The Formation and Chemical Sensitization of AgHal Heteroepitaxial Tabular Microcrystals

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Abstract

The growth of composite grains is accompanied by total or partly transformation of halide composition of microcrystals, usually, without changing the molar amount of each particle. The halide conversion process on photoemulsion heteroepitaxial tabular AgBr/AgCl microcrystals by the Br^- ions has been investigated. The experimental results were analyzed by optical microscopy. Stepwise change in morphology, structure, and composition of the particles during the conversion process is shown. The method of the formation of heteroepitaxial crystals is suggested. The algorithm of the halide conversion process allows us to control the degree of conversion, to vary the amount and halide composition of epitaxial portions. Examination of photographic properties of tabular AgBr microcrystals with corner converted epitaxial portions has been carried out. The bromide ions were used for primary converting while the bromide and iodide ions were used for secondary converting. In the latter case either the fine AgBr emulsion or the fine $AgBr_{0,96}I_{0,04}$ emulsion was added into the system. It turned out that chemical sensitization in the presence of potassium thiocyanate for converted heteroepitaxial tabular $AgBr/AgCl_{1-x}Br_x$ microcrystals is less effective because of higher fog optical density.

Introduction

Epitaxial crystals are a most interesting system both from the point of view of investigating the mechanism of the growth of microcrystals during mass crystallization and investigating the interaction of photographically active substances (sensitizers, developing substances, etc.) with the surface of the heterophase microcrystal. The formation of the corner AgCl epitaxial portion on tabular AgBr microcrystals makes it possible to control the localization of the latent image centers that allows us to increase quantum efficiency of the photoprocess and the photographic speed of the particular microcrystals [1]. However, the growth of the photographic speed of the epitaxial emulsion is accompanied by a faster growth of fog optical density in comparison with tabular AgBr microcrystals which can be deterred by halide conversion of AgCl epitaxial portion.

The process of conversion enables total or partly changing the halide composition of microcrystals without changing the molar quantity of each particle. Though this phenomenon is well-known in colloid chemistry, there are very few literary data on the conversion process mechanism. Examination of the process on real photoemulsion crystals is complicated by an extremely small size of these particles (~ 1 microns). In order to use the method of optical microscopy, regularities of the conversion have been studied for the modelling tabular microcrystals.

Experimental Results and Discussion

At the initial stage the substrate tabular AgBr microcrystals (d ≈ 50 microns) have been obtained by the method of physical ripening of the fine emulsion. For selective precipitation of AgCl epitaxial portions onto the corners of substrate tabular microcrystals, the site-director (a solution of potassium iodide) was added into the system [1]. Then, AgCl epitaxial portions were built up on the substrate by the controllable two-jet crystallization method and converted by the bromide ions by introducing the KBr solution into the system (primary conversion). Epitaxial deposits onto the corners of substrate tabular microcrystals were found to appear after the first stage (Fig. 1a). As a result of conversion the epitaxial deposits onto the corners have increased in size (Fig. 1b). The secondary conversion was carried out at the final stage of the process: either the fine AgBr emulsion (Fig. 1c) or the fine $AgBr_{0,96}I_{0,04}$ emulsion was added into the system (Fig. 1d). Unlike a conventional lateral growth of tabular microcrystals, it should be noted that the addition of fine microcrystals into the system results in the further enlargement of the resulting deposits without a new phase being formed (Fig. 1c, 1d). The schematic models of the processes proceeding in the system are submitted in Fig. 2.

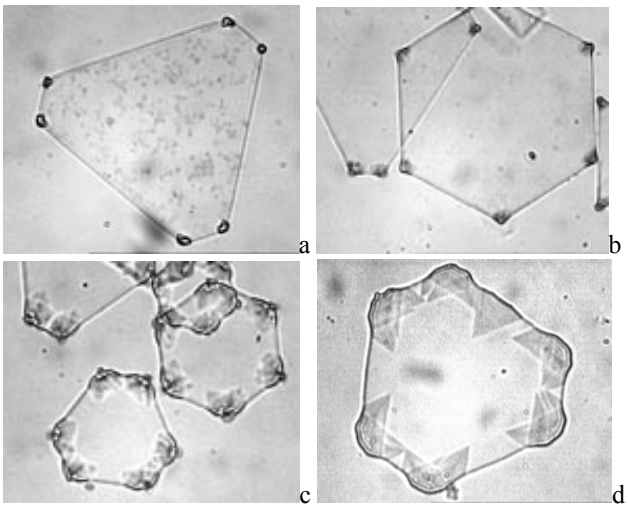

Figure 1. *Photomicrographs: a) tabular AgBr microcrystals with AgCl epitaxial portions; b) tabular AgBr microcrystals with AgCl epitaxial portions, converted KBr solution (primary conversion); c) tabular AgBr microcrystals with AgCl epitaxial portions, converted by Br^- after the addition of fine AgBr emulsion (secondary conversion by bromide ions); d) tabular AgBr microcrystals with AgCl epitaxial portions, converted by Br^- and I^- after the addition of fine $AgBr_{0,96}I_{0,04}$ emulsion (secondary conversion by the iodide ions)*

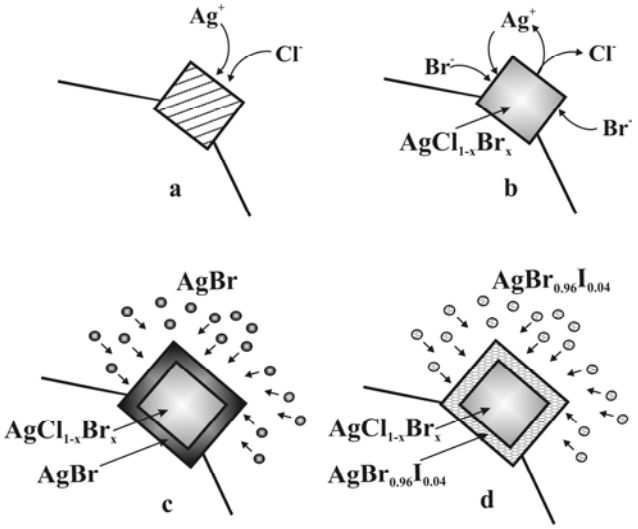

***Figure 2**. The schematic models of the first (a), second (b), and third (c, d) steps of the formation of heteroepitaxial systems*

Multistage processes allow us to form heterostructures with the pre-set properties, i.e., at the first stage it is possible to vary the content of AgCl in the epitaxial portion, at the second stage – to change the halide composition of $AgCl_{1-x}Br_x$ solid solution, the third stage allows us to form a still more heterophase system due to changing the halide composition of the fine emulsion. Thus, a three-step process of halide conversion enables the control of the degree of conversion, to vary the content of AgCl and halide composition of the epitaxial portion.

The photographic properties of microcrystals were examined after optimum conditions for the formation of tabular AgBr microcrystals with converted corner AgCl epitaxial portions were determined.

In the case of conversion by the bromide ions (Fig. 1c) (the concentration of AgCl in microcrystals made 8 % and 16 % from total mass AgHal) chemical sensitization results have shown that the photoemulsions possess a higher photographic speed compared with common tabular AgBr microcrystals. When carrying out chemical sensitization without thiocyanate potassium, the optimum values are obtained for the system in which the concentration of AgCl amounts to 16 % from total mass of AgHal. The chemical sensitization in the presence of thiocyanate potassium for converted heteroepitaxial systems turned out less effective (it is accompanied by a higher level of fog optical density). Apparently, mobility of the chemical sensitization centers increases due to thiocyanate, thereby causing the transformation of these centers into fog centers. This is also characteristic of tabular microcrystals with AgCl epitaxial portions. Therefore, it could be assumed that under the pre-set experimental conditions AgCl epitaxial portions in these systems are not converted completely. The given assumption could be supported by the results of the X-ray phase analysis of heteroepitaxial microcrystals with the various mass percentage content of chloride in the system.

In the case of conversion by the bromide and iodide ions (Fig. 1d) (the concentration of AgCl in microcrystals made 10 % and 20 % from total mass of AgHal) chemical sensitization results have shown that photographic speed of the primitive emulsion layers is higher than that of unconverted epitaxial systems of AgBr/AgCl. However, during standard chemical sensitization there occurs a significant growth of fog optical density, which can be still more intensive when increasing the mass percentage content of silver chloride in microcrystals. In our opinion, these systems possess the increased deficiency that results in initiating the direct development of microcrystals when contacting with a developing agent.

References

[1] J.E.Maskasky, Epitaxial Selective Site Sensitization of Tabular Grain Emalsions, J. Imag, Sci., 1987, V. 32, pg. 160-177.

Author Biography

Aigul B. Abisheva was born in Pavlodar (Kasakhstan) on July 19, 1980. In 2002 she graduated from Kemerovo State University, the Chemistry Faculty. Now she is a post-graduate student of Kemerovo State University, the Physics Faculty. Her field of research is mass crystallization processes of silver halides, the author of 33 scientific publications.

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