The Reactions of Electrons and Holes Leading to the Metal Clusters Formation in Silver Halides: New Quantitative Characteristics[1]

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Abstract

The new data were obtained due to kinetics investigation of loss processes of charged particles generated by a short laser pulse using microwave photoconductivity method. The influence of several factors (light intensity; preliminary UV - exposure; treatment by hyposulfite water solutions of microcrystals (AgBr 2-5 μm, AgCl 2-3 μm); AgI doping of AgBr single crystals) have been investigated. The measurements were carried out at room temperature. Basing on the analysis of the electron-ion processes kinetics the rate constants of free electron-holes recombination ($1.10^{-11} cm^3 s^{-1}$ in AgBr and $2.10^{-12} cm^3 s^{-1}$ in AgCl) has been obtained. The electron mobilities for both AgBr and AgCl were found as more than 30 $cm^2 V^{-1} s^{-1}$. It was shown that the reaction of free holes and localized electrons is limited by diffusion. The drift hole mobility ($0.8\ cm^2 V^{-1} s^{-1}$) in powder AgBr and the rate constant of free holes and localized electrons recombination ($1.4.10^{-7} cm^3 s^{-1}$) has been determined. The range of traps depth created by treatment of hyposulfite solutions in AgCl ($0.45 < \Delta E < 0.63$ eV) and the range of traps depth generated by preliminary UV exposure in microcrystals AgCl and AgBr ($\Delta E = 0.4$ eV and $\Delta E = 0.25$–0.36 eV, respectively) have been estimated. The rate constant of hole capture by centers formed by the AgI doping of AgBr single crystals ($7.10^{-9}\ cm^3 s^{-1}$) has been measured.

Introduction

One of the main problems of silver halides researches is to reveal the mechanism of the silver cluster formation under the lighting. The deficiency in quantitative data on elementary processes with charged particles participation in silver halide grains allows neither to confirm nor to reject base concepts of the various theories [1]. Among various methods used for kinetics studies of photoinduced elementary processes in silver halides, the «microwave photoconductivity» (MPH) method takes a special place as the most direct and also equally suitable method for researching of micro- and macro- samples. Due to this method at the moment, some quantitative data characterizing electron - ionic processes in microdispersible silver halide systems are obtained. We present some quantitative data on elementary stages in single crystals and powder silver halides obtained by the MPH method. These data allow to eliminate some inconsistencies in the "descriptions of mechanism of the silver clusters formation under the light" phenomenological theories, offered in different time.

Experimental

Typically we prepared powder silver halides according to a procedure reported in [2]. Its grains had a rounded shape and a size of 2 to 3 μm (AgCl) and of 2 to 5 μm (AgBr). Powders were treated with 10^{-8} - 10^{-2} mol sodium thiosulfate (STS) per mol AgHal solutions at a temperature of $20^{o}C$. The melt crystals produced by the complexes method [3]. Pure and doped single crystals grown up by Bridgman - Stockbarger method (the move speed of heater is 1 mm per hour).The MPH technique is described in [4-5]. Samples were exposed to pulsed nitrogen laser light with a wavelength of 337 nm and a pulse duration of 8−10 ns. Measurements were made at room temperature. The two-lasers technique was applied for researches of kinetics of electron-ionic processes [6]. Under the exposure by serial pulses of two lasers with the time delation, it can be observed on the photoresponse decay of the main pulse ("photoresponse-1") the photoresponse on second pulse ("photoresponse - 2").

Results and Discussion

Drift electron mobility in the powder AgBr and AgCl. Drift electron mobility is a major quantitative characteristic of electron behavior in silver halides. However, to a middle 80th years the frequently quoted point of view became conventional that the drift mobile of an electron μ_e in emulsion grains is much lower than its value in large crystals. For example, according to the data [7] for flat grains the electron mobility at room temperature is $\mu_e = 0,2$ $cm^2V^{-1}s^{-1}$, and for octahedral grains the electron mobility is $\mu_e = 0,8$ $cm^2V^{-1}s^{-1}$ [8]. For large crystals the values measured by reliable "time-of-flight" method range 40-66 $cm^2V^{-1}s^{-1} >> \mu_e$ (grains) [9].

In the paper [10] the electron drift mobility in powders AgBr and AgCl were obtained measuring the change of a quality factor of the cavity at room temperature. The obtained electron mobility values range more than 30 $cm^2V^{-1}s^{-1}$ for both AgBr and AgCl. This result, in our opinion, testifies that at the analysis of LI-formation the values of electron mobility reliably measured in grains by the "time-of-flight" method can be used for values of drift electron mobility in the emulsion silver halide grains. This can essentially influence on the calculated value of probability for electron achievement of sensitivity center in grains in different models.

Drift mobility of holes in the powder AgBr. The rate constant of recombination of free holes with trapped electrons. The special attention should be concentrated on the difference between electron mobility value in octahedral grains and macrocrystals. In the [8] the original method of drift electron mobility measurement was offered. This method bases on the analysis of influencing of treatment of microcrystals by water solution of sodium thiosulfate on the kinetics of photoresponse decay of microwave photoconductivity. The sulfur sensitization is a central element of formation process of photographic sensitization in silver halide emulsions. In the literature it was often noted that sulfur sensitization make an electron traps on the surface of the grains. It was shown in [8] by assuming that the electron motion in grains can be described by diffusive - drift problem. It has been proposed in [1] that the limit value of decay time of the photoresponse at large concentrations of adsorbent falls into time of diffusion not of electrons but holes.

The treatment of AgBr grains by water solution of sodium thiosulfate has been carried out. The characteristic half-time of MPH decreased with the concentration of water solution of sodium thiosulfate and then reached constant (plateau). It was shown, that the electron is fast trapped on a surface in result of that the recombination rate of hole and localized electrons is limited only hole diffusion to a surface. From these data the drift hole mobility at room temperature ($\mu_h = 0.8 - 1.2$ $cm^2V^{-1}s^{-1}$) and the rate constant of recombination of free hole with localized electron (as $4\pi DR=1,4\cdot10^{-7}$ cm^3s^{-1}, D – is the diffusion coefficient, R – the reaction radius) was estimated [11].

Free electron-hole recombination in silver chloride and bromide. Rate constants. Free electron-hole recombination in AgHal is one of photoelectron loss channels lowering photographic sensitivity. At the $I_0 > 10^{14}$ photon·cm^{-2} per impulse the decay law of the photoresponse becomes essential not exponential. This corresponds to electrons loss reaction of the second order.

The analysis of kinetics of decays has allowed to determine a rate constant of free electron-hole recombination at room temperature $k_{rec} = (1.5\pm0.5)\cdot10^{-11}$ cm^3s^{-1} (for single crystal AgBr), $1\cdot10^{-11}$ cm^3s^{-1} (for powder AgBr) [5] and $2\cdot10^{-12}$ cm^3s^{-1} (for powder AgCl) [2].

The trap depths created by the sodium thiosulfate treatment in powder AgCl. It was earlier noted, the detected influence of sodium thiosulphate treatment on decay time of photoresponse testifies that along with possible loss of electrons in the grains volume the loss of electrons on the grains surface gives significant contribution because of entrapment in surface traps. The data about the traps depth are important not only for understanding of mechanism of essential increasing of photographic sensitivity due to this process, but also as a whole for discovering of mechanism of latent image formation. Literary data on this problem greatly differ.

The traps depths range created by the sodium thiosulfate solutions in AgCl has been estimated on the measurements of MPH [12]: $0.45 < E_t < 0.63$ eV. The analysis of photoresponse decay kinetics of MPH was carried out in terms of the model, which was taking into account these processes: free electron-hole recombination, the trapping of holes and the trapping of electrons on two traps types, and the recombination of localized electrons with interstitial silver ions and thermal detrapping of electrons

The depth of electron traps created by the preliminary UV exposure in powder AgBr and AgCl. Similarly as LI-formation in emulsion grains under the actinic light, the influence of UV-light creates non-haloid silver clusters in the grains of powder AgBr and AgCl. These clusters serve as the electron traps. It develops in the changing of the characteristic of photoresponse decays, i.e., in the change of kinetics of electron-ionic processes.

The influence of preliminary UV-exposition on the kinetics of electron-ion reaction is shown on the fig.1 in semilogarithmic coordinates It can be seen, that the initial part of this dependence looks like «induction period», and the dependence becomes linear one in the used coordinates under the high UV expositions. Under the UV action in grains the formation of non-haloid silver clusters takes place, which are being deep electrons traps. At the same time with the increase of the UV exposures the «new» traps begin

to effectively compete with "old" one for electron trapping The influence of deep traps on photoresponse becomes noticeable when the concentration of created deep traps is high, i.e. at large expositions. The break point in the fig. 1 approximately corresponds to the relation: $\tau_s=\tau_e$. The analysis of these data has made possible to obtain the traps depth created under the preliminary UV exposure in AgCl and AgBr ($E_t=0,4$ eV and $E_t=0,25-0,36$ eV, accordingly) [13].
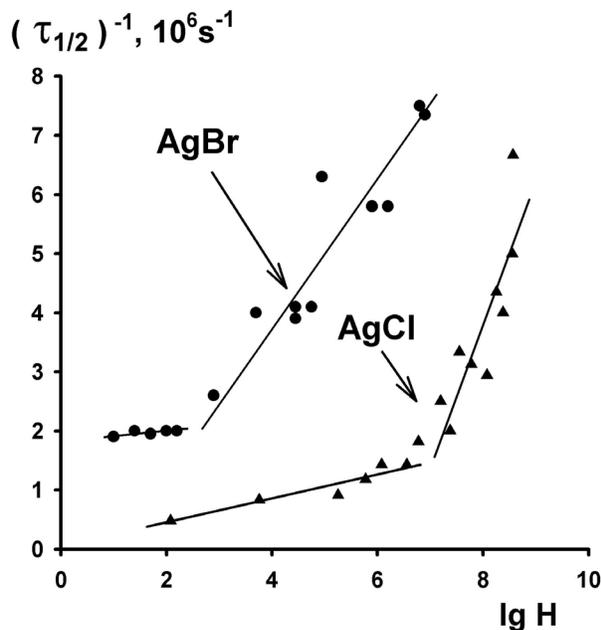

Figure 1. The dependences of the reciprocal half-times on logarithm of UV-exposure

The recombination of the trapped electrons with interstitial silver ions in evaporated layers and powders of silver bromide. The life time of silver atom. The typical results of researches using the two-lasers technique are represented in the [6]. It was detected in [14], the "photoresponse - 2" appears with the delay time $\Delta t \approx 6$ mks (vacuum evaporated AgBr layers) and $\Delta t \approx 3$ mks (powder AgBr) relatively "photoresponse - 1". The observed delay time of increase of photoresponse-2 was found in some times more, than life time of electron and the appearing of the response on the second pulse can be connected with the birth of intermediate of photolysis - the "new" electron traps, i.e. silver clusters. As can be seen from the fig. 2 the curve 4 has a maximum. The decay of curve 4 after a maximum has allowed to estimate the lifetime of atom Ag: $\tau_{Ag} = 10^{-4}$ s [14].
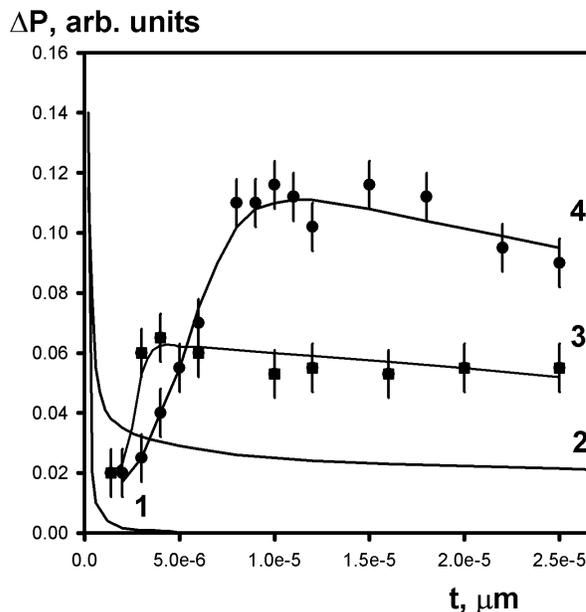

Figure 2. The dependence of the amplitudes of photoresponse-1 (A = 337 nm; $I_0 = 6 \cdot 10^{14}$ photon-cm^{-2} per impulse) and photoresponse-2 (A = 540 nm; $I_0=1 \cdot 10^{15}$ photon-cm^{-2} per impulse) on the delay time between exiting pulse: 1, 3 powder (photoresponse-1 and 2); 2, 4 evaporated layers (photoresponse-1 and 2).

The rate constant of holes trapping by centers created by the silver iodide doping of silver bromide single crystals. The special role of silver iodide in the sensitivity formation of photographic emulsions grains was repeatedly noted in literature. It is known [15], that the iodide placing in the lattice of the crystal, serves as the effective hole trap. It should be noted also, that the information about this process are important because of the problem of properties degradation of the optical silver halide fibers. The doping by silver iodide of the basis of such optical fibers improves their mechanical properties.

For an illustration of the influence of the silver iodide on the kinetics of electron-ion processes, the dependence of the inverse time of photoresponse decay of MPH on the impurity concentration in the single crystal AgBr [16] is represented in the fig. 3. It can be seen that the AgI impurity twice increases the rate of electron losses. Taking into account that the measurements were carried out at the enough low light intensity, when the recombination processes was negligible, the experiment has described by the model including the trap of electron and hole, the detrapping of localized electron and the recombination of localized electron and free hole. The rate constant of hole trapping $k_S = 7 \cdot 10^{-10}$ $cm^3 s^{-1}$ can be determined basing on the slope of the graph $\tau^{-1} \sim k_S$ [AgI].

$(\tau_{1/2})^{-1}$, $10^7 s^{-1}$
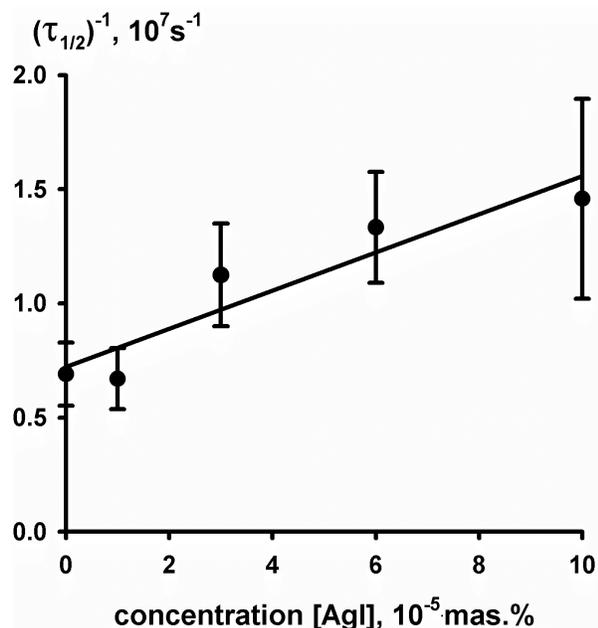
concentration [AgI], 10^{-5} mas.%

Figure 3. The dependence of inverse half-time of the fast components of photoresponse on concentration AgI in the single crystal AgBr. (3 cm microwave range).

All obtained date are summarized in the table 1.

	Sample	Value	Reference
μ_e, $sm^2 s^{-1} V^{-1}$	Powder AgBr	60	[10]
	Powder AgCl	40	
μ_h, $sm^2 s^{-1} V^{-1}$	Powder AgBr	0.8 – 1.2	[11]
k_r, $sm^3 s^{-1}$	Powder AgBr	$1{,}4 \cdot 10^{-7}$	[11]
k_{rec}, $sm^3 s^{-1}$	Powder AgCl	$2 \cdot 10^{-12}$	[2]
	Powder AgBr	$1 \cdot 10^{-11}$	[5]
	Single crystals AgBr	$(1.5 \pm 0.5) \cdot 10^{-11}$	
ΔE_{thio}, eV	Powder AgCl	0.45 - 0.63	[12]
ΔE_{light}, eV	Powder AgCl	0.4	[13]
	Powder AgBr	0.25 – 0.36	[13]
t_{Ag}, s	Evaporated AgBr	10^{-4}	[17]
k_S, $sm^3 s^{-1}$	Single crystals AgBr	$7 \cdot 10^{-10}$	[16]

Conclusion

Certainly, the present paper does not pretend to the completeness of quantitative data on electron-ionic processes in silver halides, published to the moment. The data obtained only by MPH method are represented because this method gives consistent results for measurements on the micro and macro samples. However, from our point of view, there are no reasons to search for principled differences between mechanism of the electron-ionic processes in emulsion grains and in large melted or single crystals. For interpretation of electron-ionic processes in microsystems (emulsion grains, powders, thin evaporated layers, optical fibers) the quantitative data obtained on macrosystems (single crystals, melted crystals) can be used. The essential difference between these objects is the difference in the relation between surface and volume. But the taking into account this condition does not create insuperable difficulties at interpretation of the data.

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Biography

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