Recombination rate constant of free electrons and holes in thin CdSe films

N. A. Radychev* and G. F. Novikov

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 522 1842. E-mail: rad@icp.ac.ru

The decay kinetics of electrons generated in thin CdSe films by laser pulse (wavelength 337 nm, pulse duration 8 ns) at 295 K was studied by the microwave photoconductivity method (36 GHz). Based on analysis of the photoresponse decay kinetics and the reactions of free and trapped electrons, holes, and ions, a model for the processes was proposed and the recombination rate constant of free electrons and holes in cadmium selenide was determined, being $(4—6) \cdot 10^{-11}$ cm^3 s^{-1}.

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

Although the wide use of cadmium selenide in technology is based on the well-known phenomenon of photogeneration of current carriers, quantitative data on reactions of charged particles in CdSe are virtually lacking. Presently, this situation noticeably impedes progress in the area of using cadmium selenide, because it is difficult to predict the limiting characteristics of the developed devices when these data are insufficient. Data on rate constants (cross sections) of elementary reactions resulting in the decay of excessive charges, which determine the amplitude and time characteristics of the photoresponse, are key from this point of view. One of the main reactions responsible for the time parameters of the photoresponse is the recombination of free electrons and holes. Although charge recombination was studied in many works, the problem remains unclear because of lacking quantitative data.

The most efficient method to obtain the quantitative characteristics is a study of the decay kinetics of charges in systems, whose properties can easily be changed during or immediately after the synthesis. This is difficult to perform for measurements on single crystals. Thin CdSe films prepared by the pyrolysis of complexes[1] are more appropriate, most likely, for these purposes than other materials. However, because of an insufficient time resolution of the UHF procedure in the 3-cm range used, researchers[1] restricted their consideration only by the estimation of the rate constant of recombination of free electrons and holes. In the present work, the measurements are carried out in the 8-mm range.

Experimental

Studies were carried out on CdSe films* prepared by sputtering (pulverization method) of aqueous solutions of the $\{Cd[(NH_2)_2CSe]_2Cl_2\}$ complexes on a glassceramic (Pyroceram type) support heated to 550 °C.[1—3] The complex decomposed to form a sulfide film uniformly doped with the corresponding admixtures. The typical film thickness was 5—10 μm.

The kinetics of electron decay was studied by the method of UHF photoconductivity (8-mm range). Changes in the reflection coefficient of electromagnetic waves from a resonator with a sample of small volume, which are induced by a short light pulse on the sample, were detected.[2,4,5] The time resolution of the instrument was τ_r = 10 ns. Samples were irradiated with pulses from an LGI-505 nitrogen laser (wavelength 337 nm, pulse duration τ_p = 8 ns). In measurements, the light intensity was varied by more than three orders of magnitude, using light filters and changing the beam focusing. Comparing the experimental results and calculation, the final width of the light pulse and the transition characteristic of the measuring tract were taken into account, calculating the corresponding mathematical deconvolutions. The measurements were carried out at room temperature.

Results and Discussion

A light pulse sharply decreases the loaded Q-factor of the resonator and, hence, produces a "photoresponse," *i.e.*, a change in the power of the reflected UHF wave $\Delta P(t)$ (t is the time read from the beginning of the light

---

* The samples were kindly presented by Yu. V. Meteleva.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 740—743, May, 2006.

pulse). After the end of the light pulse, the $\Delta P(t)$ function, passing through the maximum value, decreases gradually to zero. Analysis of the dependence of ΔP on the f frequency of the UHF generator[6] showed that the photoresponse $\Delta P(t) = \Delta P_Q(t) + \Delta P_f(t)$ is mainly related to a change in the Q-factor of the resonator rather than the resonance frequency f. Exposure of the sample during the experimental time produced no noticeable changes in the amplitude and shape of $\Delta P(t)$.

Taking into account the difference in mobilities[7] of electrons and holes in CdSe, it seems natural to relate the photoresponse to electrons. This assumption agrees with the results of studying the UHF photoconductivity in CdS,[2,3] CdSe,[8] and silver halides (see discussion and references in the works[5,9,10]): the changes in the UHF absorption, under the experimental conditions used in the present work, are caused by photoinduced electrons rather than positive holes.

The photoresponse decay consisted of two components, namely, the fast and slow components, whose ratio of the amplitudes and time characteristics depended on the light intensity (*i.e.*, dose of light irradiation per pulse) I_0. The plot of the total amplitude of the photoresponse *vs.* I_0 is nonlinear (Fig. 1), except for the region of low $I_0 < 10^{15}$ photon cm^{-2} (pulse)$^{-1}$, when the plot of the photoresponse amplitude *vs.* I_0 is close to linear (see inset in Fig. 1).

The characteristic decay time of the fast component of the photoresponse changed weakly with an increase in the light intensity. For the light intensities $I_0 < 10^{14}$ photon cm^{-2} (pulse)$^{-1}$, $\tau_{1/2}$ = 15—20 ns; for $I_0 > 10^{15}$ photon cm^{-2} (pulse)$^{-1}$, the $\tau_{1/2}$ value is close to the time resolution of the instrument τ_r. The photoresponse decays with a change in the intensity of the incident light by more than three orders of magnitude are shown in Fig. 2. It can be seen that the fast component is present in all curves. In all decay curves, the slow component is not exponential with a half-decay time of ~200 ns. The amplitudes of the fast and slow components in the initial time moments differ by ~10 times.

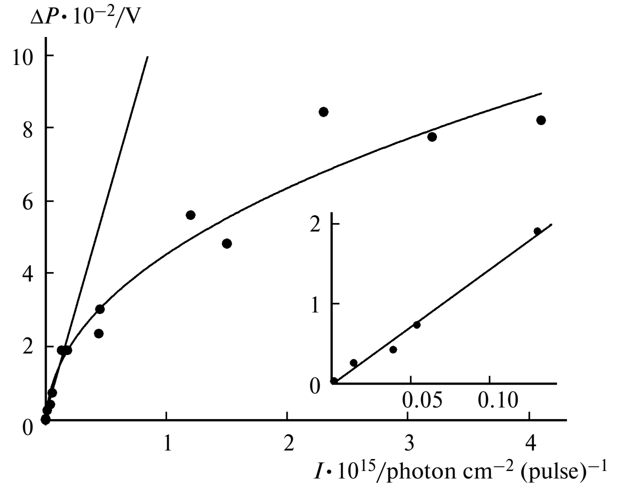

Fig. 1. Photoresponse amplitude as a function of the incident light intensity for a time moment of 30 ns after the light pulse beginning. The linear region of the plot at low radiation intensities is shown in inset.

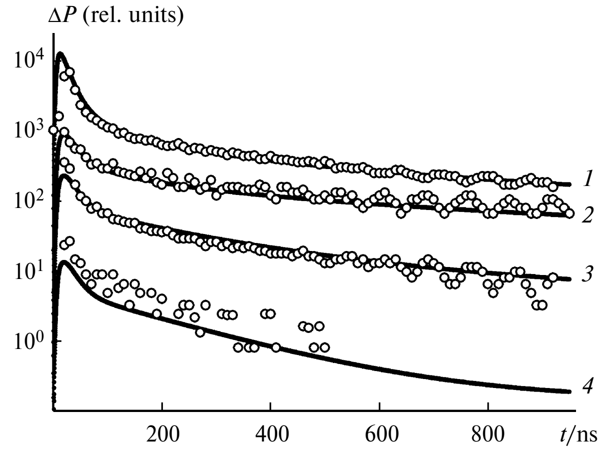

Fig. 2. Decay of the UHF photoconductivity photoresponse at irradiation densities of $4.1\cdot10^{15}$ (*1*), $1.3\cdot10^{14}$ (*2*), $0.39\cdot10^{14}$ (*3*), and $2\cdot10^{12}$ photon cm^{-2} (pulse)$^{-1}$ (*4*) (markers are experiment, solid lines are calculation).

Taking into account published data,[1] it seems natural to assume that such insignificant changes in the characteristic time of decay of the fast component of the photoresponse with an increase in the light intensity for a considerable increase in the amplitude can be caused by the recombination processes that occur within a time shorter than the time resolution of the instrument. In fact, for the maximum intensity $I_0 = 4.1\cdot10^{15}$ photon cm^{-2} (pulse)$^{-1}$, the estimation gives $\tau_{1/2}$ ~0.05 ns $< \tau_r$.

This assumption is confirmed by an analysis of the dependence of the integral of the photoresponse on I_0. Accepting for estimation that

$$\int \Delta P(t)dt \approx \Delta P\cdot\tau_r \approx \begin{cases} I_0\cdot\tau_{1/2} & \text{(recombination)} \\ I_0\cdot\tau_{tr} & \text{(trapping)} \end{cases}, \qquad (1)$$

we can approximately determine the light intensity at which the recombination and trapping rates are approximately equal. According to Eq. (1), the plot of $\Delta P\cdot I_0^{-1}$ *vs.* I_0 (Fig. 3) reflects the change in the characteristic time of the process with a change in the light intensity. Figure 3 shows that the plot of $\Delta P\cdot I_0^{-1}$ *vs.* I_0 in the logarithmic coordinates in the region of high intensities is almost linear with the unity slope. In this region, $\tau_{1/2} \ll \tau_r$. At low light intensities, $\tau_{1/2}$ is virtually independent of I_0.

Dependence of the amplitude of the fast component of the photoresponse on the light intensity. It is natural to relate the above obtained hyperbolic dependence of $\tau_{1/2}$

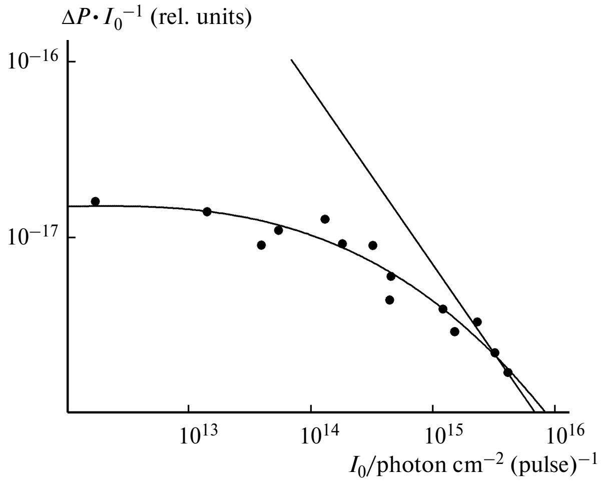

Fig. 3. Time of the half-decay of the fast component of the photoresponse decay as a function of the irradiation density.

on I_0 to the recombination of free electrons and holes formed by Eq. (2) and decaying *via* second-order reaction (3); at low light intensities electron trapping (4) competes with the recombination reaction

$$\mathrm{CdSe} \xrightarrow{W(t)} e^- + \mathrm{p}^+, \tag{2}$$

$$e^- + \mathrm{p}^+ \xrightarrow{K_\mathrm{r}} \ldots, \tag{3}$$

$$e^- + \mathrm{N} \xrightarrow{K_1} \mathrm{N}_-, \tag{4}$$

where e^- and p^+ are electrons and holes, respectively; $W(t)$ is the rate of electron and hole generation (reflects the shape of the light pulse), K_r is the rate constant of recombination of electrons and holes, N are electron traps, N_- are charged electron traps, and K_1 is the rate constant of electron trapping.

The data obtained for $\tau_{1/2}$ (see Fig. 3) make it possible to estimate approximately the product $K_\mathrm{r} \cdot K_\lambda$ assuming that the quantum yield of the internal photoeffect $\beta \approx 1$:

$$K_\mathrm{r}K_\lambda = (\beta I_0 \tau_{1/2})^{-1} \approx 0.8 \cdot 10^{-6}\ \mathrm{cm^2\ s^{-1}}. \tag{5}$$

Accepting that the absorption coefficient in CdSe[11] is $K_\lambda = 2 \cdot 10^5\ \mathrm{cm^{-1}}$, we have $K_\mathrm{r} \approx 4 \cdot 10^{-11}\ \mathrm{cm^3\ s^{-1}}$.

Dependence of the shape of the photoresponse decay on the light intensity. More precise quantitative data on the processes determining the time characteristics of the photoresponse can be obtained by an analysis of the kinetics of the photoresponse change $\Delta P(t)$ at different light intensities. The $\Delta P(t)$ values were examined, as in Refs 5 and 12, in the framework of model Eqs (2)—(4) and (6)—(12) that includes the first- and second-order reactions

$$\mathrm{p}^+ + \mathrm{P} \xrightarrow{K_2} \mathrm{P}_+, \tag{6}$$

$$e^- + \mathrm{P}_+ \xrightarrow{K_4} \mathrm{P}, \tag{7}$$

$$\mathrm{p}^+ + \mathrm{N}_- \xrightarrow{K_5} \mathrm{N}, \tag{8}$$

$$\mathrm{N}_- \xrightarrow{K_6} \mathrm{N} + e^+, \tag{9}$$

$$\mathrm{P}_+ \xrightarrow{K_7} \mathrm{P} + \mathrm{p}^+, \tag{10}$$

$$\mathrm{N}_- + \mathrm{I} \xrightarrow{K_8} \mathrm{A}, \tag{11}$$

$$\mathrm{A} \xrightarrow{K_9} e^- + \mathrm{I} + \mathrm{N}, \tag{12}$$

where P are hole traps, P^+ are charged hole traps, I are interstitial ions, A are atoms, and K_2—K_9 are the rate constants of the processes. The initial concentration of free electrons and holes was determined as the product of the generation rate by the laser pulse duration and the quantum yield of ionization.

To compare with experiment under the conditions of strongly nonuniform light absorption, the system of equations corresponding to processes (2)—(4) and (6)—(12) was numerically solved for two cases: "complete mixing of the whole reaction volume" and "mixing within thin layers." In the calculation, the thickness of the layers perpendicular to the direction of light incidence was chosen to be $\Delta x = K_\lambda^{-1}$.

Choice of parameters for the calculation of kinetic characteristics. When solving this problem, one should take into account the following conditions. The formal fitting of the kinetics of charge decay to the curves of decays of the UHF-photoresponse can hardly be substantiated, because the problem, as a whole, includes too many parameters: nine rate constants and three concentrations. Therefore, it is basically important to determine limits of changing the parameters. This can be done on the basis of analysis of the contribution of different processes to the photoresponse at different time moments after the beginning of the light pulse.

Note that for the range of light intensities used in experiment the characteristic lifetime of an electron before recombination should change by three orders of magnitude. Based on the recombination rate constant estimated for the lowest light intensity, this time is $\tau_{1/2} = (K_\lambda \beta I_0 K_\mathrm{r})^{-1} \approx 60$ ns. Therefore, the fast component observed at a low light intensity should be related to electron trapping with a characteristic time of ~20 ns.

For the estimation of the concentration of electron acceptors, note that an increase in the light intensity does not result in strong changes in the decay rate of the slow component of the photoresponse (see Fig. 2). Therefore, first, for the maximum light intensity traps are not filled; second; the slow components reflect the first-order processes. Since the initial concentration of current carriers at the maximum light intensity is $\sim 10^{21}\ \mathrm{cm^{-3}}$ and the simple estimate shows that the electron concentration would decrease by ~100 times due to recombination to a time moment of 100 ns, then the maximum concentration of acceptors N can be restricted in the calculation of the kinetics by a value of 10^{19} cm^{-3}. The real concentration of acceptors is lower, probably, due to the efficient liberation of electrons from traps. A noticeable escape of electrons from traps is indicated by the fact that the ratio of the fast and slow components (see Fig. 2, curve *4*) is by 10 times lower than that estimated above. This makes it possible to decrease (in the calculation) the initial concentration of acceptors to a level of ~10^{18} cm^{-3}.

The lifetime of an electron in a trap cannot be shorter than the half-decay time of the fast component $\tau > \tau_{1/2} \approx$ 20 ns. In the opposite case, at the lowest light intensity (see Fig. 2, curve *1*), the fast component could not appear. The upper limit of the lifetime of a charge in a trap can be estimated assuming that quasi-stationary equilibrium was established to a moment of 100 ns: $\tau \leq 10\,\tau_{1/2} \approx$ 200 ns.

As mentioned above, the slow component of the photoresponse is caused by reactions of electrons, holes, and interstitial ions with trapped charges. The ratio of contributions of these processes depends on the light intensity. At high intensities, recombination with ions is insubstantial, and the main contribution to the decay is made by recombination through localized states. At low intensities, on the contrary, the recombination of an interstitial ion with a localized electron to form an atom makes the main contribution. Since an additional exposure produced no visible changes in the photoresponse amplitude or half-decay time, it can be accepted that products of the photochemical reaction were not accumulated. Possibly, the atom that formed is unstable and decomposes. Estimation of the ion concentration from measurements of the electric conductivity in the dark gave a value of ~10^{18}—10^{19} cm^{-3}.

Recombination rate constant of free electrons and holes. The results of calculation are presented in Fig. 2 by solid lines. 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 rate was virtually independent of I_0. A comparison of the calculation and experiment made it possible to determine the recombination rate constant of free electrons and holes in cadmium selenide: K_r = (4—6) • 10^{-11} cm^3 s^{-1}.

The K_r value in cadmium selenide is higher than the known recombination rate constants of free electrons and holes: 1 • 10^{-11} cm^3 s^{-1} (AgBr)**[4,5]** and 2 • 10^{-12} cm^3 s^{-1} (AgCl).**[9]** Perhaps, this is related to the fact that the width of the forbidden band in cadmium selenide (E_g = 1.6 eV) is much smaller than those in silver halides (E_g = 3.1 eV in AgCl and E_g = 2.6 eV in AgBr).

The authors are grateful to E. V. Rabenok for help in kinetic calculations.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 03-03-32202, 03-03-96404-r2003tschr, and 06-03-32725).

References

1. Yu. V. Meteleva and G. F. Novikov, *Fiz. Tekhn. Poluprovodn.*, 2006, **40**, No. 10 [*Semiconductors*, 2006, **40**, No. 10 (Engl. Transl.)].
2. A. V. Tataurov, Yu. V. Meteleva, N. L. Sermakasheva, and G. F. Novikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 1137 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1201].
3. V. N. Semenov and A. V. Naumov, *Vestn. Voronezh Gos. Univ.*, *Ser. Khim.*, *Biol.* [*Bulletin of Voronezh State Univ., Ser. Chem., Biol. Sci.*], 2000, No. 2, 50 (in Russian).
4. G. F. Novikov, B. I. Golovanov, and M. V. Alfimov, *Khim. Vys. Energ.*, 1995, **29**, 429 [*High Energy Chem.*, 1995, **29** (Engl. Transl.)].
5. G. F. Novikov and B. I. Golovanov, *J. Imaging Sci.*, 1995, **39**, 520.
6. N. L. Sermakasheva, G. F. Novikov, Yu. M. Shul´ga, and V. N. Semenov, *Fiz. Tekhn. Poluprovodn.*, 2004, **38**, 395 [*Semiconductors*, 2004, **38**, 380 (Engl. Transl.)].
7. A. P. Georgobiani, *Usp. Fiz. Nauk* [*Sov. Phys. Rev.*], 1974, **113**, Issue 1 (in Russian).
8. S. Grabtchak and M. Cocivera, *J. Appl. Phys.*, 1996, **79**, 786.
9. G. F. Novikov, B. I. Golovanov, and N. A. Tikhonina, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 2234 [*Russ. Chem. Bull.*, 1996, **45**, 2118 (Engl. Transl.)].
10. G. F. Novikov, E. V. Rabenok, and M. V. Alfimov, *Khim. Vys. Energ.*, 2005, **39**, 1 [*High Energy Chem.*, 2005, **39**, 167 (Engl. Transl.)].
11. B. Pejova and I. Grozdanov, *Mater. Lett.*, 2004, **58**, 666.
12. E. V. Rabenok, Ph. D. (Phys.-Math.) Thesis, Chernogolovka, 2005 (in Russian).

Received February 21, 2006