

Investigation of Silver Particles Forming on Surface of Silver Bromide Micro-Crystals

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Abstract – The regularities of formation and electronic characteristic of photolytic silver on the surface of sols and microcrystals (MC) AgBr of various sizes and habits, as well primitive, as subjected to chemical sensitization was explored by transmission electronic microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) methods. XPS results were compared to condition of silver in sols and MC AgBr, synthesized at low values of pAg, and also with data for massive and disperse metallic silver.

1. Introduction

The most actual direction of the modern investigations of a surface is studying of the intentional modification of a surface as a result of external actions of the different nature. In a scientific photography those is process of silver clusters formation on a surface of AgHal MCs and other products topochemical reactions, the composition and structure which differs from matrix AgHal. The knowledge and the profound understanding of similar surface processes is necessary not only for successful creation and perfection of photographic materials and registration systems on their base, but also represents major theoretical interest. In the present paper there are represented investigations of surfaces state of silver bromide model MCs at preparation and optimization stages, before and after the UV irradiation by TEM and XPS methods. These investigations were carried out for determinations of the information on regularity of the distribution (topography) and chemical nature of silver particles.

It is known, that change of the ionic equilibrium in a solution of the AgBr MCs syntheses and other conditions of the syntheses influence upon physical characteristic, condition of a surfaces and habit AgBr MCs [1]. The ratio of the silver and halogen ions concentration on the AgHal MCs surfaces is defined not only conditions of the syntheses. On the modification of silver halides MC surfaces the light and UV irradiation, x-ray radiation of XPS spectrometer maybe affect.

Separately the problem exist to select contribution from particles of metallic silver in XPS spectra after radiation decompositions of AgBr surface, which can

influence upon value of a binding energy of electronic levels of silver and ratio atomic concentrations $[Ag]/[Hal]$.

2. TEM investigations of regularities of Ag_n-specs formation

For investigations there have been synthesized emulsion AgBr MCs ($d=0,1; 0,4$ and $1,0 \mu$) of cubic habit and AgBr MCs ($d=0,3; 0,8$ and $1,5 \mu$) of octahedral habit. The syntheses of AgBr sample and chemical sulfur sensitization (SS) were carried out on standard methods [6]. To study regularities of photolytic Ag_n particles formation on a MC surface, MCs were separated from gelatins and exposed by an impulse of light. For visualization of the smallest photolytic Ag_n-particles before preparation of carbon replicas, MCs were developed by technique of arrested development.

There are micrographs of carbon replicas of AgBr MCs in Fig. 1. These micrographs represent the most typical results of experiments. We noted that on a surface of equal MCs equal number of particles of the about identical sizes are observed. The last testifies to identical catalytic activity of centers of concentrating.

Depending on MC habit and sizes some regularities of localization of Ag_n-particles on MC surface were observed. So on ($d < 0,5 \mu$) {100} faces of MCs formation of particles preferentially on edges were observed. At $d \geq 0,5$ Ag_n specs decorate plane and edges. However on surface of octahedral MCs Ag_n specs decorate only plane of {111} faces.

The revealed regularities in topography of Ag_n particles on MC surfaces of a cubic and octahedral habit show that {111} faces are more active then {100} faces. It was also noted in paper [2]. The most activity {111} faces is the result of the most energy of {111} faces [3,4].

Our investigations have shown that Ag_n particles concentration varies in range $10^{10} - 10^{11} \text{ cm}^{-2}$ depending on habit and size of MCs and also conditions of chemical sensitization. This value is comparable to value of density of the surface states related with Br_s^- , being on the kink-sites. According to [5] concentration of Br_s^- is $10^{10} - 10^{11} \text{ cm}^{-2}$. This allows considering Br_s^- as centers of concentrating of photolytic silver.

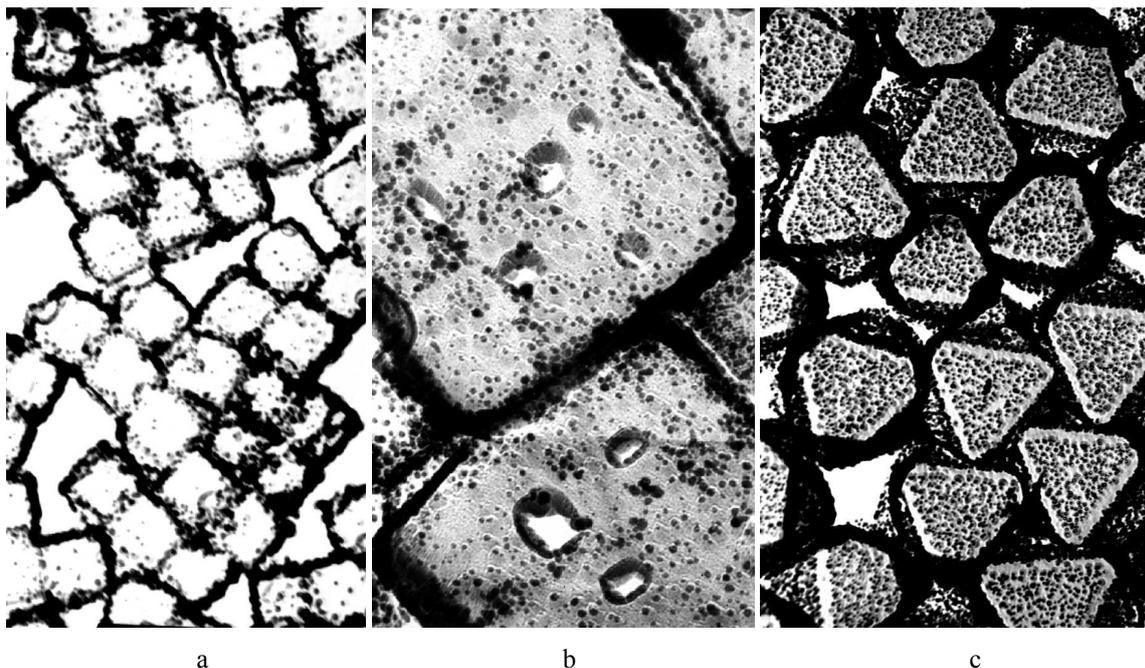


Fig. 1. Carbon replicas of AgBr MCs: a) AgBr (100), $d=0,35 \mu\text{m}$; b) AgBr (100), $d=1,0 \mu\text{m}$; c) AgBr (111), $d=0,8 \mu\text{m}$. MCs were exposed and then it were developed by D-76 solution (1:100). Samples were developed during 5 min

3. The Influence of a preliminary irradiation on XPS-spectrum of silver bromide

The syntheses of sample AgBr in excess ion silver ($p_{\text{Ag}}=1$) and chemical sulfur sensitization (+SS) were carry out on the standard methods described in [6]. Also samples MC AgBr {111} with bivalent ions cadmium with concentration 0,1 mole % have been prepared. Then samples were exposed to the long-time action by a ultraviolet radiation (+hv).

XPS-data are shown in Table 1. It is safe to say that at minimum p_{Ag} , value of a binding energy (E_b) of lines Ag $3d_{5/2}$ approaches to value E_b for metallic silver that is probably involved to plating a surface.

For samples AgBr of uncontrollable syntheses and MC AgBr with reduction p_{Ag} of increase of a binding energy and width of 3d-lines Ag and Br is observed, at simultaneous increase relations atomic concentrations $[\text{Ag}]/[\text{Br}]$. The photolysis of the same samples reduce to additional increase of values E_b of 3d-levels Ag and Br and relations $[\text{Ag}]/[\text{Br}]$. It is indicative to formation on the surface MC of complexes Ag_n , as well as Br_0 or Br_2 .

The investigation of processes of photolysis of AgBr MCs after sulfur sensitization and cadmium ions additive show similar results. Moreover, in this case the photolysis goes less intensively, than on primitive MC.

The formed photolytic silver can acidify by photolytic halogen on the surface MC. This possible explain that fact, that in irradiation samples the binding energy of silver does not increase. The decrease of the relation $[\text{Ag}]/[\text{Br}]$ occurs probably because of that that the surface fill (occupy) with the free halogen.

We shall Note, that absence of shift of 3d-lines for metallic and ionic forms of silver have not a uniquely interpretation and can be explained by compensation relaxation effects.

The key parameter characterizing a chemical condition of silver and taking into account chemical shifts of Age-lines (Ag M_{5VV}) and the contribution from relaxation effect – modified Wagner's parameter (α') (1) [7], has allowed precisely to separate in our experiments of metallic and ionic silver.

$$\alpha' = E_{\text{kin}}(\text{Ag } M_{5VV}) + E_b(\text{Ag } 3d_{5/2}) \quad (1)$$

The comparison of data in Table 1 for metallic silver with irradiated samples of AgBr MC allows to draw a conclusion that the photolytic silver has formed on a surface corresponds to metallic silver.

One of the reasons of plating of AgBr surfaces can be a X-rays of a spectrometer, however the action of a X-ray irradiation happens at initial moment of scanning of XPS-spectra and can not be precisely registered in our experiments.

According to the data in Table 1 are noted differences of electronic properties of separate clusters and aggregates of silver particles from characteristic of massive metallic sample of silver.

According to TEM data at the long-time action of UV irradiation modification of MC surface that is displayed in formation of poles and pickling is observed. In case of MCs (100) ($d < 0,5 \mu\text{m}$) silver particles concentrate preferentially near to edges of crystals. In case of MCs (111) topography of metal concentrating doesn't depend on MC sizes and proceeds preferentially on plane of {111} faces. It is necessary to note, that regularities of silver particles formation at the

long-time UV irradiation practically don't depend on conditions of chemical sensitization. It is known, that concentrating of silver in crystals of silver halides most efficiently proceeds near to the charged defects, such as dislocations and intercrystalline borders. The represented results of photodecomposition allow to making the conclusion that in emulsion MCs ($d < 0,5 \mu$) defects (dislocations and intercrystalline border) are practically absent. The higher number of metal concentrating places on a surface of large crystals can be consequence of higher concentration of various structural defects.

Table 1. The binding energy of XPS-lines, chemical shift for level Ag 3d_{5/2}, Wagner's parameter (α') (in eV) and a composition of a surface of silver, sols and MC AgBr {111} and {100} habit, before and after a sensitization and UV-irradiation

Sample	pAg	Ag 3d _{5/2}	Br 3d	α'	[Ag]/[Br]
Ag (Disperse – Sprayed)	-	368,4	-	720,2	-
Ag (Massive metallic)	-	368,2	-	720,2	-
AgBr {111} d=0,57 μ	10	367,7	69,0	718,0	0,35
	3	367,6	69,0	718,7	0,8
	1,6	368,2	69,2	719,0	1,0
AgBr {100} d=0,4 μ	10	367,7	69,1	717,7	0,3
	3	367,9	68,7	718,6	0,9
	1,6	368,0	69,0	719,1	1,1
Sols AgBr	5,5	367,4	68,1	717,5	0,8
	1	368,2	68,7	719,7	1,2
Sols AgBr + hv	5,5	368,4	68,3	720,0	1,8
AgBr {100} + hv	3	367,9	68,7	719,2	1,2
AgBr {100} + SS + hv	3	368,1	68,3	719,7	1,1
AgBr {111} + CdBr ₂ + hv	3	367,7	68,4	718,2	1,0

4. Conclusion

As a result of carried out TEM investigations it is shown that MCs (100) ($d < 0,5 \mu$) dislocations and intercrystalline borders are practically absent. It is shown, that concentration of centers, where silver particles formation proceeds, on surface of AgBr MC (111) and (100) is $10^{10} - 10^{11} \text{ cm}^{-2}$. The found quantity is comparable to quantity of Br_s⁻ that allows considering these defects as centres of concentrating of silver.

The presented XPS-data are indicative that condition of syntheses and a stages optimization and preparation of AgHal MCs can to render essential influence on a composition of surface layer AgBr.

It is experimentally shown, that division in XPS-spectra of metallic and ionic phases silver is possible by means of the analysis 3d-lines Ag, Ag_e-lines of silver (Ag M₅VV) and (α') – Wagner's parameter.

The results of the analysis for small silver clusters, which are considered as primary centres of the latent image, can be used at making of theoretical models of photographic process.

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