The Formation of Silver Particles Dispersions at Photodecomposition of AgBr Microcrystals

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Abstract – The investigation of the effect of sensitivity centers formation in AgBr octahedral microcrystals (MC) (111) at the ripening without sulfur-containing additives (natural ripening) is carried out. It is established that the sensitivity centers formation occurs during the shape modification of MC AgBr (111) owing to the disparity of the chemical potential of microcrystal facets. It directly proves the silver nature of sensitivity centers at the microcrystals AgBr (111) ripening in explored conditions. The results of experiment on the change of the octahedral AgBr (111) MC photosensitivity (S) depending on the crystal sizes (d) are discussed. For the first time it is shown that the limited concentration of the growth centers of silver particles on the surface of AgBr (100) and AgBr (111) MC makes $10^{10}$–$10^{11}$ cm$^{-2}$ that is comparable with the density of the surface states related to Br$^{-}$ ions on the kink sites. It allows to present these defects as the active centers of silver concentration.

1. Introduction

The process of the information registration in silver halide photographic systems consists in the controllable formation of the particles from clusters till the micron sizes at all stages of the materials processing. However till now there is no the unique answer to the questions on the nature of the sensitivity centers, on the reason of the photo sensitivity dependence from the sizes MC and the crystallization rate, about the regularities of the silver clusters formation on the MC surface.

2. An experimental technique

The emulsions with AgBr (111) MC have been obtained by the controlled double-jet crystallization technique [1]. The sensimetric method to the examination of the photographic performances of the photo-layers was applied. The ionic conductivity of the AgBr MC was studied by the dielectric loss method [2]. The electronic microscopy was used for measuring the sizes and shapes of AgBr microcrystals. The legitimacies of the silver particles formation on the MCs surface by the method of the coal replicas were explored.

3. The influence of the ionic equilibrium on the process of silver clusters formation on the AgBr (111) microcrystals surfaces

In Fig. 1, the results of the investigation of the photosensitivity change during the MCs AgBr (111) natural ripening at the introduction in the reactor of the small-grained emulsion microcrystals (SGE MC) with the sizes $d_{\text{SGE MC}} < d_{\text{AgBr (111) MC}}$ are given.

As follows from the obtained data given in Fig. 1, for the AgBr (111) MC the photosensitivity increase during ripening without addition of sodium thiosulfate is observed. Authors [1] this effect is termed by the natural ripening. It is obvious that the formed sensitivity centers in given requirements have cleanly silver nature. In the some cases the sensitivity level for AgBr (111) MC achieved 120–150 units, that comparably with the sensitivity values, obtained in the requirements of the usual chemical ripening of corresponding systems.

In Fig. 2 electron micrographs of AgBr MCs coal replicas after the various methods of the treatments are given. The analysis of the obtained electron micrographs of MCs coal replicas (Fig. 2) shows that during the natural ripening and storage there is the change of the microcrystals shape and facet. It is developed in the flattening of the edges and the summits of octahedrons at the ripening time till 2 hours and in the formation of the practically spherical and cubic shape at 4 hours of the ripening.

The increase of the supersaturation in the solution by the addition of the small-grained emulsion during the natural ripening of the microcrystals result in to increase of the rate of the MCs shape modification. The all obtained results allow to confirm that the cer-
tain level of the supersaturation in the solution is necessary for the sensitivity formation in the mode of the natural ripening of AgBr (111) MC.

It is known [3] that the microcrystals which are being equilibrium with the environment, take the form with the minimum free surface energy, $G$. This concept has been formulated by Gibbs-Woolf in the form of the relation:

$$ G = \sum_i S_i \gamma_i = \text{min} , $$ (1)

or

$$ \gamma_1 = \frac{r_2}{r_1} = \frac{\gamma_1}{\gamma_2} = \frac{kT}{r_1} \frac{C_\text{sol}}{C_\text{imp}} , $$

where $S_i$, $\gamma_i$, $r_i$ - area of $i$-th facet, free surface energy of $i$-th facet and distance up to $i$-th facet from centre of the crystal (a normal line to $i$-th facet), accordingly; $V_m$ - molar volume of MC, $k$ – Boltzmann constant, $T$ – temperature, $C$ – solution concentration, $C_\text{imp}$ – solubility at the crystallization temperature.

With reference to the data presented in Fig. 2, the change $r_{111}$ and $r_{100}$ means the change $\sum S_i \gamma_i$, according to requirements in the solution. Thus supersaturation in the solution, containing the microcrystals, will be natural to depend and on the distribution of microcrystals in the sizes. In this case the recrystallization process owing to the effect of Gibbs-Thomson, that will be more significant, than this distribution is less uniform. It means that the natural ripening process essentially depends on the supersaturation ($\Pi$), that is, there is threshold value $\Pi^*$. In this case, if the value of the supersaturation in the solution essentially is more or less $\Pi^*$, the sensitivity formation during the ripening occurs less efficiently. For cubic MC the requirements in the solution at natural ripening correspond $\Pi << \Pi^*$ and the sensitivity formations is not observed.

In Fig. 2 it is possible to distinguish the some MCs shapes during the modification: octahedral, cub-octahedral (tetrahedral with the various relations of the facets areas (111) and (100)) and cubic. The relation of the normal lines to facets of MC for the numbered shapes varies in following limits:

$$ \frac{\gamma_{111}}{\gamma_{100}} \cdot \frac{r_{111}}{r_{100}} < 0.57 $$ crystals will get the octahedral facet irrespective of the initial shape of MC. At $\mu_{111} > \mu_{100}$ for $\gamma_{111}/\gamma_{100} \leq 0.57$ crystals will be modified consistently up to the spherical and cubic shapes.

Thus, the sensitivity centers formation in AgBr (111) MC at the ripening without sulfur-containing additives occurs during the recrystallization owing to the distinction in the chemical potentials of the facets (111) and (100). As follows from the obtained experimental results, on the MCs surface thus the stable silver sensitivity centers (SC) are formed. Presumably, the formation plan of sensitivity centers will include the stage of the MCs dissolution with increase of the relation $r_{111}/r_{100}$:

$$ \text{AgBr} \rightarrow \text{Ag}^{+} \text{sol} + \text{Br}^{-} \text{sol} \quad (4) $$

The further plan of the sensitivity centre formation can be written down as the plurality of the electronic and ionic stages on MC surface:

$$ e^- + \text{Ag}^{+} \text{sol} + \text{Ag}_2 \text{S} \rightarrow \text{Ag}_2 \text{S} \equiv \text{SC} \quad (5) $$

$$ e^- + \text{Ag}^{+} \text{sol} + \text{Ag}_2 \text{S} \rightarrow \ldots \quad (5') $$

...Ag$_2$S, etc. with the formation of the fog centers, where Ag$_2$S – silver ion on the MCs surface defect (for example, kink-site).

The full or partial absence of the reactions 4, 5 at the AgBr (100) MCs ripening explains the difference of cubic MC from octahedral microcrystals. Thus, it is shown, that the mechanism of the sensitivity centers formation in AgBr (111) MC in the mode of natural ripening is related to the distinction in the chemical potentials of the facets of the AgBr (111) and (100) MC.

4. The influence of the AgBr (111) microcrystals sizes on the photosensitivity centers formation process

It is standard that the process of the latent image formation during the lighting of the AgBr microcrystals is the sequence of the electronic and ionic stages on the sensitivity centers. In the high-sensitivity microcrystals this sequence concentrates on the restricted number of the sensitivity centers. The degree of the optimization depends on the lifetime of the electron on
the sensitivity centers: \( \tau_e = \frac{L}{V_0} \exp \left( \frac{\Delta E_i}{kT} \right) \) (\( E_i \) – energy of the trap concerning the conduction band), and also the ionic conductivity which determines the neutralization time of the entrapped \( \tau_n = \frac{\epsilon \epsilon_0}{\sigma} \). The broadening of these quantities \( \Delta \tau_e \) and \( \Delta \tau_n \) owing to the presence of the several sensitivity centers, the inhomogeneity of the MC in the sizes and habit result in to the sensitivity decrease. Thus, the important parameters of the formation of the latent image are the energy of electronic traps \( E_i \) and the ionic conductivity \( \sigma \). As value \( \sigma \) depends on the facet and sizes of the MC, in the present paper the studying of the influence of AgBr (111) MCs sizes on the photosensitivity formed during the natural ripening is carried out.

In Fig. 3 the results of the investigations of the photosensitivity change and the fog level of AgBr (111) MC with various sizes are presented. In the table 1 the results on the change of the quantity \( \sigma \) depending on the MC sizes are given.

![Fig. 3. Sensitivity (S0.85) and the fog level (D0) vs. medial equivalent size of AgBr (111) microcrystals: S(0) – initial sensitivity, S(C) – in the mode of the natural ripening, S(C+TAI) – in the mode of the natural ripening with addition triazaindolizine (TAI)](image)

As follows from the presented in Fig. 3 results, the greatest value of the quantity \( S \) during the natural ripening is achieved for the AgBr MC with the sizes 0.9–1.1 microns. According to the data in the table 1, the value of the ionic conductivity at \( d = 1 \) micron exceeds the conductance for the macrocrystals. For the discussion of the possible reasons of the dependence \( S \) from \( d \) we shall carry out the estimates \( \tau_e \) and \( \tau_n \). It is possible to guess that the observable maximum of the photosensitivity in Fig. 3 is related or to the length of the diffusion bias of the photoelectron, or in due course the neutralizations time of the electron on the sensitivity centers an the interstitial silver ion.

### Table 1. The value of the ionic conductivity for the some MCs (111) sizes, data are average for uniform conditions of synthesis. In view of the literary data the conductance value for the macrocrystal [4] is given

<table>
<thead>
<tr>
<th>( d, \mu m )</th>
<th>( \sigma, \text{Om}^\text{-2} \text{sm}^{-1} )</th>
<th>( E_i, \text{eV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.2·10^-3</td>
<td>0.35</td>
</tr>
<tr>
<td>0.3</td>
<td>5.4·10^-6</td>
<td>0.45</td>
</tr>
<tr>
<td>0.4</td>
<td>4.5·10^-6</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>1.1·10^-6</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>10^-6</td>
<td>0.55</td>
</tr>
<tr>
<td>macrocrystal</td>
<td>4.2·10^-8</td>
<td></td>
</tr>
</tbody>
</table>

Guessing that the lifetime of the electron on the trap is determined by the recapture process of the electron an interstitial ion, it is possible to establish the connection between the activation energy of the ionic conductivity \( E_i \) and the trap energy of the entrapment concerning bottom of the conduction band \( E_i \) [5]:

\[
\tau = \exp \left( \frac{E_i - E_{\text{th}}}{kT} \right) = C \exp \left( \frac{E_i}{kT} \right),
\]

\( E_i \) – the activation energy of neutralization of the electron on the trap by interstitial silver ion, \( E_{\text{th}} \) – the activation energy of the ionic conductivity.

Thus, on measured values \( E_i \) and \( E_{\text{th}} \) it is possible to define the depth of the electronic traps and the lifetime of the electrons. According to the data [5], value \( E_i \) practically does not depend on MCs sizes and is equaled 0.07 eV. From here for \( d = 0.9–1 \mu m \), \( E_i = 0.45–0.5 \text{ eV} \). On the relations \( \tau_n = \frac{\epsilon \epsilon_0}{\sigma} \) and \( \tau_e = \frac{L}{V_0} \exp \left( \frac{E_i}{kT} \right) \) estimates Maxwell time relaxation \( \tau_n \) and the lifetime of the electron on the traps \( \tau_e \) which have made 1.1·10^-6 s and 6.3·10^-6 s, accordingly are made. Thus, the relation of these quantities testifies that the neutralization of the entrapped carrier will occur earlier, than there will be the thermal release of the trap. For the macrocrystal value \( \tau_n = 2.6·10^{-5} \text{ s} \) and is more than \( \tau_e \). In this case the probability of the participation of the several sensitivity centers during the latent image formation increases and \( S \) decreases, as is observed in experiment (Fig. 3). On the other hand, if to assume for \( \tau_n \) the found value 6.3·10^-6 s, and for \( \mu_e = 0.2 \text{ sm}^2 \text{ B}^{-1} \text{s}^{-1} \), then the length of diffusion bias \( L \) will be equal 1.2 microns, that is close to the observational value \( d \) in maximum \( S \). The last means that at \( d > d \) (Smax) the decrease of the photosensitivity occurs owing to \( L < d \).

5 The state of the surface and the limiting number of the growth centers of silver particles

According to the diffusive-drift model the surface is represented as the source of the generation of the additional Frenkel defects to the equilibrium value in volume. As \( D_{vi} \ll D_{Ag^+} \), as the result of the diffusive-
sive-drift redistribution the surface is charged negatively (here $D_{V}$ and $D_{Ag}$ — diffusion constants of the vacancy and the interstitial silver ion, accordingly). From the requirement of the equality to zero of the drift and diffusion streams, it is possible to gain the relation for the quantity of the surface potential:

$$e\Delta \varphi = (\varphi_s - \varphi_o) = \frac{kT(b - l)}{n_o b} (\Gamma_s b),$$  \hspace{1cm} (7)

where: $\Gamma_s$ — the function of the generation of the Frenkel defects pair, interreacting under the Coulomb law, $b$ — the relation of the mobilities $V_K$ and $Ag^{+}$, $l$ — the Debye shielding distance. The estimate of the quantity of the surface potential yielded with use of the numerical values of the parameters entering in (7), available in the literature yields value $e\Delta \varphi \approx -0.1$ eV that is close to experimental data. Really, the estimates of the surface potential which made immediately from the measuring of the ionic conductivity and photo-emission of electrons, the yield value $e\Delta \varphi \approx -0.25$ eV for the AgBr (111) MC and $e\Delta \varphi \approx -0.15$ eV for the AgBr (100) MC, that corresponds to the density of the charge, related with $Br^{-} 10^{10}$–$10^{11}$ sm$^{-2}$ [6]. The investigation of the regularities of the formation and silver particles growth has shown that at the storage (pBr = 3.0) of AgBr (111) MC on the surface are formed Agn specs up to $10^{10}$ sm$^{-2}$. They were directly revealed by the electron microscope (without arrested development) (Fig. 4b). At the development of these microcrystals simultaneous growth of Agn specs up to $10^{10}$ sm$^{-2}$ was observed (Fig. 4c). Thus, at the storage (pBr = 3.0) of AgBr (111) MC effect of auto-decoration of the surface take place. This fact shows that the limiting number of the active growth centers on AgBr (111) MC surface is revealed. On the irradiated AgBr (111) MC surface the formation of Agn particles up to $10^{11}$ sm$^{-2}$ is observed also (Fig. 4a). Summary, the limiting number of growing silver particles equals the density of the surface states. It allows approving that $Br^{-}$-defects on the AgBr MC surface are crystallization centers.

Fig. 4. Electron micrographs of carbon replicas of AgBr (111) microcrystals: a) irradiated microcrystals were developed by the solution D-76, b) microcrystals were storage at pHBr = 3.0 and $t = 6^\circ$C during 6 months, c) microcrystals were storage at pHBr = 3.0 and $t = 6^\circ$C during 6 months and were developed. The formation of Agn particles up to $10^{11}$ sm$^{-2}$ is observed in the all cases

References