Rate constant of the recombination of free electrons and holes in AgCl at 295 K

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The transient kinetics of the loss of electrons generated by light pulses in powdered AgCl has been studied by the microwave photoconductivity method (36 GHz) at 295 K. At high light intensities, $I_0 > 10^{14}$ photon cm^{-2} per pulse, the kinetics obeys the second-order law. The rate constant of the recombination of free electrons and holes is equal to $2 \cdot 10^{-12}$ cm^3 s^{-1}.

Key words: silver chloride; electron, hole, recombination, rate constant, kinetics; latent photographic image.

The absence of quantitative data on many elementary processes involving electrons, ions, holes, and atoms in silver halides makes it impossible either to confirm or reject different theoretical models suggested for the description of the physicochemical mechanism of the formation of the "latent photographic image," clusters of Ag containing no silver halides. Despite a great number of publications on this topic, there are not more than ten works presenting quantitative data on elementary processes in silver halides. For example, the reaction parameters of the excess electrons (capture by an acceptor[1] and recombination with a positive hole[2,3]) in AgBr and the drift electron mobility in emulsion microcrystals have been measured,[4,5] the quantitative data on nucleation processes of Ag atoms have been obtained,[6—8] the lifetime of an Ag atom has been determined,[9] and the parameters of heterojunctions in AgHal have been calculated.[10] The majority of the publications contains only qualitative results.

In this work, we attempted to determine the rate constant of the recombination of free electrons and holes, which is one of the channels of photoelectron loss in AgCl.

Experimental

The experimental procedure has been described previously[2,3,11] and is based on the registration of changes in the reflection coefficient of electromagnetic waves produced by a short light pulse from a cavity containing a sample. Measurements were carried out on two setups in 3-cm and 8-mm ranges with parameters of the registering chain RC = 35 and 7 ns, respectively (R and C are the resistance and capacitance of the input chain). One difference from the procedures described was the use of a more powerful light source, an LGI-505 nitrogen laser. The analysis of the dependence of the photoresponse amplitude on the frequency of the microwave cavity showed that the photoresponse is mainly related to changes in the quality of the cavity rather than in the resonance frequency.

Powdered AgCl was prepared by pouring equimolar amounts of $AgNO_3$ and KCl in ethanol. The residue was repeatedly washed by decanting in a 0.001 M water—ethanol solution of KCl and dried *in vacuo* for 6 h at ~20 °C and then for 1 h at 423 K. According to the data of optical and electron microscopies, the AgCl microcrystals were spherical with a mean size of 2—3 μm. Measurements were carried out at room temperature.

Results and Discussion

According to the published data,[2,3] the changes in the microwave absorption under the experimental conditions are caused by photogenerated electrons rather than by positive holes.

Our experiments showed that at low light intensities ($I_0 \leq 10^{14}$ photon cm^{-2} per pulse) the law of the decay of the microwave absorption photoresponse corresponds to an exponential function, whose time constant is independent of the light intensity but, as in the case of AgBr, is determined by the content of impurities in AgCl. In this intensity range, the photoresponse amplitude ($\Delta P(t)$) depends linearly on I_0.

At light intensities $I_0 > 10^{14}$ photon cm^{-2} per pulse (the threshold value is determined by the purity of the sample), the dependence of $\Delta P(t)$ on I_0 becomes nonlinear, and a fast component, whose decay rate increases as I_0 increases, appears in the initial region of the decay of the photoresponse amplitude. The decay rate of the slow component remains almost constant. The decay of $\Delta P(t)$ for four strongly different I_0 values is demonstrated in Fig. 1. The duration of the responses at the half-height (half-width) varies from 600 to 200 ns under these conditions.

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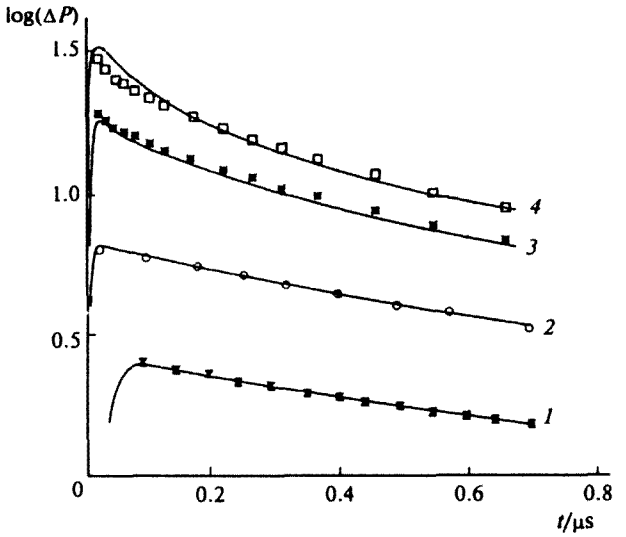

Fig. 1. Time dependences of the microwave absorption photoresponse for various light intensities, I_0/photon cm^{-2} per pulse: *1*, $2 \cdot 10^{13}$ (3-cm range); *2*, $1.5 \cdot 10^{14}$ (8-mm range); *3*, $5 \cdot 10^{14}$ (8-mm range); and *4*, $1.4 \cdot 10^{15}$ (8-mm range). The curves show the calculation results. The points mark the logarithms of the experimental values of photoresponses at characteristic moments.

This dependence of the kinetics on the light intensity is close to that obtained previously[2,3,11] for AgBr, and it was assigned to the recombination of free electrons and holes. However, the light intensity at which the recombination in AgCl is manifested is considerably higher than that in the case of AgBr, which complicates substantially the experiment and analysis of the data.

The $\Delta P(t)$ kinetics at various light intensities was analyzed in terms of a model including first- and second-order reactions:

$$AgCl \xrightarrow{W(t)} e^- + p^+, \quad (1)$$

$$e^- + N_0 \xrightarrow{k_1} N_-, \quad (2)$$

$$p^+ + P_0 \xrightarrow{k_2} P_+, \quad (3)$$

$$e^- + p^+ \xrightarrow{k_3} \ldots, \quad (4)$$

$$e^- + P_+ \xrightarrow{k_4} P_0, \quad (5)$$

$$p^+ + N_- \xrightarrow{k_5} N_0, \quad (6)$$

where e^- and p^+ are free electrons and holes, respectively; N_0 and P_0 are electron and hole traps; N_- and P_+ are charged electron and hole traps; $W(t)$ is the rate of generation of electrons and holes (which reflects the shape of the light pulse); and k_1—k_5 are the rate constants of the corresponding processes. For comparison with the experiment under the conditions of nonuniform light absorption, the system of equations corresponding to processes (2)—(6) was solved numerically for two cases: (a) "perfect stirring of the whole reaction volume" (averaging over the whole volume) and (b) "stirring within thin layers" (averaging over each layer). The layers with widths of $\sim 0.5/(\beta k_\lambda)$, where $k_\lambda = 5 \cdot 10^3$ cm^{-1} and $\beta = 0.6$ is the light absorption coefficient and the photoionization quantum yield in AgCl, respectively, were chosen for the calculation.[12]

The finite width of the light pulse and the transition characteristics of the measuring track were taken into account in the treatment of the experimental data. The experimental $\Delta P(t)$ responses were compared with the results of calculations of the corresponding convolutions of the time dependences of the electron concentrations simultaneously for several different light intensities as described previously.[2,3]

The calculated $\Delta P(t)$ dependences for different I_0 in semilogarithmic coordinates are presented in Fig. 1. It can be seen that despite noticeable changes in the light intensities, the decays of the right regions of the curves, *i.e.*, the "slow" components, are approximated satisfactorily by exponential functions, whose decay rates are almost independent of I_0. These components can be reasonably assigned to processes (3), (5), and (6).

A comparison of the calculation results with the experiment gave the value $k_3 = 2 \cdot 10^{-12}$ cm^3 s^{-1} for the recombination rate constant of free electrons and holes in AgCl. The k_3 value obtained is almost fivefold lower than the recombination rate constant of free electrons and holes in AgBr ($\sim 1 \cdot 10^{-11}$ cm^3 s^{-1}).[2,3]

The recombination rate constant determined for AgCl makes it possible to draw some preliminary conclusions concerning the mechanism of the effect of heterojunctions of the AgHal′/AgHal″ type (where Hal′ and Hal″ are different halogens) on the photographic sensitivity of emulsion microcrystals. Such a low value of the rate constant likely indicates, as in the case of AgBr, that the mechanism of the action of the heterojunctions on the photographic sensitivity cannot be reduced to the prevention of the recombination of free electrons and holes due to charge separation by the electric field of the heterojunction, as authors of many works believe. In fact, because of the low recombination rate constant of *free* electrons and holes, the recombination cannot compete with the capture of a free electron by acceptors or with the recombination with a captured (localized) hole or the recombination of a free hole with a localized electron in the space of the heterojunction at the practically important light intensities and concentrations. Probably, the effect of heterojunctions on the photographic sensitivity should be explained in a different way.

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