Brief Communications

Rate constant of free electron-hole recombination in thin cadmium sulfide films

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The transient decay kinetics of electrons generated in thin cadmium sulfide films by short laser pulses was studied by the microwave photoconductivity method (9 and 36 GHz) at 295 K. The films were prepared by the pulverization method from thiocarbamide coordination compounds. At the high light intensity $I_0 > 10^{14}$ photon cm^{-2} per pulse, the decay kinetics of photoelectrons corresponded to a reaction of the second order. Analysis of the kinetic data made it possible to determine the rate constant of recombination of free electrons and holes: $k_3 \approx 2(\pm1) \cdot 10^{-13}$ cm^3 s^{-1}.

Key words: cadmium sulfide, recombination, electron, hole, rate constant, kinetics, mechanism.

Thin cadmium sulfide films are widely used for the development of sensors sensitive to various physical and chemical effects.[1] The sensitivity of these films (in particular, for the use in reverse luminescent systems for the detection of information) depends on many factors, such as composition, structure, and specific features of synthesis. This is related to the specificity of chemical reactions involving charged particles in the films synthesized. One of the reactions that decreases the sensitivity of the films to the light and ionizing radiation is the recombination of free electrons and holes, which often results in nonradiative energy loss. Although many works[1—4] are devoted to the study of recombination, this problem remains unclear. In particular, in the recent studies of electron-hole recombination in aqueous colloids of CdS in the picosecond time scale, the authors[4] observed two components: fast (decay of 2 ps) and slow (decay of 45 ps), which were ascribed to nongeminate and geminate electron-hole recombinations, respectively. The fast component was very sensitive to the laser excitation intensity. However, this distribution of time intervals for geminate and nongeminate recombinations poorly agrees with the modern concepts on the recombination and separation of geminate pairs to free ions. These concepts are based on the studies of the initial steps of radiation chemical processes,[5] according to which the geminate recombination of ion pairs, which are bound by the Coulomb interaction, is preceded by the recombination of separated pairs (free charges), whose kinetics should correspond to a reaction of the second order. Thus, taking into account the known data,[4] one can expect that in sufficiently pure CdS (*i.e.*, when the recombination rate is lower than the rate

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of charge capture by acceptor admixtures) the recombination of free electrons and holes should be expected in the nanosecond time scale. The purpose of this work is to obtain quantitative data on this elementary process.

Experimental

Films were prepared by sputtering (pulverization method) of aqueous solutions of the $[Cd((NH_2)_2CS)_2X_2]$ complexes (X = Cl^-, Br^-, AcO^-) onto the glass-ceramic substrate heated to 450—600 °C.[6] This resulted in the decomposition of the complex to form the sulfide film uniformly doped by the corresponding admixtures (the typical film thickness was 5—10 μm).

The method of microwave photoconductivity (UHF) was used to study the decay kinetics of electrons. The experiment was based on the detection of changes in the reflection coefficient of electromagnetic waves from a cavity containing a small-volume sample. These changes were induced by the irradiation of the sample with a short light pulse. The procedure has previously been described in detail.[7,8] Measurements were carried out on two setups in UHF intervals of 3 cm and 8 mm with the parameters of the detecting circuit RC = 60 and 20 ns, respectively (R and C are the resistance and capacity of the inlet circuit). An LGI-505 nitrogen laser was used for irradiation. Measurements were carried out at ~20 °C.

Results and Discussion

The irradiation with a light pulse resulted in a sharp decrease in the loaded Q-factor of the cavity and, correspondingly, in a change in the power of the reflected UHF wave ($\Delta P(t)$, photoresponse). After the end of the light pulse, the photoresponse gradually decreased to zero. Analysis of the plot of the photoresponse amplitude *vs.* frequency of the UHF generator showed that, as previously,[9] the photoresponse was mainly related to a change in the Q-factor of the cavity rather than to a change in the resonance frequency.

At relatively low light intensities ($I_0 < 10^{14}$ photon cm^{-2} per pulse), the photoresponse decay is exponential (Fig. 1, curve *1*), the decay rate is independent of the light intensity, and the photoresponse amplitude depends linearly on the intensity. The treatment of the films with electron acceptors (Br_2) increases the rate of exponential decay of the photoresponse. These facts indicate that the photoresponse is induced by the involvement of electrons, which decay by the first-order reaction during the photoresponse decrease, in photoconductivity. This conclusion agrees with the results of the UHF photoconductivity study of silver halides[7,8,10]: under experimental conditions, changes in the UHF absorption are induced by electrons generated by the light rather than by positive holes.

At the light intensities $I_0 > 10^{14}$ photon cm^{-2} per pulse, the plot of the photoresponse amplitude *vs.* I_0 becomes

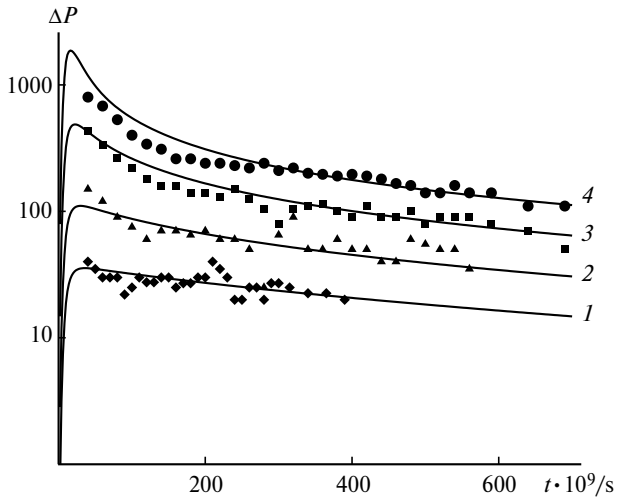

Fig. 1. Photoresponse of the UHF absorption (ΔP) as a function of time (t) for different light intensities: $I_0 = 4.6 \cdot 10^{13}$ (*1*), $1.6 \cdot 10^{14}$ (*2*), $7.5 \cdot 10^{14}$ (*3*), and $3.6 \cdot 10^{15}$ photon cm^{-2} per pulse (*4*) (solid curves are calculation, and points indicate the experimental photoresponse values at the characteristic time moments).

nonlinear, and a fast component appears in the initial region of the decay of $\Delta P(t)$, whose decay rate increases with an increase in I_0 (see Fig. 1, curves *2*—*4*). The decay rate of the slow component remains virtually unchanged and equal to that at low light intensities. The duration at the half-height of the photoresponses (half-width) in Fig. 1 changes from 30 to 700 ns.

The dependence of the decay kinetics of electrons on the light intensity can naturally be related to the recombination of free electrons and holes that decay *via* the second-order reaction. This assumption agrees with the results obtained previously for silver bromide[7,8] and chloride,[10] where the kinetics is also related to the recombination of free electrons and holes.

Analysis of the $\Delta P(t)$ kinetics was carried out, as previously,[10] in the framework of the model including reactions of the first and second order

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

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

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

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

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

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

where e^- and p^+ are free electrons and holes, respectively; N and P 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 (reflects the shape of the light pulse); and k_1—k_5 are the rate constants of the corresponding processes. The initial concentration of free electrons and holes was determined from the product of the generation rate by the duration of the laser pulse and the quantum yield of ionization (for CdS at $\lambda = 337$ nm, the quantum yield of ionization is $\beta \approx 1$).[3]

For comparison with the experiment under the conditions of strongly nonuniform light absorption ($k_\lambda = 2 \cdot 10^5$ cm^{-2} is the coefficient of light absorption in CdS,[2] $\beta \approx 1$), the system of equations corresponding to processes (2)—(6) was numerically solved for two cases: (a) complete stirring of the whole reaction volume and (b) stirring within thin layers. For calculation, the layers perpendicular to the light incidence, x, were chosen with the thickness $\Delta x = k_\lambda^{-1}$.

In the interpretation of the experimental data, we took into account the resulting width of the light pulse and the transient characteristics of the measuring tract calculating the corresponding mathematical convolutions. The rate constant was obtained as a variable parameter of the problem,[7,10] which is necessary for the best agreement of the theoretical and experimental photoresponses $\Delta P(t)$ and is independent of the light intensity.

The calculated $\Delta P(t)$ plots for different I_0 in the semilogarithmic coordinates are shown in Fig. 1: $I_0 = 4.6 \cdot 10^{13}$ (curve *1*), $1.6 \cdot 10^{14}$ (curve *2*), $7.5 \cdot 10^{14}$ (curve *3*), and $3.6 \cdot 10^{15}$ photon cm^{-2} per pulse (curve *4*). It can be seen that even at considerable changes in the light intensity the decays of the right parts of the curves, *i.e.*, slow components, are satisfactorily approximated by exponential functions, whose decay rates are almost independent of I_0. These components can naturally be related to the processes described by Eqs. (2) and (5).

The comparison of the calculated and experimental data gives $k_3 = 2 \cdot 10^{-13}$ cm^3 s^{-1} for the recombination rate constant of free electrons and holes. The k_3 value is independent of the type of admixtures within the experimental error. This fact corresponds to the status of this magnitude as a rate constant of the elementary process, which allows it to be used for the prediction of the ratio of contributions of recombination and electron capture processes in CdS under different conditions.

Note that the k_3 value is relatively low, which likely indicates the mechanism of interband recombination in CdS. This assumption is consistent with the known fact that for the exciton mechanism of recombination the rate constants are higher by 1—2 orders of magnitude. For example, $k_3 = 1 \cdot 10^{-11}$ (AgBr)[7,8] and $2 \cdot 10^{-12}$ cm^3 s^{-1} (AgCl).[10]

It should be mentioned in conclusion that the obtained k_3 value poorly agrees with the previous[4] results of studying charge recombination in CdS in the picosecond time interval. At the light intensity used in this work (1.18 photon Å^{-2}), the estimation of the half-decay period of the charge concentration from the obtained recombination rate constant gives ~5 ns. The observed[4] "nongeminate" (sensitive to the light intensity) electron-hole recombination with a half-decay time of several picoseconds should likely be attributed to the recombination of charge pairs interacting[5] with each other.

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