

ON THE CRYSTALLISATION MODEL OF PHOTOPROCESS IN AgHal

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Phenomenon of photoinduced recrystallisation in AgHal crystals was established as a result of experiments on simulation of photoprocesses in AgHal crystals [1,2]. Composition of new phase depends on the stoichiometric composition of matrix, presence of alloying impurities and on a spectral structure of irradiation. Specifically irradiation by pulsed N₂-laser UV-light leads to the growth of Ag-filaments, irradiation by UV-light of high-pressure mercury lamp leads to the growth of Ag-needles, and addition of visible light leads to the growth of filaments of main composition [1,2]. Direct observation of photoamorphisation as well as formation of quasi-liquid phase made it possible to describe all observed types of photorecrystallisation in AgHal within a framework of a vapour-liquid-crystal (VLC) mechanism, where "vapour" - mobile biographic and photogenerated point-like centres. In the case of direct reduction of AgHal by electrons through injecting electrode, VLC-mechanism becomes simpler up to liquid-crystal mechanism under the condition of matrix structure changing to body-centred cubic (bcc) or amorphisation of matrix in the region of phase boundary (PB) with injecting electrode.

Mutual influence of structures of substrate (AgHal) and epitax with properties of ion-selective electrode supposes directed diffusion of cations from body and concentration lengthways phase boundary with epitax. Such process for compositional crystals and microcrystals (MC) has been confirmed by model experiments [3] as well as by the investigation of absorption, fluorescence and excitation spectra of substrate-epitax type compositional MC [4-7]. Specifically system AgI/Ag₂HgI₄ was studied [4] and it was shown spectrally that absorption of Ag_n from the near-surface region of substrate with face-centred cubic structure has discrete character, that may be result of discrete changing of potential at phase boundary as well as of discrete character of Ag_n aggregation from molecular centres. The interdependence between: filamentary structure of γ -AgI (model centre of sensitivity (CS)) in AgCl, growth of Ag-needle from γ -AgI phase, positive potential at the point of needle and directed diffusion of Ag from AgCl to body end of needle, that supposes changing of AgCl structure in the region of PB with γ -AgI, has been shown in direct experiment [5].

The growth of filamentary crystals is characterised by the visible increasing of the volume. Analysis of characteristics of growth of filaments from AgI and Ag₂O [8,9] gave reasons to consider this process as ordered aggregation of selectively-excited molecular centres, such as Ag₂⁺¹ or Ag₃⁺¹I₂⁻ in AgI, into the chains of covalently linked through Hal⁰ molecular cations (molecular anion Hal₂⁻ is situated lengthways short axis of Ag-bipyramid. Unit cell of filamentary crystal Hal⁰-Ag₆⁺⁺-Hal₂⁻-Hal⁰ in the case of low-temperature stabilization of AgHal bcc-structure by superstoichiometric Ag may be created by photoinduced or coulomb redistribution of electron density, and Ag⁺ (centre of Ag₆) are situated in regular tetrahedral lattice sites.

Presence of catalytic (seed) Ag-centre, bcc- or amorphised matrix around it, and potential gradient in the body of AgHal permit to assume gradient-zone recrystallisation (GZR) when the movement of seed centre is directed into the body of AgHal. The prospective speed of GZR (10⁻⁴ cm/s) provides restoration of a crystal with the sizes of about 1 μ for 10 - 100 s (depending on pH of solution and number of catalytic centres of

development). The GZR model of electrochemical restoration of AgHal is correct in the case when an energy barrier for n-type electrical conductivity in the initiating Ag-centre is low enough. For the substantiation of this assumption in the case of AgBr or Ag₂S filamentary crystals one can note, that covalent radius of Br⁰ and ion radius of Ag⁺ are close (1.14 Å and 1.13 Å), and in Ag_{2+x}S CS there are Ag⁰S⁻ centres, in which radiuses of Ag⁰ and S⁻ are equal to 1.44 Å (that is equal to potential gradient 0.2 - 0.3 eV at PB between AgBr and Ag_{2+x}S).

The localisation of photoexcitation on the low-intensive continuous UV-irradiation was simulated at β-AgI/γ-AgI, where γ-AgI phase was created by the deposition of thin (1 μ) coat of Ag (diameter = 0.5 mm) and following heating of the crystal up to the temperature of the β-α phase transition (150 °C). As a result of later irradiation by halogen lamp and by Ar⁺-laser (514 nm; < 50 mW/cm²) at room temperature the bunch of Ag-filaments grows from the area of Ag-coat in 1-2 s.

Within a framework of the concept of unity of all stages of photoprocess in AgHal the role of chemical maturing consists not only of formation of CS, but also of concentrating of Ag⁺ near PB of MC-CS, and in this case structure of AgBr changes and ionic mobility increases up to superionic. Possibility of bcc-structure in alloyed AgBr was shown by microcalorimetry of standard emulsion MCs in comparison with known temperature region of structural phase transition in AgI. In this context the high concentration of mobile Ag⁺ can not be related to CS, but only to MC. This fact follows from the electrometry of emulsion MC of a different structure and permits to explain etching hollows around the area of development as a consequence of greater chemical activity of AgHal in conditions of high ion mobility. Thus the ionic stage of photoprocess is the result of photochanging of potential of a double electrical layer on PB MC-CS and can be considered as photodevelopment [10].

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