

Kinetics of Photoconductivity in ZnSe Crystals upon Photoexcitation of Deep Centers

L. I. Bruk, O. S. Gorya, V. A. Korotkov, L. E. Kovalev,
L. V. Malikova, and A. V. Simashkevich

Moldova State University, ul. Mateevicha 60, Kishinev, 277009 Moldova

It has long been known that investigation of the spectral characteristics of photoconductivity (PC) in wide-band-gap semiconductors does not provide full information on the position of photosensitive centers in the forbidden band. The broad spectrum of intrinsic and impurity PC consists of several overlapping bands. In the long-wavelength region, impurity photoeffect is superimposed over the falling-off spectrum of intrinsic PC. In addition, measurements of steady-state PC are incapable of revealing photoinsensitive recombination and trapping centers. Those levels that were not excited prior to illumination of the semiconductor may provide no contribution to PC and may appear either photoinsensitive or indistinguishable from dominant channels of recombination and trapping on other centers. Preliminary excitation may alter the state of these levels to such a degree that they will show up as a spike in the PC relaxation curve [1 - 6].

In this paper, we report kinetic studies of the PC and the effective cross section for photon capture (CSPC) in the photosensitivity range of zinc selenide single crystals containing trace impurities.

Relaxation of the PC and CSPC after optical excitation can be described in terms of a two-level model [5, 6]. In the band gap of ZnSe ($E_g = 2.68$ eV at 300 K), there are two localized levels: a deep level S , which is situated in the middle of the gap and related to a fast recombination center with comparable capture cross sections for electrons and holes, $S_{nS} = S_{pS} \approx 10^{-17}$ cm², and a photosensitive acceptor level A , whose capture cross section for electrons is larger than that for holes, that is, S_{nA} is far less than S_{pS} (Fig. 1a). Equilibration on levels A and S proceeds first through the $V-A$ channel and then through the $S-V$ channel.

Within the framework of this model, the concentration

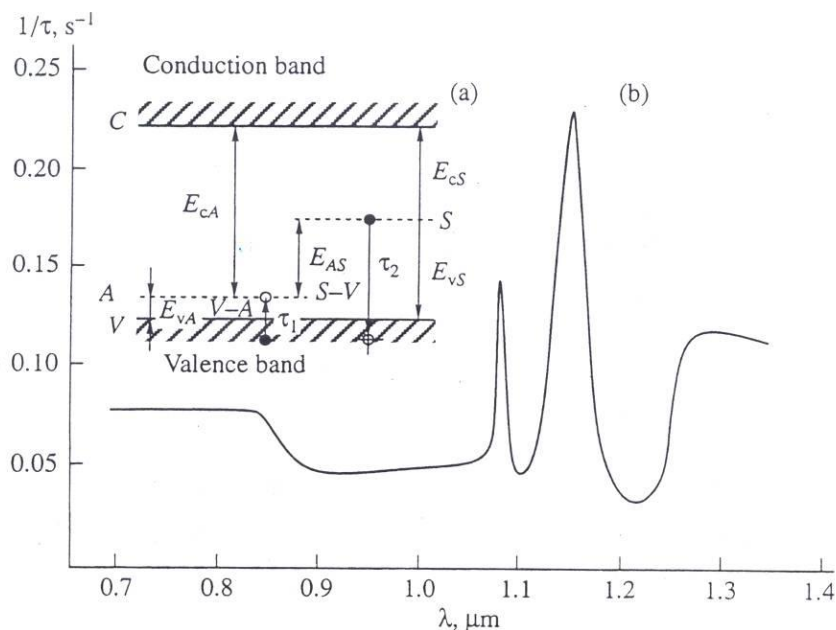


Fig. 1. (a) Two-level model; (b) spectral dependence of inverse relaxation time $1/\tau$ (preliminary excitation at $0.490 \mu\text{m}$).

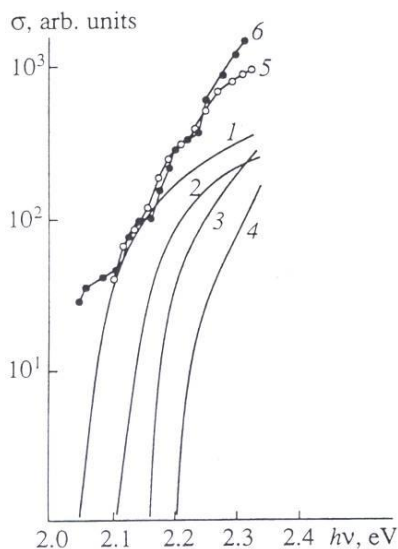


Fig. 2. (1 - 4) Calculated CSCP spectra; (5) their sum; (6) experimental spectrum.

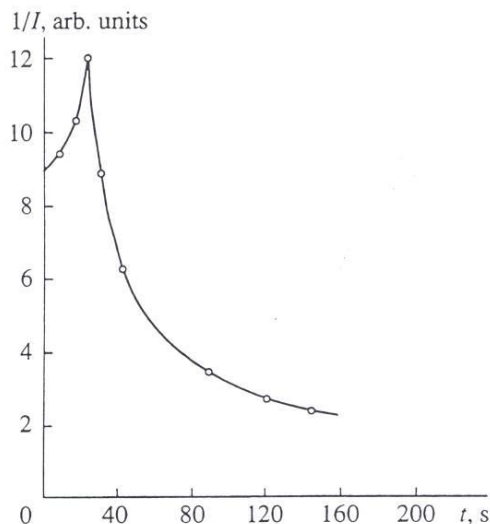


Fig. 3. Relaxation of the CSCP on deep centers; observation at $\lambda = 0.950 \mu\text{m}$ after photoexcitation at $\lambda_{\text{pr}} = 0.475 \mu\text{m}$.

of electrons on the *S*-center, m_S , at time t is given by [5]

$$m_S = \frac{m_{S_{\text{max}}} m_{S_{\text{st}}} \exp \left[\frac{m_{S_{\text{st}}} t}{m_{S_{\text{max}}} \tau_2} + \frac{\tau_1}{\tau_2} (1 - e^{-t/\tau_1}) \right]}{m_{S_{\text{st}}} + m_{S_{\text{max}}} \exp(\tau_1/\tau_2) [\exp(m_{S_{\text{st}}} t / m_{S_{\text{max}}} \tau_2) - 1]}, \quad (1)$$

where $m_{S_{\text{max}}}$ and $m_{S_{\text{st}}}$ are defined by the boundary conditions $m_S|_{t=0} = m_{S_{\text{max}}}$ and $m_S|_{t=\infty} = m_{S_{\text{st}}}$, respectively; τ_1 is the characteristic time of electron transfer from the valence band to the acceptor level (level *A*); and τ_2 is the characteristic time for level *S*.

Given that $\tau_1 \ll \tau_2 = \tau$ and that photocurrent is proportional to m_S , expression (1) can be written as

$$\frac{I_{\text{ph}_{\text{max}}}}{I_{\text{ph}_{\text{st}}}} \ln \left[\frac{(I_{\text{ph}_{\text{st}}}/I_{\text{ph}_{\text{max}}}) - 1}{I_{\text{ph}_{\text{st}}}/I_{\text{st}}} \right] = \frac{1}{\tau} t, \quad (2)$$

where $I_{\text{ph}_{\text{st}}}$, $I_{\text{ph}_{\text{max}}}$, and I_{ph} are steady-state, maximum, and instantaneous values of photocurrent, respectively.

In appropriate coordinates, relation (2) represents a straight line with a slope $k = 1/\tau$. With the designation $Y = kT$, the coefficient k is given by

$$\frac{1}{\tau} = \frac{\langle Yt \rangle}{\langle t^2 \rangle} = \frac{1/n \int_{i=1}^n Y_i t_i}{1/n \int_{i=1}^n t_i^2} = \frac{\int_{i=1}^n Y_i t_i}{\int_{i=1}^n t_i^2}, \quad (3)$$

where subscript i refers to the i th point in the photocurrent relaxation curve. By measuring $1/\tau$ at different

observation wavelengths and at a fixed excitation wavelength, we can determine the spectral dependence $1/\tau = f(\lambda)$. This dependence, obtained at a wavelength of preliminary excitation $\lambda_{\text{pr}} = 0.490 \mu\text{m}$ (Fig. 1b), suggests that there are two *S*-levels in the band gap (1.14 and 1.06 eV below the bottom of the conduction band), both of which feature an increased probability of recombination.

The position of the *A*-centers can also be determined from the spectral dependence of the CSCP. These dependences for deep centers in high-resistivity ZnSe were measured and calculated using a technique [7] relying on the fact that the population of an impurity level does not change upon irradiation at different wavelengths if the photocurrent is maintained constant by adjusting the intensity of incident light. With this condition, the CSCP spectrum is determined by the dependence of light intensity I on photon energy:

$$\sigma_{\text{ph}}^0(h\nu) = \text{const}/I(h\nu). \quad (4)$$

A typical CSCP spectrum is shown in Fig. 2. From the inflections in curve 6 (experimental data), we determined the energies (relative to the bottom of the conduction band) of the corresponding levels to be $E_{\text{cA}} = 2.05, 2.11, 2.16,$ and 2.21 eV . The calculated individual CSCP spectra for these centers are shown by curves 1 - 4, and their sum is shown by curve 5, which is in reasonable agreement with the experimental curve. Thus, our results provide evidence that the photosensitive levels in question are due to *A*-centers and can be satisfactorily described by the two-level model proposed here.

The above technique was also used to investigate the relaxation of the CSCP on deep centers after photoexcitation. We found "spikelike" relaxation of the CSCP

(Fig. 3). Preliminary excitation causes electron transitions from the photosensitive level (*A*-center) to the center responsible for the spike (*S*-center) via the conduction band. These transitions change the charge state of the *S*-center and increase the average photoionization cross section. As the electrons are removed from the *S*-center (owing to recombination with holes originating from the valence band), the photoionization cross section reverts to its initial value. Thus, the spike-like relaxation of PC after photoexcitation of deep centers is due to relaxation of the CSPC on *S*-centers.

CONCLUSION

Based on a two-level model, we obtained a relation between the recombination probability and the instantaneous value of photocurrent.

Spectral and relaxation dependences of the photocurrent and CSPC were used to determine the ionization energy of *S*-centers, the carrier lifetime on these centers, and its dependence on the concentration and depth of the *A*-centers.

The spike-like relaxation of PC and CSPC after photoexcitation of deep centers is accounted for by relaxation of the CSPC on *S*-centers.

REFERENCES

1. Lashkarev, V.E. and Rybalka, V.V., Spikelike Relaxation of Photoconductivity in Cu-Doped HgS, *Ukr. Fiz. Zh.* (Russ. Ed.), 1965, vol. 10, no. 2, pp. 166 - 172.
2. Berkovskii, F.M. and Ryvkin, S.M., Photoinduced Charge Exchange on Impurity Centers and Photo-emf Kinetics in Germanium, *Fiz. Tverd. Tela* (Leningrad), 1963, vol. 5, no. 2, p. 381.
3. *Fizika Soedinenii A^{II}B^{VI}* (Physics of II-VI Compounds), Georgobiani, A.N. and Sheinkman, M.K., Eds., Moscow: Nauka, 1986.
4. Gaplevskaya, S.P., Zavertannaya, L.S., and Rvachev, A.L., Some Features of Photoelectric Memory in Cadmium Sulfide, *Ukr. Fiz. Zh.* (Russ. Ed.), 1974, vol. 19, no. 2, pp. 292 - 298.
5. Gorya, O.S., Spectral Memory of Photoconductivity in High-Resistivity ZnSe, *Fiz. Tekh. Poluprovodn.* (Leningrad), 1989, vol. 23, pp. 2090 - 2093.
6. Gorya, O.S., Spectral Memory of Photoconductivity in High-Resistivity ZnSe, *Fiz. Tekh. Poluprovodn.* (Leningrad), 1990, vol. 24, p. 1496.
7. Baubinas, R.V., Vaitkus, Yu. Yu., and Senulis, F.D., Spectral Dependences of the Photon Capture Cross Section from Infrared Quenching and Impurity Photoconductivity in Single Crystals of CdSe, *Litov. Fiz. Sb.*, 1978, vol. 17, no. 1, pp. 109 - 116.