

CRYSTALLISATION MODEL OF PHOTOPROCESS IN AgHal

V.A. Reznikov, A.V. Barmasov and V.E. Kholmogorov

Institute of Physics, St.Petersburg State University St.Petersburg, Russia, 198904.

With a help of spectroscopic methods it is shown for some emulsion compositional substrat-ionoselective epitaxy microcrystals (MC), as well as for the AgHal macrocrystals of the same structure, that photoinduced formation of Ag_n particles may be described as photorecrystallisation from the solid solution with the structure, stabilised at 290 K by a superstoichiometric Ag from substrate. In this case one can consider Ag_6^{++} bipyramids (component of the cationic subsystem) to be an elementary particle of such system.

Ag_n formation was simulated by a photolysis in β -AgI as a result of photoinduced phase transition β - γ - α . All observed types of photorecrystallisation in AgHal can be described within a framework of a vapour-liquid-crystal (VLC) mechanism, thus morphology and stoichiometric composition of a new phase depends on a history of crystal and on a spectral structure of radiation. The growth of filaments of Ag from the volume of AgI also can be described as a VLC mechanism (under some assumptions) too.

The growth of filamentary crystals is characterised by the visible increasing of the volume, that permits to suppose that they are formed by the aggregation of selectively-excited $Ag_2^+I^0$ or $Ag_3^+I_2^-$ molecular centres. Assumed structure and composition of temperature-stable initial molecular centres were estimated by the analysis of properties and conditions of growth of new phase. One may suppose $I^0-Ag_6^{++}-I_2^-I^0$ (I_2^- pairs are located in the centres of Ag_6^{++} bipyramids) to be an elementary Ag-centre. In this model stability of positive potential of Ag_n is maintained by the displacement of its electron density at I_2^- .

The local character of recrystallisation in β -AgI and collective character of the process (metallisation of the whole volume) in α -AgI points to the localisation of photoexcitation in the area of biographic structural defects. 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 coat of Ag 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 Ar^+ -laser (514 nm; $< 50 \text{ mW/cm}^2$) the bunch of surface-oxidised ribbon-like or Ag-filaments grows from the area of γ -AgI in 1-2 s. This fact as well as formation of Ag-spire from γ -AgI in AgCl crystal may be regarded as photodevelopment.

It was shown that the morphology of filamentary crystals was the same both in the case of photo- or electronic irradiation of macro- and microcrystals of AgHal. Amorphisation of AgHal (AgBr) substrate may be assumed as a result of directed diffusion and concentrating of Ag^+ on the phase border (PB) substrate-epitaxy. So the photographic AgBr MC may be considered as such system: semiconductor - solid electrolyte - solid solution. Presence of catalytic (seed) Ag-centre, amorphised matrix around it, and gradient of potential in the volume of AgHal permit to assume gradient-zone recrystallisation (GZR) on Ag-centre when its movement is directed into the volume of AgHal. The prospective speed of GZR (10^{-4} cm/s) provides restoration of a crystal with the sizes of about 1μ for a time less than 100 s. The GZR model of electronic restoration is correct in the case when an energy barrier for n-type electroconductivity in the initiating Ag-centre is low enough. For the substantiation of this assumption in the case of AgBr or Ag_2S filamentary crystals one can note, that covalent radius of Br^0 is equal to 1.14 Å, ion radius of Ag^+ is 1.13 Å, and in $\text{Ag}_2\text{X}_2\text{S}$ centres of sensitivity (CS) there are Ag^0S^- centres, in which radiuses of Ag^0 and S^- are equal to 1.44 Å.

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 microcrystal-CS, and in this case electrochemical restoration in reality is electrochemical crystallisation on Ag_n . In this context the high concentration of mobile Ag^+ can not be related to CS. 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.

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