

CRYSTALLIZATION and PHOTOGRAPHIC PROPERTIES of HETEROCONTACT AgBr/AgCl MICROCRYSTALS

Boris Sechkarev, Larisa Sotnikova, Fyodor Titov, Timothy Larichev, Tanya Ignatieva, Alex Utechin
Kemerovo State University, Kemerovo, Russia

Abstract

The process of formation of heterocontact core-shell microcrystals AgBr/AgCl and AgBr(I)/AgCl and also epitaxial systems is investigated. In work the research of an opportunity of formation silver chloride shell on AgBr and AgBr(I) core is carried out. The shell growth was realized by two ways: controllable double-jet crystallization and recrystallization of fine emulsions. The influence of pAg, rate of addition of reagent solutions, temperature of synthesis and recrystallization, presence of the solvent on process of mass crystallization of silver chloride on $AgBr_xI_{1-x}$ microcrystals is investigated. The optimal conditions of crystallization of monosize AgCl shells on AgBr and $AgBr_xI_{1-x}$ microcrystals with AgCl epitaxes both by method of double-jet crystallization and by method of recrystallization of fine emulsion are established. The obtained heterocontact systems have allowed to increase a photosensitivity of photolayers and to reduce a time of photographic processing.

Introduction

Now to physic and chemical properties of AgHal microcrystals for manufacturing of photographic materials show higher requirements, which can not be achieved within the framework of the traditional approaches. To optimize photographic process in AgHal photomaterials it is possible by use of new types of emulsion microcrystals, allowing to increase efficiency of photoprocess by means of more effective utilization of energy of light, reduction of light scattering in layers, localization of the latent image and increase of efficiency of photographic processing.

One of the ways of the decision of this problem is the using of heterocontact microcrystals such as the isometric "core-shell" microcrystals with cores and shells of various halide composition and also epitaxial system with various halide composition of a substrate and epitaxes. The special position among heterocontact systems is occupied by chloride containing microcrystals. The silver chloride has considerably smaller absorption and photosensitivity in a short wave part of a spectrum (400-450 nm) than silver bromide or bromoiodide. Therefore for reception green and red of photosensitive layers in color photomaterials preferably to use chloride containing photographic emulsions. Besides the time of photographic processing of AgCl emulsion layers is much less owing to high solubility of silver chloride.

The present work is devoted to search of paths of reception of heterocontact systems AgBr/AgCl and AgBr(I)/AgCl and to comparative research of the sensitometric characteristics of resulting systems.

Experimental results and discussion

For investigation of an opportunity of formation of AgCl shells on AgBr and AgBr(I) cores the emulsions containing microcrystals AgBr or $AgBr_{0.96}I_{0.04}$ of a cubic habit (d=0,4 a micron, C_v=12%) and a fine emulsion AgCl (d=0,06-0,01 micron) were synthesized. The shell was grow by two ways: by a method of controllable double-jet crystallization[1], and by method of fine emulsion recrystallization[2].

In case of the method of controllable double-jet crystallization the influence of temperature and pCl value on formation of AgCl shell was investigated. It was established that at pCl=1 the crystallization of silver chloride took place at angles of core AgBr microcrystals (Figure 3.2 a, b). The reason the formation of epitaxes in this case is the increased surface activity of angles of microcrystals (in comparison with the basic surfaces). The continuation of process of epitaxial growth by the way of increase of crystallizing mass

results in propagation of already formed epitaxes and is not accompanied by formation of a new phase crystals.

At reducing of concentration of chlorides ions up to pCl=2 the monosize shell on cubic AgBr microcrystals is formed (figure 2a). The obtained microcrystals have high enough monodispersity (C_v=20%).

It is necessary to note that at growing of shell by a method of double-jet crystallization the rate of addition of reagents solutions must be below "critical" level to prevent the formation of a new phase particles[3]. We determine that the critical rate for our experimental conditions of synthesis is $0,7*10^{-3}$ M/mines.

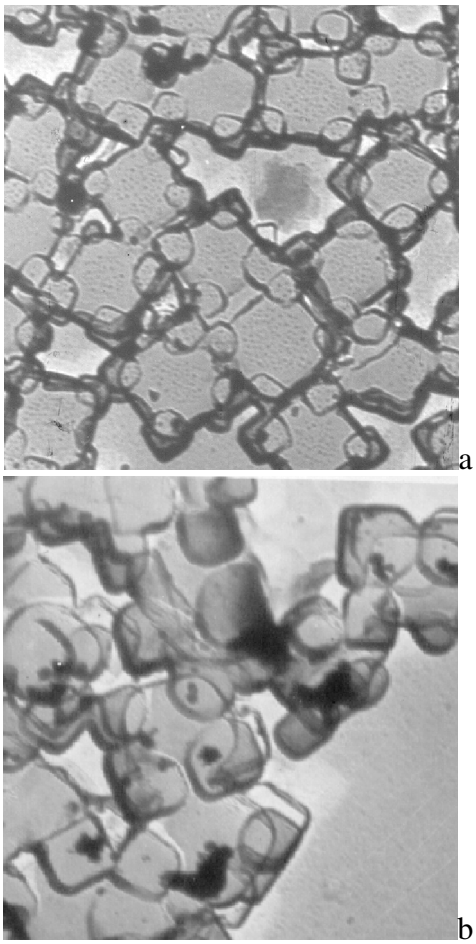

Figure 1. An electronic microphoto of coal replica of microcrystals AgBr with angular epitaxes AgCl (pCl=1, t°=45°C).
a) AgBr:AgCl=2:1; b) AgBr:AgCl=1:1

At crystallization of an shell by the method of two-jet crystallization at pCl=3 with the subsequent decreasing in the end of synthesis down to 1,5 the microcrystals was obtained which presented on a Figure 2b. In this case, apparently, there is a formation of fine microcrystals, which coalesce with sides of core microcrystals with the further recrystallization.

For research of temperature effect on process of formation of AgCl shell the crystallization was carried out in an interval of temperatures from 40 up to 60°C. The optimal temperature of crystallization, at which the monodisperse microcrystals are formed, is 45°C. At smaller temperature besides of process of crystallization of the shell there is a formation of a new AgCl microcrystals and its further growth. At temperature more than 45°C the dissolution of silver bromide crystals take place which results to a rounding of sides and to sticking of microcrystals. This so significant temperature effect on process of epitaxial is explained by strong dependence of the solubility AgCl on the temperature[4].

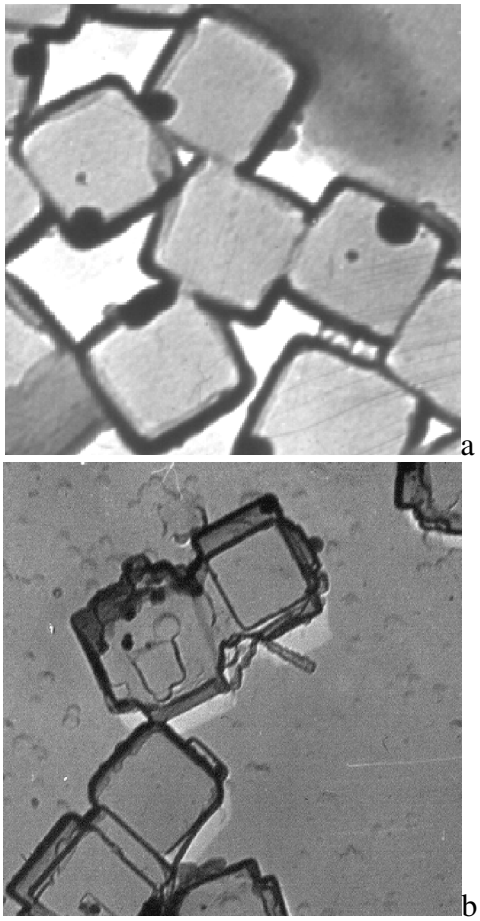

Figure 2. An electronic microphoto of coal replica of:
a) AgBr microcrystals with AgCl shell (pCl=2, t°=45°C); AgBr:AgCl=1:1
b) AgBr with AgCl epitaxes on {100} surface (pCl=3, t°=45°C); AgBr:AgCl=1:1

The research of process of formation of AgCl shell on microcrystals AgBr by a method of recrystallization of fine

emulsions also was carried out. The recrystallization of a mix core and fine emulsions was carried out at temperature 50 ^{o}C, and at pCl value varied from 1 up to 2. Time of crystal transformation was 50 mines.

It is revealed that at carrying out of process of recrystallization at chloride ions excess (pCl=1) already after 10 minutes of physical ripening the AgCl agglomerates were formed which at the further physical ripening continued to growth. The formation of a silver chloride shell on a AgBr core in our experimental conditions does not occur. The surface dissolution of AgCl microcrystals and their aggregation is observed that results in formation of large microcrystals of the imperfect forms.

At pCl=2 there is a formation of an shell. The crystal transformation is finished within the first 10 minutes and in subsequent the insignificant growth of microcrystals due the Ostwald ripening is observed only. Because of high solubility of AgCl the processes of recrystallization proceed much faster than for AgBr. The recrystallization of silver chloride proceeds also more depth that is even the small difference in a size of microcrystals is moving power for dissolution of small microcrystals (because of their high solubility pK_{sp}=9.8). The increase of an average equivalent diameter of microcrystals and decrease C_v (with 45 up to 15 %) is also observed.

The research of influence of the silver halide solvent (25% water solution of NH_4OH) on process of recrystallization of fine emulsion at the presence of core microcrystals has shown that in system the dynamic equilibrium between two fractions of microcrystals is established. It is connected to coexisting of competing processes: the growth of nucleus microcrystals due to Ostwald ripening and the back process of "dissolution" of microcrystals due to formation of ammoniac complexes of silver $[Ag(NH_3)_2]^+$ (pK_{12}=7,2). Therefore the re4crystallization of the fine emulsion is retarded and after finishing of the process of physical ripening there are core microcrystals and some of fine microcrystals.

The epitaxial AgBr/AgCl microcrystals and the core-shell AgBr/AgCl microcrystals were subjected to sulfur-plus-gold (S + Au) sensitization. The photographic properties of obtained layers were investigated by a standard sensitometric technique. The results are presented in a figure 3.

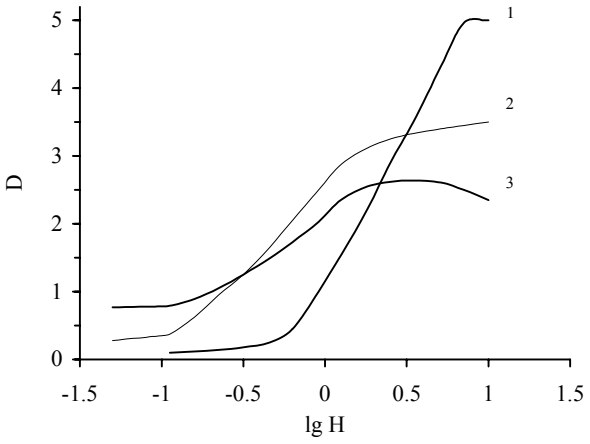

Figure 3. The characteristic curves of emulsion layers:
1- core emulsions AgBr, time of development - 8 mines.
2- systems AgBr/AgCl with angular epitaxes, time of development - 4 mines.
3- core-shell AgBr/AgCl, time of development - 4 mines.

From the graph it is possible to see that the emulsion layer 3 has high enough optical density of a fog and effect of solarization at the large expositions. The effect of solarization, apparently, is caused by amplification of processes of recombination on inner interface border, which are a source of an inefficiency of formation of the latent image.

Epitaxial systems allow to increase a photosensitivity six times besides that the time of display is reduced in 2 times. The very insignificant growth of optical density of a fog can be suppressed by utilizing developing solutions with a low of silver halide solvent concentration.

Thus, the carried out experiments have allowed to establish optimal conditions of crystallization of the monosize AgCl shell on microcrystals of composition $AgBr_xI_{1-x}$ and on $AgBr_xI_{1-x}$ microcrystals with AgCl epitaxes. The obtained heterocontact systems have allowed to increase a sensitivity of photographic layers and to reduce the time of photographic processing.

References

1. Yu.A.Breslav, V.V.Peisakhov, L.Y.Kaplun. *Advanced of Sci. Photogr. (Russia)*, **24:** 5-46 (1986).
2. E.I. Kagakin, T.A. Larichev, *J. Sci. and Appl. Photogr.*, **40**, 57-59 (1995)
3. B. A. Sechkarev, *Micr. Res. and Techniq.*, **42**, 145-147 (1998)
4. T.H.James, Ed., The Theory of Photographic Process, 4th ed., Macmillan, New York, 1977.