INCREASE OF PHOTOSENSITIVITY AND INTENSITY OF LUMINESCENCE IN PHOTOTHERMAL DISSOCIATION OF DONOR-ACCEPTOR PAIRS IN CdS

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As shown by investigations of different semiconductors (CdS and CdSe, ZnS and ZnSe, GaSe, GaAs, $CdSiP_2$, and others), the main type of photosensitivity center (i.e., center of "slowest" recombination), is an acceptor in an n-type sample (cf., e.g., [1]) and a donor in a p-type sample (e.g., [2]). The same centers, as shown by joint investigations of luminescence and photoconductivity [3], are centers of the effective recombination luminescence that results from radiative decay of the majority carriers by these centers.

Such a situation is governed to a considerable degree by the charge state of the centers. Thus, deep acceptors (A) in n-type semiconductors, being compensated and thus negatively charged, attract the non-equilibrium holes, which are captured in the Coulomb field, with a large capture cross section $S_{pA}^{-} \sim 10^{-12} - 10^{-14}$ cm^2 [1], greatly exceeding the "geometrical" capture cross section $\sigma \sim 10^{-15} - 10^{-16}$ cm^2. The succeeding radiative capture of the electron is produced already by a neutral center (if the acceptor is singly charged), with a cross section equal to $S_{nA}^{0} \sim 10^{-19} - 10^{-21}$ cm^2 [1, 3].

The large cross section S_{pA}^{-} makes the centers A under consideration readily able to compete with capture of holes by other (i) recombination centers. Even if the A-center concentration is not very high, $N_A \sim 10^{15} - 10^{16}$ cm^{-3}, they carry frequently the main share (g_A) of the entire recombination flux, $g_A = S_{pA}N_A/\sum_i S_{pi}N_i$. The sample exhibits good photosensitivity and luminescence (in the given band) if $g_A \sim 1$.

A change, for any reason, in the value of S_{pA} should change the recombination flux through the A centers, and hence the luminescence and the photoconductivity. For example, an increase of S_{pA} by K times with the filling of all the recombination centers kept unchanged (for simplicity) leads to an increase of the flux (g_A) through the A centers by a factor $K/[g_{0A}(K - 1) + 1]$, where g_{0A} is the initial flux through the A centers.

An effective reason for the change of the cross section S_{pA} should be the clustering of this center with an ionized donor (D^+), as a result of which the A^- centers ceases to be negatively charged and becomes practically neutral under equilibrium conditions (dipole), $(A^-D^+)^0$. The cross section for hole capture should decrease appreciably in this case, from S_{pA}^{-} to σ,[1)] and the cross section for the capture of an electron (by a positively charged complex) should increase from S_{nA}^{0} to $S_{n(DA)}^{+}$.

To the contrary, in the case of decay of the complex $(A^-D^+)^0$, which captures holes weakly, into centers A^- and D^+ that do not interact with each other, the cross section for the capture of holes by the A^- centers increases sharply from σ to S_{pA}^{-}, and the electron capture cross section decreases. This leads to

[1)] The cross section for hole capture by dipole centers should have a value intermediate between σ and S_{pA}^{-} and should vary with the distance d between the donor and acceptor like $d^{1/2}$ [4].

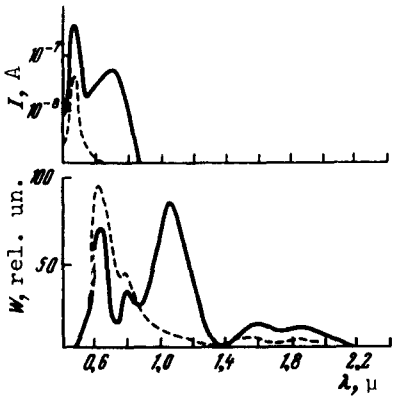

Fig. 1

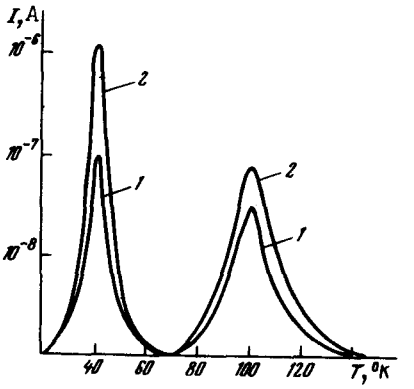

Fig. 2

Fig. 1. Spectra of photocurrent I and luminescence W in a CdS crystal before (dashed lines) and after (continuous lines) of the occurrence of the sensitizing photochemical reactions.

Fig. 2. Curves of thermostimulated current before (curve 1) and after (curve 2) the occurrence of the PCR. The increase of the peak at 40°K is due to the increase of the concentration of the corresponding trapping centers, and the increase of the peak at 100°K is due to sensitization of the crystal at a constant concentration of trapping centers.

an increase of the photocurrent and of the intensity of the corresponding luminescence.

We have apparently succeeded in observing such a photothermal pair decay process in CdS and CdSe single crystals, in which the so-called sensitizing photochemical reactions (PCR) take place [5].

In these crystals, usually subjected to prior thermal annealing and quenching, illumination in the interval from room to lower temperatures (-100°C) there occurs a considerable increase (up to 10^2 times) of the photosensitivity [5], accompanied by an increase in the intensity of the luminescence band λ_{max} = 1.03 - 1.06 μ in CdS [6] (Fig. 1). This luminescence, as established earlier [3], is connected with radiative capture of electrons by the main acceptor photosensitivity centers in CdS (the so-called r-centers [1]). A detailed investigation of these processes has shown that both are due to the occurrence in the crystal, as a result of the PCR, of a large number (up to 10^{16} cm^{-3}) acceptor photosensitivity r-centers of the same type as those causing the photosensitivity of ordinary CdS crystals [5 - 7].

Two significant circumstances characterize the considered PCR processes.

1. Simultaneously with the occurrence of new r-centers, shallow donors (E_c - 0.05 eV) are always produced and have the same concentration as the r-centers. The shallow donors are apparently connected with the interstitial Cd_i^+. They become clearly manifest in the spectra of thermostimulated conductivity at low temperatures (Fig. 2).

2. For both types of centers to be produced, it is necessary to have not free electrons but free holes [7]. The latter can be produced not only by the intrinsic light or by bipolar injection of carriers from electrodes, but also by using infrared illumination that excites in the v-band holes previously produced by the light and fixed on the deep centers in the crystal.

The first of these facts indicates, in our opinion, that the donor-acceptor pairs $[(\text{r-center})^- Cd_i^+]^0$ produced by the thermal treatment decay during the course of the PCR into independent components $(\text{r-center})^-$ and Cd_i^+.

The second fact explains this process well. Indeed, the complex under consideration, the two components of which are retained by the Coulomb forces, can capture at the PCR temperature only a hole, and not an electron, since the acceptor center is quite deep (E_v + 1.0 eV), and the donor center is too shallow (E_c - 0.05 eV).

As a result of capture of the hole, the Coulomb attraction between the pair components vanishes and the Cd_i^+ ion, which moves easily in the CdS lattice, diffuses away from the neutral acceptor to a distance such that they practically cease to interact.

The measured activation energy of this process [5] is 0.15 eV.

We assume that the described mechanism, based on an appreciable decrease of the cross sections for carrier capture by the centers when they cluster together, may be one of the causes of such phenomena as aging of luminors and electroluminors, the so-called degradation of opto-diodes, the decrease of luminescence intensity when strongly doped by co-activator donors (i.e., it can cause in this case the concentration quenching of the luminescence). Pair dissociation, on the other hand, can lead, in addition to the phenomena described, also to a rapid increase of the photocurrent and luminescence intensity in the case of short-duration heating of samples, etc.

Gurevich and co-workers [8] have investigated in detail the process of clustering of donor and acceptor centers $(Ga_{Zn})^+$ and $(V_{Zn}Ga_{Zn})$ in Zn, processes that lead to a change in the luminescence spectrum. In our opinion, the considerations described above can explain the results of their observation, namely the decrease of the intensity of the new luminescence band due to the neutral complex $[V_{Zn}, (Ga_{Zn})_2]^0$, compared with the intensity of the luminescence connected with the acceptor complex $(V_{Zn}Ga_{Zn})^-$.

[1] V.E. Lashkarev and M.K. Sheinkman, Phys. Stat. Sol. 11, 429 (1965).
[2] I.Ya. Gorodetskii, V.V. Makarenko, A.D. Shneider, and M.K. Sheinkman, Ukr. Fiz. Zh. 11, 1137 (1966).
[3] M.K. Sheinkman, In: "Elektrolyuminestsentsiya tverdykh tel" (Electroluminescence of Solids), Naukova Dumka, Kiev, 1971, p. 77.
[4] V.V. Antonov-Romanovskii, Fiz. Tverd. Tela 13, 853 (1971) [Sov. Phys.-Solid State 13, 705 (1971)].
[5] N.E. Korsunskaya, I.V. Markevich, and M.K. Sheinkman, Phys. Stat. Sol. 13, 25 (1966).
[6] I.B. Ermolovich, N.E. Korsunskaya, and M.K. Sheinkman, Fiz. Tverd. Tela 9, 2893 (1967) [Sov. Phys.-Solid State 9, 2275 (1968)].
[7] N.E. Korsunskaya, I.V. Markevich, and M.K. Sheinkman, ibid. 10, 522 (1968) [10, 409 (1968)].
[8] M.A. Il'ina, V.B. Gutan, and A.M. Gurvich, Zh. prikl. spektrosk. 14, 838 (1971).