Crystallization and Chemical Sensitization of Epitaxial AgBr(I)/AgCl Tabular Crystals

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Abstract

The process of epitaxial growing of a AgCl phase on tabular crystals AgBr after modification of a surface of substratum tabular crystal by an iodide is investigated. The influences of concentration of an potassium iodide and potassium chloride, pAg and pH of a crystallization, rate of addition of reagents and temperature on process of epitaxial growth are investigated. The conditions of formation of an AgCl phase at corners and edges of a tabular crystal are received.

The kinetics of a chemical sensitization of the received AgBr(I) tabular crystals with angular epitaxes AgCl is investigated. The influence pAg, temperature, concentration of a sensitizer on efficiency of a chemical sensitization is considered. It is shown that the presence of AgCl epitaxes at corners of a AgBr(I) tabular crystal allows to increase a photosensitivity of photolayers on the basis of these systems up to 1,5 - 2 times, in comparison with emulsion layers of AgBr(I) tabular crystals without epitaxes.

Introduction

The widely used in photographic technology tabular crystals have a number of essential faults. Despite of the large surface of a tabular crystal, the optimum concentration of dyes - spectral sensitizers correspond to the 10% filling of their surface, therefore the specific amount of dyes per unit of weight AgHal remains approximately same, as well as for isometric microcrystals. Increase of the linear size of tabular crystals more than 1.5-2.0 micron result in reduction of a photosensitivity. The chemical sensitization for AgHal is more effective on sides' {111} than on sides' {100} because of the {111} faces has the smaller activation energy of reactions with sodium thiosulfate. It was possible to expect that the latent image form preferably on {111} sides of tabular crystals. However really the latent image is located on lateral twinned surfaces of tabular crystals. As was established[1,2] both on primitive and on chemically sensitized tabular crystals the development centers are randomly formed along lateral sides. To increase a photosensitivity of tabular crystals it is necessary to limit the number of the centers of the latent image and to increase the quantum efficiency of these centers in photoprocess. An opportunity to control the localization of the latent image for the first time was shown on an example of photographic emulsions containing the epitaxial microcrystals AgCl/β-AgI.[3] These crystals contained a substratum β-AgI with AgCl epitaxes. After exposition of such epitaxial crystals the photoelectrons induced mainly in β-AgI phase, transfer to AgCl phase and form the latent image. This process allows separating photoelectrons and holes, owing to the recombination decreases. Besides the more soluble AgCl phase allows to carry out selective chemical sensitization.

The angular epitaxes AgCl on tabular crystals AgBr(I) also allow to control the localization of the latent image.[4] The energetic accounts of the band structure of AgHal show that the relative position of a bottom of a conductivity band in AgCl is above than bottom of a conductivity band in AgBr. Therefore the generated in silver bromide photoelectrons can not be transferred through a heterocontact boarding to an AgCl phase. However because of distinctions in structure of a lattice these two phases have rather high concentration of dislocations in field of a heterocontact. These dislocations can be positively charged and therefore its are traps for photoelectrons.

The purpose of the present work is the reception of tabular crystals AgBr with angular epitaxes AgCl and research of their photographic properties.

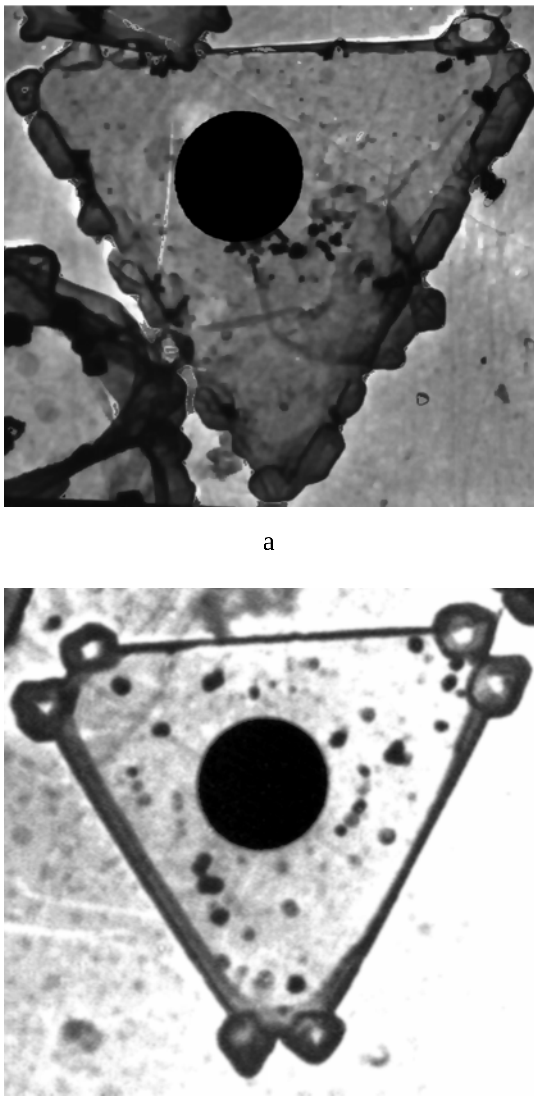
Results and Discussion

Crystallization of Epitaxial Systems.

The synthesis of the emulsion with substratum AgBr tabular crystals was carried out by a method of a controlled double jet crystallization by the standard technique.[5] The received AgBr tabular crystals had the following parameters: d=2.0 microns; C_V=50 %; S_T=85 %; h=0.1 microns.

It is known[6-8] that in the case of AgHal for epitaxial growing of a phase on the substratum microcrystal it is necessary to modify a surface of this microcrystal. As modifiers the inorganic salts forming low soluble compounds with silver ions or organic j-aggregating dyes can be used. The necessary condition is the adsorption of these compounds on a surface of AgBr tabular crystals. The growing AgCl epitaxes on tabular crystals AgBr without preliminary modification of a surface of the substratum crystal results in reception of "rough" flat microcrystals due to unselective growth of a AgCl phase on all surface of a tabular crystal. The sensitometric research of such emulsion have shown that it has a high level of fog density and is unpromising for the further using.

Modifying a surface of the substratum microcrystal is necessary first of all for stabilization of growth of the main sides of tabular crystal. Therefore we chose potassium iodide as the modifier for tabular crystals. Because of a high difference in solubility AgI (pK_{sp}=16.1) and AgCl (pK_{sp}=9.8), the silver chloride will not be crystallized on a surface of an AgBr microcrystal after iodide conversion. However, on edges and, especially, on corners of a microcrystal because of surface energy excess the formation of an AgCl phase is possible.



a

b

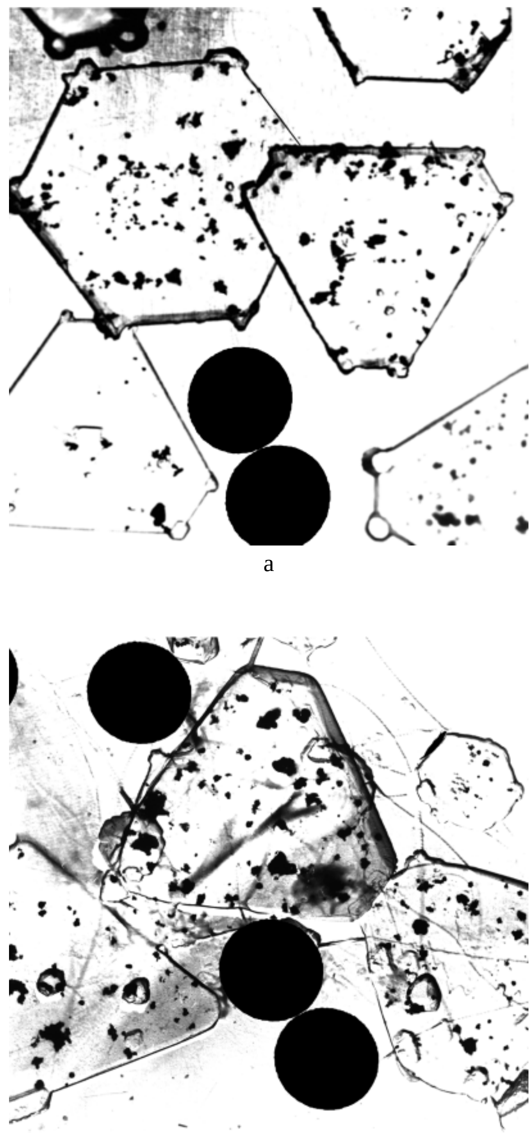
Figure 1. Electron micrographs of carbon replicas of AgBr microcrystals with AgCl epitaxes. The modifier (iodide) concentration: a) 5×10^{-3} mol/mol Ag b) 10^{-2} mol/mol Ag Internal standard latex, d=0.914 μm, Cv=5%

The process of epitaxial growing AgCl is carried out in three stages:

1. Synthesis of the substratum emulsion with tabular crystals AgBr.
2. Modification of a surface of the main sides of tabular crystals by an adsorption on them of silver iodide.
3. Epitaxial growing of AgCl.

For definition of optimum conditions of AgCl epitaxial growing on AgBr tabular crystals the influences of the following factors on process of synthesis were investigated:

- The concentration modifying KI (10^{-3} up to 10^{-2} mol/mol Ag);
- The pAg value of a crystallization of epitaxes (7.5 up to 8.6);
- The amount AgCl (1 up to 4 mol/mol AgHal);
- The rate of addition of reagent (W) during growing of epitaxes (1.0 up to 2.0 mmol/min).



a

b

Figure 2. Electron micrographs of carbon replicas of AgBr microcrystals with AgCl epitaxes. The pAg value: a). pAg = 7.5 b). pAg = 8.6. Internal standard latex, d=0.914 μm, Cv=5%

The results of experiments are presented on figures 1 and 2. At pAg=7.5 angular and lateral epitaxial grow is observed at concentration of iodide from 5×10^{-3} up to 7×10^{-3} mol/mol Ag. The increase of concentration of KI up to 10^{-2} mol/mol Ag results in formation only of angular epitaxes, and further increase of concentration - to formation of a fine phase of silver chloride. At pAg=8.6 the epitaxes are formed at concentration up to 7×10^{-3} mol/mol Ag. There is a excess of a halide ions at high pAg value that results in unepitaxial growth AgCl.

The unepitaxial growth of an AgCl phase is also observed at the large concentration of iodide ions. In all cases the epitaxial growth of chloride is observed at AgCl:AgBr(I) molar ratio more then 2:100.

For the chosen factorial space we establish optimum conditions of reception of angular epitaxes AgCl on tabular crystals AgBr: pAg=8.0; [AgCl]=2-4 mol %; $[I^-]=7\times10^{-3}$ mol/mol Ag; $W=1\times10^{-3}$ mol/min.

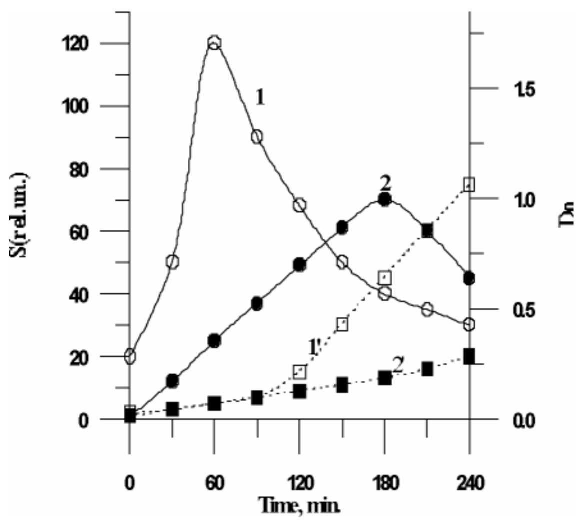


Figure 3. The kinetic of chemical sensitization of emulsion with epitaxial tabular microcrystals AgBr/AgCl (1, 1') and without epitaxes (2, 2').

Chemical Sensitization of Epitaxial Systems.

The chemical sensitization of the AgBr tabular crystals with angular epitaxes AgCl, synthesized on an optimized prescription was carried out on standard technique[5]: T=49°C; pBr=3.0; pH=6.8. As a sensitizer the sodium thiosulfate in concentration from 5×10^{-6} up to 5×10^{-5} mol/mol Ag was used. The sensitized emulsion was covered on polymeric support, dried up and exposed on a sensitometer FSR-41 at T_c = 5000 κ during 0.05 sec. The photographic processing was carried out in a standard developer UP-2 during 8 min. For comparison the comparative - substratum emulsion with AgBr tabular crystals with an adsorbed iodide but without epitaxes was used.

The kinetics of a chemical sensitization of a comparative and epitaxial emulsion is presented on figure 3. At concentration $Na_2S_2O_3$ 1.5×10^{-5} mol/mol Ag the comparative achieves the maximal photosensitivity for 180 min, whereas an epitaxial emulsion for 60 min. Besides the value of the maximal photosensitivity for epitaxial systems in is higher 2 times than for comparative at a constant level of a fog optical density. This result indirectly confirms our assumption that the AgCl epitaxes allow locating the formation of the latent image centers on border of a heterocontact. Since the solubility of AgI is much lower than AgCl therefore the achievement of the maximal photosensitivity of a comparative need the much greater time. Besides at $Na_2S_2O_3$ concentration 5×10^{-5} mol/mol Ag the epitaxial emulsion fast fogs whereas the comparative achieves S_{max} for 90 min at insignificant increase of a level of fog density. As chemical sensitization of epitaxial systems needs considerably smaller amount of a sensitizer, it is possible to consider that the number of the centers of a sensitization on such microcrystals is limited. However, it is necessary to note that for epitaxial systems the growth of a photosensitivity is accompanied by faster growth of fog density.

The increase of temperature of a chemical sensitization from 49°C up to 55°C result in decrease of a photosensitivity with simultaneous growth of fog density. Obviously, it is connected with a partial dissolution of AgCl epitaxes and formation of the fog centers on all surfaces of a tabular crystal. At smaller concentration of a sensitizer of the tendency of decrease of a photosensitivity and fog increase remains former, but the speed of process is slowed down a little. At temperatures lower then 49°C the chemical sensitization proceeds inefficiently. The maximum level of a photosensitivity S_{max} varies rather insignificantly, but the time of its achievement increase and the increase of a fog level of optical density is observed. The dependence of efficiency of a chemical sensitization on value pAg has extreme character and the maximum of a photosensitivity at a minimum level of fog optical density achieved at pAg=8.0.

On the basis of the carried out researches it is possible to conclude, that using in photographic technology of heterocontact systems as tabular crystals AgBr with angular epitaxes AgCl is perspective. However, the process of a chemical sensitization of these systems essentially differs from a chemical sensitization of usual tabular crystals and requires realization of the further researches.

References

1. R. L. Daubendiek. US Pat. 4,414,310 (1983).
2. J. C. Solberg, R. H. Piggin, H.S. Wilgus US Pat. 4,433,048 (1984).
3. H. S. Wilgis US Pat. 4,434,226 (1984).
4. J. E. Maskasky, *J. Imag. Sci.*, **32,** 160-177, (1988).
5. Yu. A. Breslav, V. V. Peisahov, L. A. Kaplun, Synthesis and Properties of T-crystals, Moscow, USSR, 1986, P. 86.
6. J. E. Maskasky, Eur. Pat. 0,213,963 (1987).
7. J. E. Maskasky, Eur. Pat. 0,213,964 (1987).
8. L. Eshelman, *Proceedings of IS&T's PICS Conference*, Portland, Oregon, USA, 1998, P. 314-316.