ION IRRADIATION

R. Miksova [1], A. Mackova [1], A. Jagerova [1], P. Malinsky [1], Z. Sofer [2]

[1]Nuclear Physics Institute of the CAS, v. v. i. - Rez (Czech republic), [2]Department of Inorganic Chemistry, Institute of Chemical Technology - Prague (Czech republic)

Structural modification after medium heavy ion irradiation were characterized by Rutherford backscattering spectrometry in the channelling mode (RBS-C) for pristine a silicon-on-insulator material (SOI). The irradiation of SOI was provided using $^{6}C^{n+}$, $^{7}N^{n+}$ and $^{8}O^{n+}$ ions at fluencies 1×10^{14} and 1×10^{15} cm^{-2} and energies 0.4, 3 and 5 MeV to follow the interplay of electronic and nuclear stopping and its influencing of the damage accumulation. The relative number of disordered atoms in the surface irradiated layer was extracted from RBS-C spectra (using as a probe He ions 2 MeV), simultaneously with the fine scan analysis to follow the ion channelling effects in the modified crystalline lattice. The back-scattered yield variation during RBS-C analysis around the aligned direction was experimentally determined as a function of the ion incoming angle. The fine scans shape was discussed in connection to the theoretical calculation done by Lindhard theory. The discussion of the ion penetration through modified SOI structure crystalline layer in channelling direction was supported by MC simulation (FLUX code) of He ion flux maps in gradually modified Si crystalline upper layer taking into account the experimentally determined relative number of vacancies from RBS C.

RBS-C measurement show as that the ion irradiated samples exhibit increase of the disorder after irradiation by 0.4 MeV $^{6}C^{n+}$, $^{7}N^{n+}$ and $^{8}O^{n+}$ ions at ion fluence of 1×10^{15} cm^{-2} (~3% with connection of the ion mass). For other energy increase, the disorder after irradiation is less than 1.5%.

Thanks/Acknowledgement

The research has been carried out at the CANAM (Centre of Accelerators and Nuclear Analytical Methods) infrastructure LM2015056. The work was supported by Czech Science Foundation (GACR No. 15-01602S) and SGS UJEP project.

P02.065-TFC273

STUDY OF PARTICULATES IN AGGESE THIN FILMS DEPOSITED BY PLD

J. Conde Garrido, J. Bobadilla, J.M. Silveyra
Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Sólidos Amorfos / CONICET, INTECIN - Buenos Aires (Argentina)

Pulsed laser deposition (PLD) is a technique for fabricating thin films that, because of its simplicity, offers great experimental versatility. It allows the stequiometric transfer of mass from the target to the substrate and the physical properties of the films are, in many cases, superior to those obtained by other techniques.

The main limit for the application of PLD in micro/nano-devices is the presence of particulate at the surface of (and sometimes even inside) the films.

In this work, we deposited thin films by PLD of the AgGeSe system on Si wafers. We tested various deposition parameters and studied the films through SEM. We present the dependence of the number of particulates and their sizes on the deposition parameters.

On examining the targets after ablation, we found that the bigger particulates originate from the tips of the cones that form on the target's surface during the ablation.

Thanks/Acknowledgement

The authors would like to acknowledge the financial support of Universidad de Buenos Aires, CONICET and ANPCyT.

P02.066-TFC281

CONTRIBUTION OF THE SURFACE CONTAMINATION OF URANIUM COMPOUNDS ON THE QUANTITATIVE ANALYSIS BY ELECTRON PROBE MICROBEAM ANALYSIS

E. Brackx [1], O. Dugne [2], E. Excoffier [1], C. Gueneau [3], J. Braun [4]

[1]CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes SA2I LMAC - Bagnols Sur Ceze (France), [2]CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes - Bagnols Sur Ceze (France), [3]CEA, Nuclear Energy Division, Service of the corrosion and the behaviour of Materials in their Environment, (SCCME), CEA, University of Paris-Saclay - Gif Sur Yvette (France), [4]CEA, Nuclear Energy Division, Service of Applied Metallurgical researches (SRMA), CEA, University of Paris-Saclay - Gif Sur Yvette (France)

Electron Probe Microbeam Analysis (EPMA) is largely used for nuclear fuels to support R &D studies as fuel fabrication, post irradiation examination, chemical compatibility between fuel and structural materials and severe accident post-test (CORIUM) to determine chemical composition of material with high accuracy.

Uranium materials (metallic alloys or ceramic) are sensitive to oxidation even at room temperature after metallographic preparation; it induces an overestimation of oxygen measurements. In some case, it could be difficult to distinguish the difference between an oxidized surface and an oxide compounds based on EDS measurements. The quantification of light elements (C, N, O) in uranium compounds could be altered by surface contamination or native oxidation in a range of few nm and 100 nm.

Electron probe microanalysis (EPMA), originally developed for determining the composition of bulk samples, has become well established techniques for determining thickness but also composition of multi-elements thin films deposited on a substrate. The present contribution is related to the optimisation of analyses by EPMA of uranium compounds in taking into account surface contamination or native oxidation. The raw measurements could induce wrong interpretation or phase diagram.

Some example of quantification operated on reduction of UO2 in molten salts media (1123 K), UC obtained by arc melted fabrication, Uranium samples obtained by interaction at high temperature for severe accident research could be presented. Auger Spectroscopy, XPS and SIMS could be used to complete the quantification of the oxidation.

P02.067-TFC291

ELECTRICAL CHARACTERIZATION OF THIN FILM CHALCOGENIDE GLASSES FOR GAS SENSORS

J. Conde Garrido, J.M. Silveyra, O. Cuellar Rodrigues, M.A. Ureña
Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Sólidos Amorfos / CONICET, INTECIN - Buenos Aires (Argentina)

Among the several applications that chalcogenide glasses have, one of the latest is their use as sensitive materials for the detection of gases. Although many materials have been successfully tested as sensitive membrane for gas sensors, chalcogenide glasses have the advantage of not requiring high temperatures for the detection of gasses. Tellurium based membranes were the subject of many investigations during the last decade [1], but other chalcogenide systems are being studied as well [2,3].

In this work, we studied the electrical properties of GeTe and GeSe3 thin film glasses deposited by pulsed laser deposition (PLD). We measured the conductivity of the films by DC measurements and AC spectroscopy. We performed the measurements under various temperatures and under vacuum and NO2 atmospheres. We encountered in both systems that their conductivity changes in the presence of NO2, which means that they are both good options for sensing NO2. On account of these results, in future work, we will study whether the addition of other elements to the membrane will improve the electrical response of the sensor.

Thanks/Acknowledgement

The authors would like to acknowledge the financial support of Universidad de Buenos Aires, CONICET and ANPCyT.

References

[1] D. Tsiulyanu, M. Ciobanu, Impedance Characterization of Gas Sensitive S-Te Based Quaternary Chalcogenides, 3rd International Conference on Nanotechnologies and Biomedical Engineering pp 382-388, DOI: http://dx.doi.org/10.1007/978-981-287-736-9_92

[2] V. Georgieva, Tz. Yordanov, V. Pamukchieva, D. Arsova, V. Gadjanova, and L. Vergovless, Gas Sensing Properties of Ge-As-S Thin Films, AIP Conference Proceedings 1203, 1079 (2010); DOI: http://dx.doi.org/10.1063/1.3322314

[3] Ping Chen, Maria Mitkova, Dmitri A. Tenne, Kasandra Wolf, Velichka Georgieva, Lazar Vergov, Study of the sorption properties of Ge20Se80 thin films for NO2 gas sensing, Thin Solid Films, Volume 525, 15 December 2012, Pages 141-147, ISSN 0040-6090, DOI: http://dx.doi.org/10.1016/j.tsf.2012.09.077.

P02.068-TFC340

P-AR-XPS INVESTIGATION OF SPINTRONIC MEMORY BUILDING BLOCKS

M. Mahjoub [1], B. Pelissier [1], A. Trifu [2], J. Nath [2], M. Miron [2]
[1]CNRS, LTM, MINATEC Campus, F-38054 - Grenoble (France), [2]CNRS INAC-SPINTEC, F-38000 - Grenoble (France)

Ferromagnetic metals and oxides are the building blocks of spintronic memory devices such as magnetic tunnel junctions (MTJ) [1]. Composed of at least two distinct ferromagnetic metals separated by an oxide, the MTJ can store information as the relative orientation of the magnetization of the two ferromagnets. The information can be read using the tunnel magnetoresistance: a low resistance state corresponds to the parallel alignment, while the anti-parallel magnetic configuration produces a high resistance state. Writing the information relies on a phenomenon called Spin Transfer Torque [2] (STT), which involves the transfer of angular momentum from one magnetic layer to the other by an electric current.

Both reading and writing of the magnetic memory require a tunneling current to be applied from one ferromagnetic layer to the other and through the oxide. In this context, the precise control of the oxidation state at the interface between the ferromagnet and the non-magnetic oxide becomes crucial.

Here we report a study of the interfacial oxidation of a Co thin film through a Pt capping layer. This study is performed using the parallel Angle-Resolved X-ray photoelectron spectroscopy (pAR-XPS) [3]. We find that a thin (1-2 nm) Pt layer is sufficiently thin to protect Co from natural oxidation, but allows a controlled interfacial oxidation when using an oxygen plasma (Fig.1).

Thanks/Acknowledgement

This work has been supported by the French ANR program «Investissements d'Avenir", contract ANR-10-EQPX-33

References

[1] Yusa, Shinji et al, Nature materials 3.12, 868-871, 2004.

[2] Slonczewski, John C et al, journal of magnetism and magnetic Materials 159. 1-2, 1996.

[3] L. Fauquier, B. Pelissier et al, Microelectronic Engineering, vol 169, 24-28, 2017.

P02.069-TFC343

FABRICATION OF GRAPHENE/MOS2NANOCOMPOSITE FOR FLEXIBLE ENERGY STORAGE

S. Khasl, M. Namdar
University Of Tabriz - Tabriz (Iran, islamic republic of)

In the present work,MoS2 decorated graphene nanocomposite powders were synthesized by laser scribing method.Theobtainedflexible light-scribed graphene/MoS2composites are very suitableas micro-supercapacitors and thus their performance was evaluated at different concentrations. The GO/MoS2composite was synthesized using a chemical mixing of GO solution withMoS2/Dimethylformamide (DMF)solution.Themixtures with various concentrations of MoS2were then coated on a LightScribe DVD disk and laser scribed to reduce GO and create aMoS2/laser-scribed graphene (LSG) composite. Four different concentrations of MoS2/LSG composites (pristine rGO, 1:100, 1:75 and 1:50 MoS2/LSG) were utilized as supercapacitor electrode and the electrode with the best performance was selected for flexible micro-supercapacitor applications.

References

[1] D Pech, M Brunet, H Durou, P Huang, V Mochalin, Y Gogotsi, PL Taberna, ... Nature nanotechnology 5 (9) (2010) 651

[2] Chmiola J, Largeot C, Taberna PL, Simon P, Gogotsi Y. Science 328 (2010) 480.

[3] Simon P, Gogotsi Y. Nat Mater 78 (2008) 45.

[4] Mai LQ, Yang F, Zhao YL, Xu X, Xu L, Luo YZ. Nat Commun 2 (2011) 381.

[5] J. M. Sieben, E. Morallón and D. Cazorla-Amorós, Energy 58(2013) 519.

[6] J. T. Zhang, J. W. Jiang, H. L. Li and X. S. Zhao, Energy Environ Sci. 4(10) (2011) 4009.

[7] Yiqing Sun, Qiong Wu and GaoquanShi , Energy Environ. Sci. 4(4) (2011)1113.

[8] S. Stankovich, D.A. Dikin, GH. Dommett, KM. Kohlhaas, EJ. Zimney, EA. Stach, RD. Piner, ST. Nguyen and RS. Ruoff, Nature 442 (2006) 282.

[9] JR. Miller, RA. Outlaw and BC Holloway, Science 329(5999) (2010) 1637.

P02.071-TFC365

MONITORING NITROGEN IN NICKEL THIN FILMS WITH TOF-SIMS

L. Volgger [1], P. Frank [2], H. Hutter [1]
[1]Technische Universität Wien - Vienna (Austria), [2]Infineon Technologies Austria AG - Villach (Austria)

Impurities and dopants have a significant influence on the properties of metals. Therefore, the analysis and determination of these amounts are inevitable. In many fields of modern industry, metal thin films are necessary and desired to reduce the amount of resources and the size of the product. To examine thin films in a nm range a measurement method with a high depth resolution is required. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a method that combines the required depth resolution with high mass resolution. ToF-SIMS provides an excellent detection limit for many elements, but on the other hand, some elements have a low secondary ion yield and therefore are barely detectable. Nitrogen for example is one of those elements. It can form nitrides, which can have negative effects on the mechanical properties. One possibility to cope with this problem is the detection of CsN^+-clusters by using a Cs primary beam [1]. Especially in organic mass spectrometry observing CN^--cluster are a solution for this problem [2]. The secondary ion yield of cyanide ions is several orders of magnitude higher than the yield of nitrogen ions. However, inorganic samples like metal thin films are lacking carbon and modern sputter techniques allow a reduction of impurities, so that the formation of CN^- is very unlikely. Therefore, it is necessary to supply the sample with an external carbon source.

In this work we tried to monitor the nitrogen amount in sputtered nickel thin films. To provide the carbon for the formation of cyanide ions, CH_4 gas was lead onto the sample surface. A CH_4 partial pressure between 0 and 10^{-6} mbar was chosen to observe a possible saturation of the CN^- signal. In addition, samples with different amounts of nitrogen were investigated to determine a correlation between the nitrogen amount in the sample, the CH_4 partial pressure and the detected signal.

References

[1] Y.Li, S. Wang, S.P. Smith, Applied Surface Science, Vol. 252, Issue 19, pp. 7066-7069 (2006)

[2] R. Peteranderl, C. Lechene, Journal of the American Society for Mass Spectrometry, Vol. 15, Issue 4, pp. 478-485 (2004)

P02.073-TFC407

LOCAL MECHANICAL PROPERTIES OF BENZOXAZINE COATINGS AS A FUNCTION

E. Pospisilova [1], A. Renaud [2], M.G. Olivier [2], A. Delcorte [1], B. Nysten [1]
[1]Institute of Condensed Matter and Nanoscience (IMCN), Universite catholique de Louvain (UCL) - Louvain-La-Neuve (Belgium), [2]Materials Engineering Research Center (CRIM), Univeristy of Mons (UMons) - Mons (Belgium)

In 2017, the use of bio-toxic chromates has been banned. This change in law has affected aeronautical industry, where chromates were used for anti-corrosion treatments of aluminum alloys. New materials are studied to replace the chromates and poly-benzoxazines exhibit promising properties [1]. In this study we focus on para-phenylenediamine benzoxazine (P-pPDA), that have been already studied by Electro-chemical Impedance Spectroscopy (EIS) and exhibit excellent barrier properties. However, it seems that fully cross-linked P-pPDA coatings delaminate from the aluminum alloy during saline tests [2]. The decrease of the curing temperature to avoid the delamination of the coating while preserving the mechanical properties of the alloy as well as the barrier properties of the coating is necessary. A decrease of curing temperature leads to partially cross-linked P-pPDA coating. In the case of partially cross-linked epoxy resins, local mechanical properties proved to be heterogeneous at the nanoscale [3], however in the case of benzoxazines this information is missing. Therefore, a study dealing with partially cross-linked P-pPDA coatings and their local mechanical properties has been conducted using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Atomic Force Microscopy (AFM). Partially cross-linked coatings were obtained by spin-coating a laboratory synthesized P-pPDA solution on silicon wafers and applying curing cycles in the temperature range from 100°C to 200°C. An original procedure was developed to measure the cross-linking degree of P-pPDA coatings locally, at the surface and long the depth, using the ToF-SIMS intensities of molecular and fragment ions, after calibration of the SIMS data with differential scanning calorimetry (DSC) for a first set of samples. In a previous study, AFM in Force Volume mode was used to study the adhesion force as a function of the cross-linking degree of P-pPDA. Here, AFM in Peak Force Tapping mode is used to evaluate several mechanical properties at the same time. As a result the adhesion force, modulus and energy dissipation are studied as a function of the cross-linking degree of the P-pPDA coatings.

References

1. H. Ishida, D. Allen, *J. Polym. Sci. B: Polym. Phys*. 34 (1996) 1019–1030
2. M. Poorteman, A. Renaud, J. Escobar, L. Dumas, L. Bonnaud, P. Dubois, M.-G. Olivier, Prog. Org. Coat. 97 (2016) 99 – 109
3. A. Bahrami, X. Morelle, L.D. H. Minh, T. Pardoen, C. Bailly, B. Nysten, *Polymer* 68 (2015) 1 - 10

P02.089-TFC459

FABRY-PEROT RESONATORS FOR SURFACE ENHANCED RAMAN SPECTROSCOPY

L. Vanco [1], M. Kadlecikova [2], M. Vojs [2], P. Michniak [2], M. Marton [2], V. Vretenar [1], M. Kotlar [1]

[1]University Science Park Bratislava Centre, Slovak University of Technology in Bratislava, Vazovova 5, 812 43 - Bratislava (Slovakia), *[2]Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in Bratislava, Ilkovicova 3, 812 19 - Bratislava* (Slovakia)

Exceptional signal enhancement, fluorescence quenching and detection limits reaching single molecule sensitivity promote surface enhanced Raman spectroscopy (SERS) as one of the most promising application of nanostructures. Molecules brought to vicinity (< 30 nm) of metal nanostructures exhibit strong Raman scattering proportional to the fourth power of incident intensity of electric field. Concerning large area, cheap and rapid deposition process and stability of SERS spectra in terms of intensity, vacuum evaporated metallic islands used for SERS have an advantage in comparison with other plasmonic nanostructures. However, they feature relatively weak plasmonic enhancement. Interference of light can increase SERS signal in the case of partially absorbing active substrates, e.g. for vacuum evaporated metallic islands. Our contribution deals with the impact of optical Fabry-Pérot resonances on the intensity of surface enhanced Raman spectra. We were focused predominantly on the relation between intensity of SERS bands and reflectance of interference plasmonic structures. We prepared multilayered Si/SiO_2 substrates with different thicknesses of oxide layer (59 to 453 nm) which were decorated by evaporated silver islands. The structures were utilized as active plasmonic and adhesive substrates for a probe of electromagnetic effects – rhodamine 6G. Except of plasmonic enhancement, we also observed interference enhancement of the SERS spectra by the factor of 16 for optimal SiO_2 thickness. Since both, excitation and scattered light can interfere in SiO_2 layers, we related the intensity of SERS bands to the respective reflectances and to the multiple of both reflectances.

Thanks/Acknowledgement

This contribution was created with the support of the Ministry of Education, Science, Research and Sport of the Slovak Republic within the Research and Development Operational Programme for the project "University Science Park of STU Bratislava", ITMS 26240220084, co-funded by the European Regional Development Fund and with the support of the project VEGA 1/0947/16.

References

[1] Ľ. Vančo, M. Kadlečíková, J. Breza, M. Vojs, P. Michniak, M. Marton: Interference enhancement in SERS spectra of rhodamine 6G: Relation to reflectance, Vibrational Spectroscopy (2017), vol. 90, pgs. 31-37.

P02.090-TFC473

INVESTIGATION OF THE FORMATION OF NI-TI INTERMETALLIC LAYERS PRODUCED BY CATHODIC ARC ELECTRON-METAL ION TREATMENT

N. Sezgin, E. Kacar, K. Kazmanli, M. Urgen
Metallurgical and Materials Engineering, Istanbul Technical University - Istanbul (Turkey)

In this study, Ni-Ti intermetallic phases were obtained by a novel cathodic arc plasma treatment. The method is called as cathodic arc electron metal ion treatment. During this process, AC bias was applied to the substrates and in-situ heating was achieved with electrons during coating process. AC bias application has positive and negative bias voltages in a cyclic manner. In the positive cycle, electrons are directed to the substrate and the substrate is heated; in the negative cycle, metal ions deposit on the surface. Therefore desired phases can form in a one shot process including coating and diffusion. For Ni-Ti system, the formation of phases were investigated for 2 different diffusion couples: Ni substrate – Ti cathode and Ti substrate – Ni cathode. The formation sequence difference of the phases were determined related to diffusion couples. For 2 different couples, time (5- 45 min) and temperature dependent (850 °C-1100 °C) experiments were performed to figure out the formation reactions of the intermetallic phases. The samples were analyzed by SEM, EDS, XRD methods.

TRI - Tribology

P02.077-TRI128

DETERMINATION OF STABLE TOOL WEAR ZONE BY ADVANCED VIBRATORY ANALYSIS, IN MACHINING C45U STEEL WITH A P30 CARBIDE TOOL.

H. Zaida, A.M. Bouchelaghem, F. Boutaghane
Laboratory of Industrial Mechanics (LMI), Badji Mokhtar University - Annaba (Algeria)

During very long machining operations, tool wear must be considered in all phases of technical-economic studies of manufacture and production. According to Koren and Lenz, the total wear is the result between the wear of diffusion and the wear of abrasion. The wear of the cutting tool is also a total wear, it results from the abrasion and the diffusion of the particles of materials in contact, tool - workpiece. The wear of the cutting tool is characterized by its phases of running-in, stability that is linear in time and accelerated wear. The monitoring of its evolution is often carried out by indicators of overall level or frequency analysis with comparison with the thresholds which are given by the standards, ISO 3685 for example. We propose in this paper the follow-up of its evolution by advanced vibratory analysis and propose the determination of the transition points of its main phase of sustainability.

References

[1] Dimla E., Dimla Snr. Sensor signals for tool-wear monitoring in metal cutting Operations – a review of methods. International Journal of Machine Tools & Manufacture .4. 2000- 1073-1098

[2] Siddhpura A., Paurobally R. A review of flank wear prediction methods for tool condition monitoring in a turning process, Int J Adv Manuf Technol. 2012. 65 .1–4. 371–393.

[3] Serra R., Rmili W., Ouahabi A. Suivi de l'usure des outils de coupe en tournage à sec de la fonte FT25 par analyse vibratoire. 19ème Congres Français de Mécanique. Marseille. 2009.

[4] González-Laguna A., Barreiro J. Design of a TCM system based on vibration signal for metal turning processes. Procedia Engineering. 132. 2015. 405 – 412.

[5] D. E. Dimla, Snr. The Correlation of Vibration Signal Features to Cutting Tool. International Journal of Machine Tools & Manufacture. 2002. 19.705–713

P02.078-TRI154

WEAR AND CORROSION BEHAVIOUR OF CR13NI5MO2 SUPERMARTENSITIC STAINLESS STEEL PIPE FOR OIL AND GAS APPLICATIONS

C. Ramoul, S. Tlili, K. Slimani, O. Ghelloudj
Centre de Recherche en Technologies Industrielles CRTI (Algeria)

Wear and corrosion are one of the most severe undesired phenomena of deterioration of materials, Corrosion Resistant Alloys (CRA) like a supermartensitic stainless steel is one of many materials developed for oil and gas applications. This study focuses on the electrochemical characterization behavior of a supermartensitic stainless steel Cr13Ni5Mo2 in NaCl and (NaCl +Na2SO4) solutions and friction wear in dry and lubrication condition of Cr13Ni5Mo2 against alumina ball . Polarization curves and electrochemical impedance measurements were obtained for different experimental conditions. The effect of heat treatment on the mechanical and corrosion properties was evaluated by treated quenching at 1050 °C for 15 minutes and tempering for 1 hour at (550 - 650 and 750 °C). A variety of examination techniques were used like optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS). The results showed that the heat treated sample at 550 °C exhibited better corrosion resistance than the other samples treated at 650 et 750 °C in 0,5 M Na2SO4 and 5% NaCl + 0,5 M Na2SO4 solutions.

Keywords: Engineering, 13Cr Supermartensitic stainless steel , heat treatment, corrosion, wear

References

[1] T. H. Lee, S. J. Kim, and C. G. Lee, J. Kor. Inst. Met. & Mater. 38, 659 (2000).

[2] T. H. Lee, S. J. Kim, and Y. C. Jung, J. Kor. Inst. Met. & Mater. 38, 667 (2000).

[3] A.Davydov, K .V. Rybalka, L. A. Beketaeva, Corros. Sci. ,47(2005) 195

[4] M.Stratmann,J.Müller, Corros. Sci. ,36(1994)327.

[5] Q.Yu1,2, The Electrochemical Behavior of 15-5PH Stainless Steel in Acidic Solutions Int. J. Electrochem. Sci., 10 (2015) 2035 - 2044

.

P02.079-TRI231

INFLUENCE OF HEAT TREATMENT ON THE STRUCTURE AND ABRASION WEAR OF A105N STEEL

A. Gharbi, K. Bouhamla, O. Ghelloudj, C.E. Ramoul
Research Center in Industrial Technologies (CRTI), P.O. Box 64, Cheraga 16014 - Algérie (Algeria)

Wear is the removal of material from a surface by very different mechanisms such as abrasion, erosion, fatigue and corrosion. In the industrial sector, the cost of repairing used parts is very high; the solution in this case is to choose an anti-wear material. To choose an anti-wear material, the first factor is the identification of wear type; however, the conditions of use in the industry are complex so the choice of materials is difficult.

Usually the choice of material depends on several factors such as high hardness, high resistance to abrasive wear and low friction coefficient. Thermal treatments are proposed in order to improve these properties.The objective of our work is to study the influence of heat treatment on the structure and abrasion resistance behavior of A105N steel.

Samples solution treatment is carried out at a temperature of 900 °C for 2 h then quenched in water. Experimental techniques such as optical microscopy, SEM, EDX and abrasion wear test are used to highlight the effect of heat treatment on the wear resistance of the steel.

The microstructural characterization shows that in the initial state, the structure is composed of ferrite and perlite, after tempering, the structure is composed of perlite and bainite. The wear tests by abrasion show a clear difference on the weight losses of up to 50% following the quenching treatment.

Keywords: Wear ; Abrasion ; Steel ; Heat treatment; A105N

References

[1]. Sanjay S. Rathore, Vikram V. Dabhade, Hardenability of sinter-forged Fee2Cu-0.7C-xMo alloys,Journal of Alloys and Compounds 664 (2016) ,p.133-140.

[2]. Shi-guang Peng, Ren-boSong, TingSun, Fu-qiangYang, PengDeng, Chun-jingWu, Surface failure behavior of 70Mn martensite steel under abrasive impact wear, Wear 362-363(2016), p.129–134.

Authors Index