Experimental determination of the dependence of the free electron—hole recombination rate constant on the band gap in semiconductors of the $A^{II}B^{VI}$ and $A^{I}B^{VII}$ types

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A correlation between the recombination rate constant of free electrons and holes (k_r) and the band gap (E_g) of semiconductors (AgCl, AgBr, $Cd_xZn_{1-x}S$, CdSe, CdTe, and their solid solutions) at 295 K was found. The experimental data were obtained by the UHF photoconductivity (36 GHz) using current carrier generation by laser pulses (λ = 337 nm, pulse duration 8 ns). A decrease in E_g in a range of 1.5—3 eV increases k_r by 1.5 orders of magnitude according to the law close to exponential.

Key words: recombination, electron, hole, rate constant, band gap.

Two key processes, namely, separation and recombination, determine changes in the charged particles generated in the matter by the light or ionizing radiation. The most part of technical applications using compounds of the $A^{II}B^{VI}$ and $A^{I}B^{VII}$ types are based on the process of charge separation, whose characteristics determine the sensitivity and time parameters of various devices, *e.g.*, solar energy converters, sensors for radiation detection, systems of information transfer and recording, and others. In these substances electron-hole recombination processes most frequently result in irretrievable energy losses, except for some types of recombination luminescence. However, quantitative data on the characteristics of this process are virtually lacking, although their absence noticeably retards progress in the area of application of these compounds, impeding prediction of the limiting characteristics of the developed devices.

Note that quantitative regularities of recombination of free (that have never been captured by traps) electrons and holes in semiconductors of other types are not quite clear, despite the fact that the problem on the relationship of the recombination rate constant (k_r) and the properties of semiconductors were discussed in a series of publications. For instance, on the basis of the estimates for the k_r values in the Ge and Si semiconductors ($\sim 5 \cdot 10^{-14}$ and $\sim 3 \cdot 10^{-15}$ cm^3 s^{-1}, respectively), which were obtained using the dependence of the absorption coefficient on the band gap (E_g) and the principle of detailed balancing, it was assumed that the rate constant should increase with a decrease in E_g. Although it should additionally be substantiated that the principle of detailed balancing can be applied to an electron that underwent the thermalization step after its generation, this concept met no basic objections so far.

Meanwhile, in the recent decade there were several attempts to experimentally determine the rate constants k_r/cm^3 s^{-1} (cross sections) of electron-hole recombination in compounds of the $A^{II}B^{VI}$ and $A^{I}B^{VII}$ types: $1 \cdot 10^{-11}$ (AgBr (powders), E_g = 2.6 eV,[2] $2 \cdot 10^{-12}$ (AgCl (powders), E_g = 3.1 eV;[3] $(3\pm1) \cdot 10^{-13}$ (CdS, E_g = 2.5 eV)[4]; $(3\pm1) \cdot 10^{-11}$ (CdTe, E_g = 1.6 eV)[5]; $(4—6) \cdot 10^{-11}$ (CdSe, E_g = 1.8 eV).[6] However, no relationship was revealed between the obtained constants and the properties of substances.

In the present work, we attempted to verify some earlier published data on the rate constants of electron-hole recombination in compounds of the $A^{II}B^{VI}$ and $A^{I}B^{VII}$ types and to supplement partially these data.

Experimental

New measurements were carried out for CdS and $Cd_{0.5}Zn_{0.5}S$ films and AgBr single crystals. The synthesis of CdS has been described earlier.[6]

To prepare the $Cd_{0.5}Zn_{0.5}S$ films,* 0.01—0.05 *M* aqueous solutions of neutral $[Me(N_2H_4CS)_2Cl_2]$ complexes were sprayed onto a glassceramic support heated to 550 °C. The complex decomposed to form a film.[4,7,8] Glassceramics was chosen as a support because of good adhesion of the sulfide films due to many silanol groups on the glassceramic surface.[8] The typical film thickness was 5—10 μm.

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* The samples were kindly presented by Yu. V. Meteleva (Institute of Problems of Chemical Physics, Russian Academy of Sciences).

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Single crystals of AgBr were obtained by the complex method,* including purification of the starting silver nitrate with inorganic sorbents, zone smelting of silver nitrate, synthesis of silver halides by precipitation from an $AgNO_3$ solution with the corresponding hydrogen halide, thermal treatment of silver halides in an atmosphere of halogen agents, and zone smelting of silver halides. High-purity single crystals of silver halides were grown from the prepared melted crystals by the Bridgeman method (heater movement velocity 1 mm h^{-1}).

The kinetics of electron decay was studied by the UHF photoconductivity method (8-mm range). Changes in the reflection coefficient of electromagnetic radiation from a resonator of the TE_{101} type containing a small-volume sample were detected. The changes in the sample were induced by a short light pulse.[2,9]

The time resolution of the procedure was 10 ns. Samples were irradiated with pulses from an LGI-505 N_2-laser (λ = 337 nm, pulse duration τ_p = 8 ns). The light beam was blinded to separate a uniform light spot. The light intensity was varied within more than three orders of magnitude using light filters and changing beam focusing. When compared the experimental results with the calculation, the final light pulse width and the transient characteristic of the measuring tract were taken into account calculating the corresponding mathematical convolutions. The measurements were carried out at room temperature.

Results and Discussion

Irradiation with a light pulse results in a sharp decrease in the loaded Q-factor of the resonator and the appearance of a "photoresponse", a change in the power of the reflected UHF wave, $\Delta P(t)$ (t is the time counted from the light pulse onset).

After the end of the light pulse, the $\Delta P(t)$ value passes through a maximum and gradually decreases to zero. The dependence of ΔP on the f frequency of the UHF generator are virtually symmetric relative to the resonance frequency f_0. According to earlier published data,[10] this fact indicates 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 Q rather than the change in the resonance frequency f.

Exposure of the sample during experiment induces no changes in the amplitude and shape of the $P(t)$ dependence.

Since the mobilities of electrons and holes in CdS [11] and AgBr [12] are different, it is reasonable to attribute the photoresponse to photogenerated electrons:

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

where $W(t)$ is the generation rate of current carriers (reflects the shape of a light pulse); e^- and p^+ are electrons and holes, respectively. This assumption agrees with the results of studying the UHF photoconductivity in CdS [4,8] and silver halides (see discussion and Refs 2, 3 and 13): the changes in the UHF absorption under the used conditions of weak disturbance ($\Delta P/P_0 \ll 1$, where P_0 is the incident radiation power) are caused by electrons born by the light rather than positive holes, namely, $\Delta P(t) \sim n$ (n is the concentration of electrons).

The kinetics of photoresponse decay was approximately of the same type on all types of the samples studied. The photoresponse decays consisted, as a rule, of two components: fast (in the time interval $\tau_p \le t \le 0.5$ μs) and slow (in the time interval 100 ns $\le t \le$ 5 μs). However, the ratio of amplitudes and the time characteristics depended on the dose of photoirradiation per pulse I_0 (light "intensity") and the type of the sample.

The photoresponse amplitude in the $Cd_{0.5}Zn_{0.5}S$ films (band gap in $Cd_{0.5}Zn_{0.5}S$ is[14] 2.85 eV) even at $I_0 \ge 2 \cdot 10^{13}$ photon cm^{-2} pulse^{-1} is nonlinear (see inset in Fig. 1, *a*). Two components are observed in the decays (see Fig. 1, *a*), and the decay rate of the fast component increases with an increase in the light intensity (see Fig. 1, *b*): at $I_0 \approx 10^{13}$ photon cm^{-2} pulse^{-1} the time of half-decay of the fast component is $\tau_{1/2} \approx 200$ ns (see Fig. 1, *b*, curve *4*) and at $I_0 \approx 10^{14}$ photon cm^{-2} pulse^{-1} $\tau_{1/2} \approx 30$ ns (see Fig. 1, *b*, curve *1*). On the contrary, the rate of the slow component is virtually independent of the light intensity (see Fig. 1, *a*).

This difference in the behavior of the response components is caused by different contributions to the photoresponse from the decays of current carriers of the first and second orders at different time moments. At rather low light intensities the first-order processes predominate, and the processes of the second order are prevailing at high intensities. In the framework of this explanation, the observed increase in the fast component decay with an increase in I_0 (see Fig. 1, *b*) can reasonably be attributed to the increasing competition between the processes of electron decay of the second (2) and first (3) kinetic orders:

$$e^- + p^+ \xrightarrow{k_r} \ldots, \quad (2)$$

$$e^- + N \xrightarrow{k_1} N_-, \quad (3)$$

where k_r is the recombination rate constant of electrons and holes, N are the electron traps, N_- are the negatively charged electron traps, and k_1 is the rate constant of electron trapping.

Therefore, the nonlinear dependence of the photoresponse amplitude on I_0 becomes clear (inset in Fig. 1, *a*). Such a dependence is caused by the noticeably decay of electrons during the light pulse *via* the second-order reaction.

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* The samples were kindly presented by N. V. Lichkova (Institute of Microelectronic Technology and Ultra-High-Purity Materials, Russian Academy of Sciences).

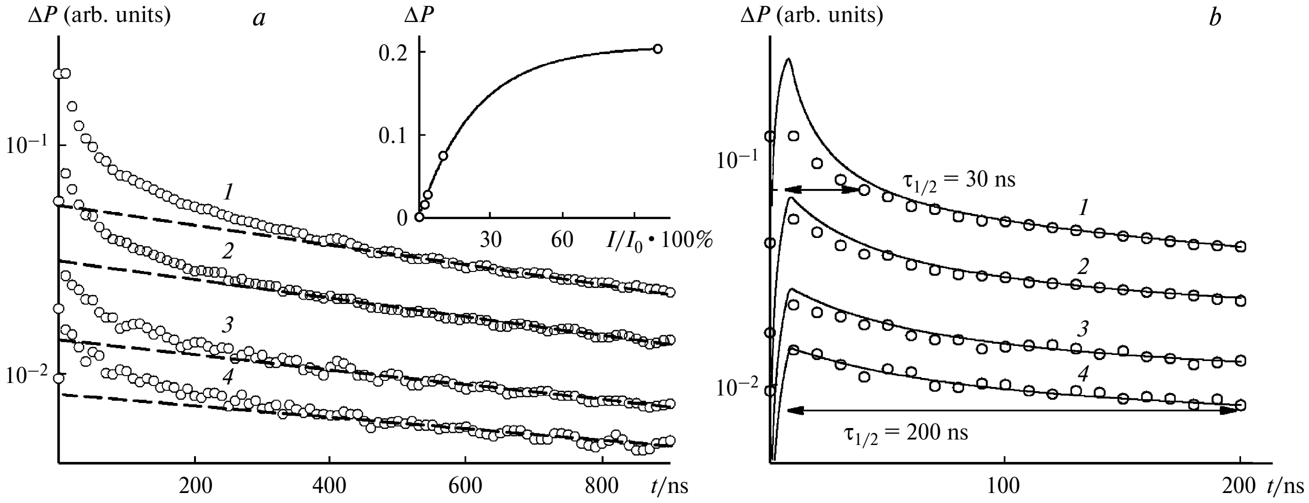

Fig. 1. Photoresponse (ΔP) of the $Cd_{0.5}Zn_{0.5}S$ film obtained at 500 °C and $I_0 = 4.4 \cdot 10^{14}$ (*1*), $4.4 \cdot 10^{13}$ (*2*), $1.7 \cdot 10^{13}$ (*3*), and $8 \cdot 10^{12}$ photon cm^{-2} pulse^{-1} (*4*) (points); straight lines show the approximation of the slow components of the decays (*a*) and solid lines show calculation (*b*). The dependence of the photoresponse amplitude on I_0 is shown in inset.

The following processes in the matter involving photogenerated current carriers can be presented:

$$p^- + P \xrightarrow{k_2} P_+, \quad (4)$$

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

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

$$N_- \xrightarrow{k_6} N + e^-, \quad (7)$$

$$P_+ \xrightarrow{k_7} P + p^+, \quad (8)$$

$$N_- + \text{ion}^+ \xrightarrow{k_8} \text{at}, \quad (9)$$

$$\text{at} \xrightarrow{k_9} e^- + \text{ion}^+ + N, \quad (10)$$

where P are the hole traps, P_+ are the charged hole traps, ion$^+$ are the interstitial ions, at are the metal atoms, k_2—k_9 are the rate constants of the processes. The initial concentration of free electrons is determined by the product of the generation rate by the laser pulse duration and photoionization quantum yield. However, direct comparison of the results of calculation of the charge decay kinetics in reactions (3)—(10) with the experimental photoresponse decays is inefficient, because the problem includes, as a whole, too many parameters: nine rate constants and three concentrations. Therefore, one should either choose experimental conditions in such a way that so many processes would not be needed to describe the photoresponse decays, or some rate constants (or the range of their acceptable changes) should preliminarily be determined by an independent method. This simplification of the problem becomes possible in the case when the changes in the shape of the photoresponse decrease is observed with a change in the light intensity by several orders of magnitude due to the kinetic features of processes of the first and second orders. This is accomplished in experiment (see Fig. 1). It can be seen that the theoretical curves (solid curves in Fig. 1, *b*) agree satisfactorily with experiment. Since the experiment was carried out under conditions of nonuniform light absorption, the system of equations corresponding to processes (2)—(10) was numerically solved for two cases: "complete mixing of the whole reaction volume" and "mixing within thin layers." The thickness of the layers perpendicular to light incidence was chosen in the calculation as $\Delta x \approx K^{-1}_{\lambda}$ (K_{λ} is the light absorption coefficient with the wavelength λ). The best agreement with experiment at the recombination rate constant of free electrons and holes $k_r \approx (6–8) \cdot 10^{-12}$ cm^3 s^{-1}.

As in microdispersed powders, the photoresponse decays consisting of two components were observed in the AgBr single crystals. A linear dependence of the photoresponse amplitude on the light intensity is observed at $I_0 < 10^{14}$ photon cm^{-2} pulse^{-1}, and the characteristic decay time is independent of I_0. The dependence becomes nonlinear with an increase in I_0, and the decay time decreases, indicating an increasing role of decay processes of the second order.

The decays of the UHF photoresponses of the AgBr single crystal at different light intensities are presented in the semilogarithmic scale in Fig. 2. At rather long times the photoresponse decays are described by exponential dependences with the characteristic times independent of the light intensity. When the light intensity increases to $I_0 \approx 1.4 \cdot 10^{15}$ photon cm^{-2} pulse^{-1} (curve *1*), a "new" faster

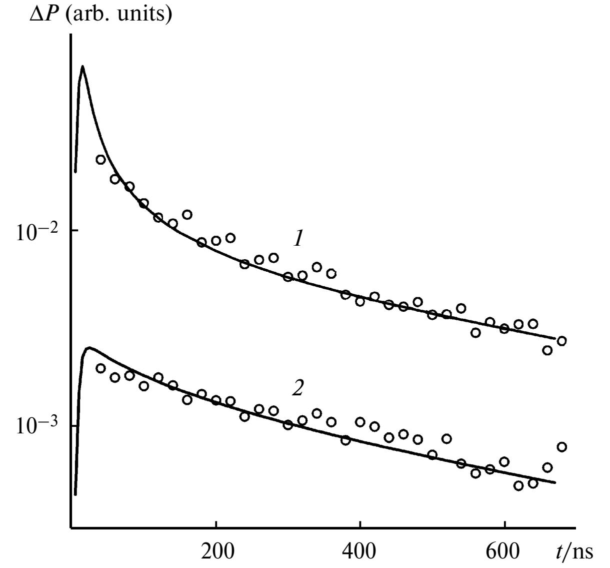

Fig. 2. Photoresponse of the AgBr single crystal at $I_0 = 1.4 \cdot 10^{15}$ (*1*) and $2.8 \cdot 10^{13}$ photon cm^{-2} pulse^{-1} (*2*), solid lines show calculation.

component appears at short times, and its decay rate increases with an increase in I_0. This component is not observed at lower I_0 (curve *2*), *i.e.*, the recombination of free electrons and holes at these light intensities does not compete with the decay processes of the first order.

The results of numerical calculations are shown by solid lines in Fig. 2. Analysis of the experimental conditions showed that the theoretical yield of holes from traps and recombination of a localized hole with a free electron make an insignificant contribution to the photoresponse decay. The calculated recombination rate constant of free electrons and holes in the AgBr single crystal is $k_r = (1.5 \pm 0.5) \cdot 10^{-11}$ cm^3 s^{-1}. The obtained k_r value agrees with that for the AgBr powders.[2] This indicates that the obtained rate constant does characterize an elementary process in the volume with the cross section independent of the type of the sample.

The verification of the results of determination of the electron-hole recombination rate constant in CdS films based on measurements of the UHF photoconductivity showed that the earlier[6] published values of the rate constant* is unfortunately mistaken. Although new measurements of the decay kinetics at different incident light intensities confirmed that the nonlinear dependence of ΔP on the light intensity was observed in the CDS films at high light intensities, as in the $Cd_{0.5}Zn_{0.5}S$ films, and this boundary turned out to be at $I_0 > 10^{13}$ photon cm^{-2} pulse^{-1}. At the low light intensity $I_0 \leq 10^{12}$ photon cm^{-2} pulse^{-1} the dependence was linear (region of processes of the first order), although the photoresponse decays also consisted of two components with half-decay times of 70 ns and 1.13 μs. The calculations of the kinetics of the UHF photoconductivity decays at different light intensities in the interval $6 \cdot 10^{11}$ photon cm^{-2} pulse^{-1} $\leq I_0 \leq 4 \cdot 10^{14}$ photon cm^{-2} pulse^{-1} gave the recombination constant of free electrons and holes equal to $2(\pm 1) \cdot 10^{-11}$ cm^3 s^{-1}.

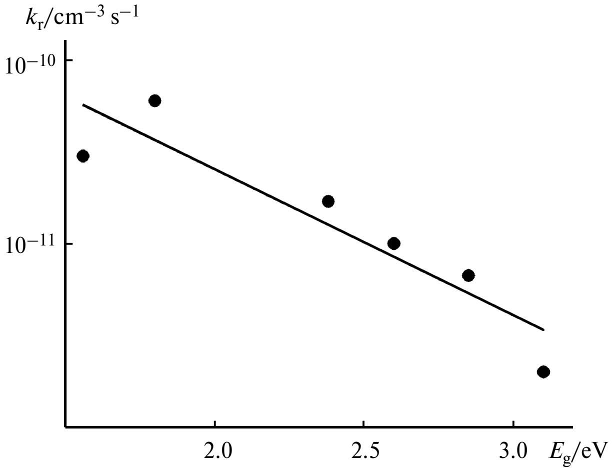

Fig. 3. Recombination rate constant (k_r) of free electrons and holes *vs*. band gap (E_g) of the semiconductor.

The results of determination of the rate constants of recombination of free electrons and holes obtained in the present work and published earlier are given in Fig. 3. It can be seen that the rate constant increases from $2 \cdot 10^{-12}$ to $3 \cdot 10^{-11}$ cm^3 s^{-1} with a change in the band gap of the semiconductor from 3.2 eV for AgCl to 1.5 eV for CdTe. The dependence presented in the semilogarithmic coordinates is linear within the experimental error. Therefore, the empirical dependence of k_r on E_g can formally be written as the exponential function

$$k_r = k_r^0 \exp\{-\alpha_r E_g\}, \tag{11}$$

where $\alpha_r \approx 1.5$ eV^{-1}.

It seems of interest to extrapolate dependence (11) to the regions of low and high energies of the band gap. For the extrapolation to $E_g = 0.4$ eV we have $k_r = (2-3) \cdot 10^{-10}$ cm^3 s^{-1}, which is close to the preliminary results of studying PbS.* The extrapolation to the energies of radiative transitions in Si and Ge** also gives the value that does not contradict to the estimates.[1]

Undoubtedly, the obtained dependence (11) needs special detailed discussion. It can be assumed that it reflects a decrease in the probability of electron and hole recombination with an increase in the band gap in the semiconductor, because it is necessary to distribute an increasing portion of the energy evolved upon recombination (phonons).

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* The authors apologize for the mistake in the previous work[6] caused by disrepair of the light intensity meter.

* Private report by N. L. Sermakasheva.

** http://www.ioffe.ru/SVA/NSM/rintroduction.html

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