The Comparison of the Electron-Capture Cross-Sections of Different Impurity Centers of the AgBr(Irⁿ⁺) and AgBr(I, Irⁿ⁺) (n=3, 4)Emulsion Microcrystals

A.Yu.Akhmerov, S.A.Zhukov, O.I.Sviridova, Z.N.Palamarchuk, V.M.Belous; Research Institute of Physics; Odessa National University;Odessa/ Ukraine

Abstract

Photographic (room temperature) and luminescence (T=77K) properties of AgBr and AgBr(I) MC containing different concentrations of $Ir^{n+}(n=3,4)$ ions are compared. It is observed that sulfur sensitization of cubic $AgBr(Ir^{n+})$ MC leads to increase of sensitivity, whereas this effect is not seen in the case of octahedral $AgBr(Ir^{n+})$ or $AgBr(I, Ir^{n+})$ MC. According to the luminescence data it is found that sulfur sensitization of cubic AgBr(Ir^{n+}) MC promote formation of $(Ag_2S)_pAg^+$ - or $(Ag_2S)_q$ clusters (q > p, d > 20Å), which can compete with Ir^{n+} centers for photoelectrons localization that determines sensitivity increase. In contrast to the case of cubic MC, sulfur sensitization of octahedral $AgBr(Ir^{n+})$ and $AgBr(I, Ir^{n+})$ MC leads to Ag_2S_{-} , $(Ag_2S)_{2-}$ centers and $(Ag_2S)_n$ clusters $(n < p, d < 20\text{\AA})$, which do not compete with Ir^{n+} centers for capture of photoelectrons. Therefore, sulfur sensitization of octahedral MC does not lead to the sensitivity increase. We conclude that sensitivity centers formed in the course of sulfur sensitization are different in cubic and octahedral MC.

Experimental

The described below results were obtained during the study of the properties of the following emulsions: AgBr-emulsions, containing cubic MC with the average dimension (d) of $0.8 \cdot \mu m$ and $0.25 \cdot \mu m$ (on condition that the emulsions are indicated as A and B accordingly) and AgBr(I) (3-mole%AgI) emulsions with the $0.25 \cdot \mu m$ dimension cube-octahedral MC (C-emulsion). The MC habitus was determined on the base of the electron-microscopic observations. Introduction of tri- (III) or quadrivalent (IV) iridium ions was made under the solution emulsification by the use of potassium halide, holding different amounts of potassium hexachloriridate extra. The sulfur sensitization of the all listed emulsions was carried out under the following equal conditions: temperature -47°C, pAg 8.6, the sodium thiosulfate concentration – $4.6 \cdot 10^4$ mole Na₂S₂O₃ 5H₂O/mole AgHal.

As it follows from sensitometric results given in the table the presence of trivalent or quadrivalent iridium in the MC volume reduces the emulsion photosensitivity (surface developer, the developing duration is 8 min). The indicated desensitization made by iridium and connected with the electron-capture centers forming in the MC and with the advent of the electron-hole recombination additional channels [85] that verify luminescent results. According to it introduction of trivalent (III) or quadrivalent (IV) iridium ions into the MC is accompanied by the emulsion microcrystals low temperature (T=77K) photoluminescence quenching. However, despite all the studied emulsions desensitization by the introduced iridium (as an example, these results are given only for Aemulsion in the table). The emulsions photosensitivity after the sulfur sensitization (the photosensitivity maximum value was achieved under the sensitization duration $t_2=1.5-2.0$ hours) depends on the habitus, dimension, concentration of the introduced iridium and the MC halide composition.

If for A-emulsion the sulfur sensitization leads to the photosensitivity raise even for the MC holding the iridium ions then in the case of B, C-emulsions the presence of iridium in the MC are accompanied by the photosensitivity reduction (the table). The obtained results about the different influence of iridium on the photosensitivity under the sulfur sensitization allow us on the base of the luminescent and sensitometric emulsion properties comparison to find out which sulfur-silver centers must be created under the sensitization, in order they could win the competition with the "iridium" centers in the electrons localization and to ensure thereby the photosensitivity rise. In addition, the obtained results allow us to have known which centers have a smaller value of σ_e in comparison with the "iridium" ones that leads to the desensitization. The luminescence spectrums of the emulsions with the various duration of the chemical ripening were measured under 77K. Monochromatic radiation with λ =500·nm was used for luminescence excitation. As everybody knows, only the sulfursilver centers luminescence is aroused in this case [2]. Therefore, it is possible to conclude about the change of the sulfur-silver clusters concentration and their dimensions correspondingly on the base of the luminescence intensity change and the luminescence maximum change in the ripening process.



Fig.1. The luminescence spectrums of the A(a), B(b), C(c) emulsions with the various sulfur-sensitization duration $(t_2, hours)$): 1 – 0.0; 2 – 0.5; 3 – 1.0; 4 – 2.0; 5 – 3.0; 6 – 4.0; 7 – 6.0. The emulsion grains contained 10 ⁻⁶ potassium hexachloriridate mole/mole AgBr.

As an example in the fig. 1 the luminescence spectrums of the sulfur-sensitized emulsions with various duration of sensitization (t_2) and with the definite iridium (IV) admixture concentration in

the MC (10^{-6} mole potassium hexachloriridate /mole AgHal) are given.



Fig.2. The intensity dependences in the infrared luminescence band maximum of A(a), B(b), C(c)-emulsions on the sulfur-sensitization duration. The emulsion grains contained the following concentrations of the potassium hexachloriridate admixture (mole/mole AgBr): 1 - 0 (no admixture); $2 - 10^{-6}$; $3 - 5 \cdot 10^{-6}$; $4 - 10^{-5}$. The curve 1 is dotted on Fig.a.

The measurements of a similar nature were also made for the emulsions with other iridium (IV) admixture concentrations in the MC. The dependences of the luminescence intensity (I_{lum}) and the luminescence maximum spectral location (λ_{max}) of A, B, C – emulsions on t₂ were derived on the ground of the obtained results



Fig.3. The dependences of the infrared luminescence band maximum spectral location (λ_{max} , nm) of A(a), B(b), C(c – emulsions on the sulfur-sensitization duration. The emulsion grains contained the following concentrations of the potassium hexachloriridate

(fig.2, 3).

admixture (mole/mole AgBr): 1 - 0 (no admixture); $2 - 10^6$; $3 - 5 \cdot 10^7$ ⁶; $4 - 10^{-5}$. The curve 1 is dotted on Fig.a.

The luminescence rise for all studied emulsions in the near infrared spectral region under the sulfur sensitization proves that the sulfursilver clusters arise on the MC surface because of the mentioned sensitization [2]. The experimental results, shown in fig. 1-3, let us derive the following conclusions.

In the case of A - emulsion, the evolution of the sulfur-silver clusters is typical for cubic MC [17,24,26] and is characterized by the clusters dimensions fast enough growth, which is proved by the long-wave displacement λ_{max} from 820 to 1020 nm in the sensitization process and by the absence of a luminescence intensity considerable growth (fig.2a and 3a). It is obvious that a relatively small number of the sulfur-silver clusters arise on the surface of the cubic emulsion MC in the thiosulfate adsorption case. Their dimensions rise as at the expense of Ag₂S- molecules association arisen and migrating on the MC surface, as following the absorption of the sulfur sensitizer on (Ag₂S)_n-cluster of the definite dimensions that determines at once the cluster dimension rise according to the autocatalytic law. The photosensitivity maximum is achieved in the area t2=1.5 - 2.0 hours for the emulsion without iridium (the fog density is not more, than $D_0=0.04$) at the same time the value $\lambda_{max}=880 \cdot nm$ (1.14eV) that corresponds to the cluster's dimension d≈30Å [3]. Introduction of the iridium ions into the MC of A-emulsion does not change the general view of the dependence of I_{lum} and λ_{max} on $t_2,$ however, the value of λ_{max} is slightly greater than in the case of the MC without iridium, under $t_2=1.5-2.0$ hours when the photosensitivity maximum is achieved. This says that such sulfur-silver clusters that have slightly greater dimensions, than the ones of the reference emulsion, in this case determine the photosensitivity. Sulfur-silver clusters of relatively great dimensions (d>20Å) are able to adsorb the silver ions, transforming at that into the positive impurity centers [2]. Then it follows from the obtained results that the photosensitivity rise is bound up with the arise of those very clusters of the $(Ag_2S)_pAg^+$ -type or $Ag^+(Ag_2S)_pAg_{m-1}$ -type $(perhaps,(Ag_2S)_pAg_m^+,m<4)$ [2] which have got the greater electron-capture cross-section than the electron-capture (or electron-recombination) cross-section of the center holding the iridium ion. Though the AgBr-MC of B-emulsions had the cubic habitus, however, unlike A-emulsion, the change of λ_{max} under the sulfur sensitization is observed only in the range from 760 nm to 870.nm (fig.3b). This shows that in this case under the sensitization the clusters form with smaller dimensions than the ones of Aemulsion. Obviously, the MC with d=0.25·µm synthesis conditions assist in the surface defects concentration rise that influences the adsorption of the sulfur sensitizer and the evolution of the sulfursilver clusters, arising at that. Introduction of iridium ions into the MC brings the dependences I_{lum} and λ_{max} on t_2 nearer to the case, typical for the MC with the octahedral habitus-under the rise of t₂ the considerable rise of I_{lum} and not very sudden (only in the range from 800·nm to 850·nm) displacement of λ_{max} are observed (see also [2]). Such result evidently shows that the surface defects concentration rises greatly under the introduction of the iridium ions into the MC with $d=0.25 \cdot \mu m$ that leads to the impurity centers formation through the first-order reaction under the sensitization [2]. As it follows from the luminescent investigations, the luminescence band of the clusters with λ_{max} =820·nm is observed for B-emulsion with the maximum photosensitivity (t₂=1.5 hours). This value λ_{max} is greatly smaller than the one for the case of A– emulsion. Then in this case, under the sulfur sensitization the sulfur-silver clusters with smaller dimensions, than the ones for A– emulsion, arise on the MC surface. Mentioned clusters cannot win the competition with the "iridium" centers in the localization of the photoelectrons, created by the light in the MC, and so the introduction of iridium into the MC is accompanied by the photosensitivity decrease for B–emulsion (see the table).

Potassium B- emulsion hexachloriridate A- emulsion C- emulsion concentration, mole/mole AgBr S_{0.85} before the sulfur Maximum value of S_{0.85} Maximum value of S_{0.85} Maximum value of S_{0.85} sensitization after the sulfur after the sulfur after the sulfur sensitization sensitization sensitization Iridium Iridium Iridium Iridium Iridium Iridium (III) (IV)(III) (IV) (IV) (IV) 0 0.85 12.0 1.8 26 10^{-7} 0.65 0.52 22.0 23.5 10^{-6} 0.37 0.46 21.0 39.0 1.2 26 $5 \cdot 10^{-5}$ 0.8 23 10^{-5} 0.1 0.1 19.5 16.0 0.5 17 $5 \cdot 10^{-5}$ 0.23 13 10^{-4} 0.2 0.1 11.0 19.0

Table. The photosensitivity (S_{0.85} lux⁻¹ c⁻¹) of A, B, C-emulsions containing different amounts of iridium before and after the sulfur sensitization

The results of the luminescent measurements obtained for C – emulsion completely correspond to the MC with the octahedral habitus case - the sharp rise of the luminescence intensity and the small change of λ_{max} follow the rise of t_2 (the value λ_{max} does not depend on t_2 for the emulsion without iridium, fig.3c). However, the introduction of the iridium ions into the MC influences the mentioned dependences somewhat (obviously, because of the MC defects change), however, in this case also the value λ_{max} for the emulsions with the maximum photosensitivity (t_2 =1.5 hours) is greatly smaller, than the one for the case of A–emulsion. As it was pointed out earlier (see the table), the introduction of the iridium ions into the MC of C–emulsion is accompanied by the photosensitivity decrease. Such result should be expected on the base of the explanation given for B–emulsion.

Thus, the experimental results described earlier prove that under the sulfur sensitization of the emulsion microcrystals, which differ in the dimension, habitus, halogen-silver composition, the sulfursilver centers, different by the dimensions and the charge state, arise. Only in the cubic MC case, $(Ag_2S)_pAg_m^+(m<4)$ and $(Ag_2S)_q(q > p)$ clusters with the dimension d>20Å are the photosensitivity centers which are able to concentrate the photolytic silver near themselves. The mentioned clusters do not arise for the MC with the octahedral habitus [2]. Perhaps in this case the dimers $(Ag_2S)_2$ (+DK $(Ag_2S)_2$ -centers), situated near the positively charged MC surface defects, are the photosensitivity centers [4]. The dimensions of these centers are greatly smaller (d<20Å [5]), than the ones of the clusters $(Ag_2S)_pAg_m^+(m<4)$ or $(Ag_2S)_q(q>p)$. Hence, DK $(Ag_2S)_2$ -centers can not win the competition with the "iridium" centers in the photoelectron capture. In addition, it must be taken into account that sulfur sensitization of octahedral MC leads to the $(Ag_2S)_n(n < p)$ clusters rise, which are the traps not for the electrons, but for the holes [2] (appearance of the luminescence bands in the region from 700 to 870 nm is connected with these clusters [2]). The indicated clusters assist in the photosensitivity rise by their hole-acceptor function only.

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Author Biography

Alexander Akhmerov received his BS in physics from the Odessa National University, Ukraine (1975) and his PhD in physics and mathematics (1989). Since then he has worked in the Research Institute, Odessa National University, Ukraine. His work has focused on the development of spectral sensitization and supersensitization of silver halide emulsions using luminescent investigations.

The Synergetic Action of Chemical and Spectral Sensitizations on Cubic {100} AgBr Microcrystals

Afonkina J. N., Sotnikova L. V., Sechkarev B. A., Ryabova M. I.; Kemerovo State University, Kemerovo, Russia

Abstract

The given work is devoted to comparative research of influence of adsorption of dye on a surface of cubic {100} AgBr microcrystals, subjected to various types of chemical sensitizations, on a level of photographic sensitivity and optical density of the fog of photographic layers on their basis.

Influence of the nature thyacarbocianin Dyes on sensitometric characteristics of photographic layers with the centers of photographic sensitivity received at sulfur, sulfur – plus - gold, reduction and reduction – plus - gold chemical sensitizations is investigated.

It has been established, that the level of photographic sensitivity and optical density of the fog of photographic layers is determined by the nature of a spectral sensitizer besides adsorption of some dyes results in decrease in optical density of the fog. Investigating efficiency of a spectral sensitization of cubic [100] AgBr microcrystals depending on type of the centers of photographic sensitivity, mutual influence of chemical and spectral sensitizations has been shown.

Introduction

One of most important aspects in modern photographic practice is the search of the techniques of improving of efficiency of the photographic process on halide silver (AgHal) microcrystals (MC) to increase photographic materials' sensitivity. The most important stages for effective formation of the photographic speed surface centers are chemical and spectral sensitizations. The process of spectral sensitization is a less investigated and more interesting method of photographic speed increase in AgHal C. One of the difficulties in achieving the highest photographic speed during spectral sensitization is the desensitization effect of secondary oxidation-reduction processes of Dye (D). Therefore, to achieve the highest photographic speed it is necessary to eliminate these processes.

It is common knowledge that the fog optical density values of a photographic layer at spectral sensitization always increase [1]. However, on the basis of our experimental data it was found out that the introduction of certain carbocyanine D on tabular MC reduces the fog optical density values achieved during chemical sensitization [2] without photographic speed decrease and the maximum optical density of darkening decrease. The goal of the paper is to determine the influence of the chemical nature of impurity centers (IC) on spectral sensitization by one and the same Dye.

Experiment

Synthesis of the photographic emulsion

The emulsion containing cubic AgBr MC with the average equivalent diameter d = 0,80 mcm and the variation factor $C_v = 8\%$ was synthesized by the two-jet crystallization method [3]. The electronic microphotograph of the emulsion is given in Fig. 1.



Figure 1. The electronic microphotograph of cubic AgBr MC.

Chemical sensitization (CS)

IC of the different chemical nature $((Ag_2S)_nAg_mAu_k, (Ag_2S)_nAg_m, Ag_n^0, Ag_n^0Au_k)$ were formed on the surface of cubic AgBr MC by means of different types of CS. The conditions for CS AgBr MC were adjusted for each type of CS. Four types of CS resulting in IC of the different chemical nature were investigated, namely: sulfur CS ((S)-CS) by Na_2S_2O_3, sulfur-plus-gold CS ((S+Au)-CS) by Na_2S_2O_3 and HAuCl_4, reduction CS ((Sn+Au)-CS) by SnCl_2 2H_2O and reduction-plus-gold CS ((Sn+Au)-CS) by SnCl_2 2H_2O and HAuCl_4.

The conditions for sensitizations and the sensitometric characteristics of the photographic layers (relative photographic speed (S_{rel}), fog optical density values (D_0) and maximum density of darkening values (D_{max})) are submitted in Table.

Spectral sensitization (SS)

To determine the degree of the influence of the chemical nature of IC on SS by the same Dye during CS, the Dye (D-1) was added into the emulsion.



The D-1 concentration in the emulsion was $6,2 \ 10^{-5}$ mole/mole Ag. After the adsorption of D-1 onto the surface of cubic AgBr MC with the IC of the different chemical nature, the photographic layers were coated on the support. Then, chemically and spectrally sensitized photographic layers were subjected to sensitometric tests and the photographic speed and fog optical

density values were compared. The values of the photographic characteristics of the emulsion layers are submitted in Table. The characteristic curves of chemically and spectrally sensitized photographic layers for different types of CS are presented in Fig. 2.

Sensitometric characteristics and the conditions for chemical and
spectral sensitizations of the photographic emulsion:

CS additives, x 10 ⁻⁵ mole/mole Ag			Sensitometric characteristics received at CS			Sensitometric characteristic received at SS by D-1		
[Na ₂ S ₂ O ₃]	[HAuCl ₄]	[SnCl ₂]× 2H ₂ O	S _{cs}	Do	D _{max}	S _{SS}	D。	D _{max}
7,2	-	-	20	0,18	3,11	30	0,17	4,89
7,2	1,7	-	30	0,33	4,53	50	0,14	5,11
-	-	5,4	10	0,30	2,51	40	0,45	4,42
-	1,7	5,4	25	0,39	3,73	100	0,88	4,55

These characteristic curves show the influence of Dye-1, depending on the type of chemical sensitization, on photographic speed of cubic AgBr MC.







- the sample after (Sn+Au)-CS and adsorption of D-1 Figure 2. Characteristic curves of photographic layers with IC received for different types of CS.

Based on the experimental data, photographic speed increase values (S) due to adsorption of D-1 during CS for different types of IC were calculated. S was calculated by the formula: $S = S_{SS} - S_{CS}$, where: S_{CS} - photographic speed received at CS; S_{SS} - photographic speed received at SS.

The values of S are submitted in Fig. 3.



Figure 3. Dependence of photographic speed increase (S) from the time of sensitization after adsorption of D-1.

It is seen that the dependence of photographic speed increase on the time of sensitization after adsorption of D-1 for different types of CS is extreme to a greater or lesser extent with the exception of (S)-CS for which insignificant increase in photographic speed is observed during the first 45 min. During (S+Au)-CS appreciable photographic speed increase (~ two-fold increase) occurs within 30-90 min followed by photographic speed decrease due to fog optical density increase. During (Sn)-CS there occurs gradual increase of S (for 90 min) followed by its decrease due to fog optical density increase. Sharp increase in photographic speed during (Sn+Au)-CS occurs from the first minutes of the introduction of HAuCl₄ and proceeds for 90 min. Thus, (Sn+Au)-CS allows us to receive the maximum absolute photographic speed increase during SS. On the other hand, from the CS data (see Table) it is evident that the reduction sensitization is least effective. (S)-CS allows us to obtain photographic speed values twice as much as the values during (Sn)-CS. The inclusion of gold atoms into the structure of IC results in photographic speed increase both for (Sn)-CS and for (S)-CS, and there occurs twofold increase in fog optical density during (Sn)-CS. Thus, the best sensitometric characteristics are achieved during (S+Au)-CS.

The experimental data show that the influence of adsorption of D-1 on IC, having a different chemical nature, on photographic speed can be different depending on the IC type.

During (S)- S and (S+Au)-CS the adsorption of D-1 does not actually affect photographic characteristics of the layers because of desensitization. Our experimental data agree to the data [4] on weak SS of Ag₂S centers by cyanine D. Desensitization effect, in this case, is explained by the recombination of photoelectrons and holes of D on Ag₂S centers. However, during (S+Au)-CS fog optical density values after the adsorption of D-1 decrease.

The interaction of D-1 with the Ag^0 centers formed during (Sn)-CS appeared more effective. It is known that photographic layers with the (Sn)-CS centers are least subjected to desensitization by D [1]. Silver clusters (the centers of (Sn)-CS) are the acceptors of both electrons and holes depending on their size [5]. A characteristic property of (Sn)-CS is its ability of forming a great amount of inner electron and hole traps in spite of the fact that the inclusion of gold into the structure of IC stabilizes silver clusters and catalyses their development but photographic speed values of the layers with the Ag^0 and $Ag^0_nAu_k$ centers remain low (see Table). However, these centers eliminate the desensitization effect caused by D-1. For the photographic layers with the $Ag^0_nAu_k$ centers there was observed six-fold increase in photographic speed at rather high fog optical density values.

Hence, the optimum photographic properties cannot be obtained when using only one type of IC. To exclude the desensitization effect caused by D we decided to use mixed sensitization, viz, $Na_2S_2O_3$, $HAuCl_4$ and $SnCl_2 2H_2O$ were used as chemical sensitizers. In this case $SnCl_2 2H_2O$ acted as a reductone*.

The characteristic curves showing a consecutive change of the photographic response of the layers depending on the conditions for mixed (Sn+S+Au) sensitization are submitted in Fig. 4.





Figure. 4. Characteristic curves of chemically $(\Box - (S+Au)-CS, \bullet - (Sn+S+Au)-CS)$ and spectrally $(\circ - (Sn+S+Au)-CS + D-1)$ sensitized photographic layers.

It is seen that characteristic curves after the application of $SnCl_2 2H_2O$ as a reductone, fog optical density values decrease significantly. The adsorption of D-1 results in further decrease in fog optical density and, thereby, in appreciable layer photographic speed increase. The method proposed for this type of sensitization is rather perspective since high photographic speed values are achieved by systematically decreasing fog optical density values.

Conclusion

Having investigated the efficiency of spectral sensitization of cubic AgBr C depending on the type of photographic speed centers, it is shown that chemical and spectral sensitizations influence each other. Also, it was found out that the introduction of Dye reduces fog optical density values achieved at (S+Au)- and (Sn+S+Au)-CS if they are not too high. The impurity centers $-Ag^0_n$, $Ag^0_nAu_k$ during spectral sensitization are least subjected to the desensitization effect caused by Dye.

It is stated that sensitizers and dyes for each photographic material should be thoroughly selected to achieve the optimum photographic characteristics.

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Author Biography

Juliya N. Afonkina was born in Kemerovo (Russia) on June 25, 1980. In 2002 graduated from the State University of Kemerovo, Chemistry Faculty. Since 2002 she worked on General Physics departments of Kemerovo State University as a Scientific Researcher. Now she is Postgraduate student of the General Physics department of Kemerovo State University. Her field of research is chemical sensitization processes of silver halide photographic emulsions. The author of 23 scientific publications.

The Formation and Chemical Sensitization of AgHal Heteroepitaxial Tabular Microcrystals

E. V. Prosvirkina, A. B. Abisheva, T. A. Larichev and B. A. Sechkarev; Kemerovo State University; Kemerovo, Russia

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 \approx 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 1. 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

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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.