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Your preferred conference topic:	Ferroelectrics, functional oxides and topological insulators
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# Effect of postannealing crystallization of FE:HfO<sub>2</sub> on dynamics of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> formation at SiO<sub>2</sub>/FE:HfO<sub>2</sub> interface depending on valence of doping impurity

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Correlation between crystallization phases of ferroelectric HfO<sub>2</sub> affected by valence of impurity atom and composition and extension of the transition layer formed at the SiO<sub>2</sub>/HfO<sub>2</sub> interface in the model systems Si-sub./SiO<sub>2</sub> (7,5 nm)/Si(Al):HfO<sub>2</sub> (9,5 nm)/TiN (9 nm) was studied. Formation of a Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> at the interface SiO<sub>2</sub>/HfO<sub>2</sub> was revealed and dependence of its thickness and stoichiometry on the formation of the tetragonal phase P4<sub>2</sub>/nmc of HfO<sub>2</sub> was established. It is shown that doping with aluminum followed by annealing prevents the formation of a tetragonal phase and reduces both  $d_{\text{silicate}}$  and  $X$  by about 20% (with respect to undoped HfO<sub>2</sub> annealed at the same temperature).

## Introduction

Today's exponentially growing demand for the storage and processing of digital information requires revolutionary approaches to building data processing and storage. Ferroelectric (FE) memory is a promising candidate for the basis of a new type of logic-in storage class memory (SCM), which should combine the advantages of NAND charging memory (scalability and non-volatility) and DRAM memory (speed). HfO<sub>2</sub>-based ferroelectrics are main candidate materials for active layer in ferroelectric memory unit cell now due to the CMOS compatibility of HfO<sub>2</sub> and its good scalability potential.

For successful implementation of FE:HfO<sub>2</sub> it is necessary simultaneously to achieve high value of remnant polarization ( $P_r$ ) by stabilization of polar orthorhombic phase Pca2<sub>1</sub> of HfO<sub>2</sub> and high enough number of stable cycles of  $P_r$  direction changing (endurance). Unfortunately, in general  $P_r$  value and endurance properties are anticorrelated and significant endurance issues are still crucial for implementation of FE:HfO<sub>2</sub> [1] in spite of known ways of  $P_r$  value improvement. Endurance issues generally can be related to formation of transition chemical compounds at interfaces between HfO<sub>2</sub> and metal or dielectric layers [2,3]. At the same time  $P_r$  value depends on fraction of polar orthorhombic phase. Thus the question arises whether crystallization of FE:HfO<sub>2</sub> and dynamics of, for example, Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> formation at SiO<sub>2</sub>/FE:HfO<sub>2</sub> interface are correlated? In this regard, different HfO<sub>2</sub> doping and annealing conditions, which are equally optimal for optimizing the  $P_r$  value can affect endurance characteristics in different ways. The current work aims to contribute to understanding the evolution of the composition and extension of the transition layer formed at the SiO<sub>2</sub>/FE:HfO<sub>2</sub> interface in model FE-memory unit cells and its correlation with different postannealing recrystallization of HfO<sub>2</sub> affected by valence of impurity atom (Al or Si). At the moment comprehensive study of an effect of the ionic

radius of the impurity [4] on stabilization of ferroelectric phase of HfO<sub>2</sub> is known. But there is no information on the effect of chemical properties of the impurity. The choice of Al and Si is due to the fact that these elements are characterized by different valences at almost the same ionic radius.

## Experimental methods

Si-sub./SiO<sub>2</sub> (7,5 nm)/Al(Si):HfO<sub>2</sub> (9,5 nm)/TiN (9 nm) multilayer structures were grown as described in [5]. Al doped (5.5%) and Si doped (3.6%) HfO<sub>2</sub> films were synthesized by ALD from HfCl<sub>4</sub> and H<sub>2</sub>O precursors at 300° C on top of 7.5-nm-thick SiO<sub>2</sub> layers thermally grown on low doped p-type Si(100). After PVD of TiN annealing was carried out in N<sub>2</sub> at 850 °C for 60 s (Al-doped HfO<sub>2</sub> and the undoped HfO<sub>2</sub> reference) or at 1000° C for 30 s (Si-doped HfO<sub>2</sub> and the undoped HfO<sub>2</sub> reference). The samples before and after doping and annealing process were studied. Crystal structure characterization was carried out by grazing incidence X-ray diffraction (GIXRD) realized with Bruker "D8 DISCOVER" system at "Research Centre for X-ray Diffraction Studies" of research park of SPbSU and by OK-near edge X-ray absorption fine structure (NEXAFS) measured at BEAR beamline of Elettra synchrotron, Trieste, Italy. Formation of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> at SiO<sub>2</sub>/FE:HfO<sub>2</sub> interface was studied by X-ray photoelectron spectroscopy performed at P22 HAXPES beamline of the storage ring PETRA-III at DESY in Hamburg, Germany and by transmission electron microscopy realized by analytical transmission electron microscope Carl Zeiss Libra 200 FE at "Interdisciplinary Resource Centre for Nanotechnology" of research park of SPbSU.

## Results

GIXRD diffractograms are shown in Fig.1. A joint analysis of all the curves allows one to conclude that the original HfO<sub>2</sub> film (unannealed and undoped) has a polycrystalline structure, which is a mixture of monoclinic (m-) phase and tetragonal (t-) or orthorhombic (o-) phase (see non-monoclinic peaks around 30° and 36°). This means that initial crystallization of HfO<sub>2</sub> occurs during the synthesis process. Annealing of undoped films doesn't change crystal structure significantly. The most important to note a strong effect of annealing of Si/Al doped HfO<sub>2</sub> films manifested in intensive main peak located around 30° that means a prevailing content of t- or o-phases with only an insignificant contribution from the m-phase in Si(Al):HfO<sub>2</sub> annealed films. Unfortunately, it is hard to distinguish t- and o-phases from GIXRD because the peak around 30° is a mixture of signals from (111) and (101) planes of the o- and t-phases, respectively. Due to this reason oxygen K-edge

NEXAFS was analyzed because of high sensitivity of HfO<sub>2</sub> OK-NEXAFS to symmetry of oxygen coordination which is different in t- and o-phases. Weighted summation of model spectra of pure m-, t- and o-phases shows that comparable contributions of the t- and o-phases present in the structure of Si-doped HfO<sub>2</sub> annealed at 1000° C and the predominant contribution of the o-phase is inherent in Al-doped HfO<sub>2</sub> annealed at 850° C.

Si2s photoelectron spectra of all samples were measured at 7 keV excitation energy and decomposed to Si-, SiO<sub>2</sub>-, SiO<sub>x</sub>-, Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>-components using CASA XPS software. Then binding energy difference between SiO<sub>2</sub>- and Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>-components and relative intensities were analyzed. The thickness of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> and the stoichiometry X were calculated from this analysis and the results are shown in Fig.2.

A strong dependence of the thickness and stoichiometry X of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> on the annealing and doping conditions can be revealed. The thicker Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> layer is more Hf-rich (X and d<sub>Silicate</sub> are correlated). It is worth comparing doped/undoped samples annealed under the same conditions. Doping with Si (3,6 %) slightly reduces the d<sub>Silicate</sub> in the sample annealed at 1000° C but within error range. On the contrary, doping with Al (5,5 %) reduces d<sub>Silicate</sub> by about 20% upon annealing at 850° C. It can be assumed that it is doping with Al that significantly affects the formation of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> at the SiO<sub>2</sub>/HfO<sub>2</sub> interface during annealing, in contrast to Si doping.

Thus nature of HfO<sub>2</sub> crystallization process during annealing determines the formation of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> sublayer at the common SiO<sub>2</sub>/HfO<sub>2</sub> interface already formed before annealing during ALD of HfO<sub>2</sub>, and the control of HfO<sub>2</sub> crystallization by impurity doping affects the thickness and stoichiometry of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>.

## Conclusion

We established that as-deposited ALD-HfO<sub>2</sub> film before annealing already has polycrystalline structure and an initial layer of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> is formed between SiO<sub>2</sub> and HfO<sub>2</sub> layers. Further, upon annealing the thickness of the Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> and the content of hafnium in it increase. We have established for the first time that the recrystallization of HfO<sub>2</sub>, which depends on the dopant valence, has a different effect on the dynamics of changes in the thickness and stoichiometry of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>. Doping with silicon promotes the formation of tetragonal crystallites common to HfO<sub>2</sub> and Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub>, simply facilitating the crystallization of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> without a significant change in its thickness and stoichiometry compared to the sample without impurities annealed at the same temperature. On the contrary, doping with aluminum leads to a predominance of the orthorhombic phase compared to the tetragonal one in HfO<sub>2</sub> that reduces both the thickness and the stoichiometry of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> by about

20% compared to the undoped sample annealed at the same temperature. The results obtained in this work are important for problems of stabilization of memory window value of ferroelectric field effect transistor during program/erase cycling from point of view capacitive coupling of ferroelectric/insulating dielectric in gate oxide stack.

## References

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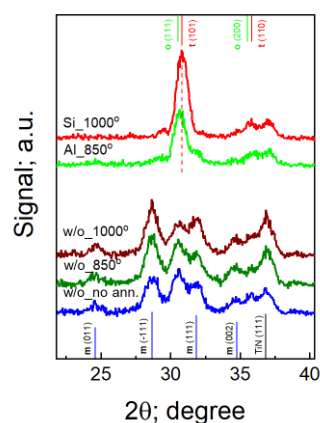


Figure 1. GIXRD diffractograms of annealed or unannealed and Al(Si) doped or without (w/o) doping Si-sub./SiO<sub>2</sub> (7,5 nm)/Al(Si):HfO<sub>2</sub> (9,5 nm)/TiN (9 nm) samples in 22.5°- 40° range. Reference patterns for monoclinic P2<sub>1</sub>/c (m-), tetragonal P4/nmc (t-) and orthorhombic Pca2<sub>1</sub> (o-) phases of HfO<sub>2</sub> are shown.

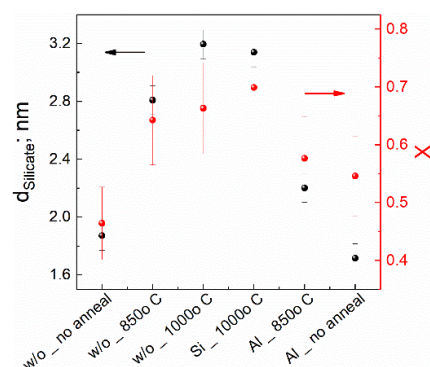


Figure 2. Results of calculation of Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> thickness (d<sub>Silicate</sub>) (left) and stoichiometry X (right) based on relative intensities of Si, SiO<sub>2</sub> and Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> components and binding energy difference between SiO<sub>2</sub> and Hf<sub>x</sub>Si<sub>1-x</sub>O<sub>2</sub> components in decomposed Si2s HAXPES spectra, respectively.

