DEEP CENTERS INFLUENCE ON PHOTORESPONSE CHARACTERISTICS IN HIGH-RESISTIVITY ZnSe

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ABSTRACT

The photocurrent peak after preliminary optical excitation with specific wavelength in high resistivity ($\rho \approx 10^{12} \Omega * cm$), unintentionally doped ZnSe monocrystals was observed. To study photocurrent "flash" phenomenon, the photocurrent relaxation spectra, photon-capture cross-section (PCCS) spectra and photo-electron paramagnetic resonance (photo-EPR) were investigated. Two-levels model involving the recombination of an S-center and an acceptor A has been developed to obtain the relation between recombination probability and instantaneous photocurrent value. The S-centers ionization energies (1.06eV and 1.14eV from the bottom of the conduction band) and charge carriers life times were determined. The acceptor's positions in ZnSe band gap are equal to 2.05, 2.11, 2.16 and 2.21eV from the bottom of the conduction band. The photocurrent and PCCS "flash" nature as well as complicated photo-EPR are associated with the relaxation of S-centers attributed to Fe ion in the band gap of semi-insulated ZnSe.

INTRODUCTION

The optical properties of wide energy band gap II-VI compound semiconductor ZnSe material system have received much attention of late because they may prove useful for photodetectors, photodiodes, and laser diodes [1, 2], working in blue and blue-green range of the spectrum. The efficiency of such devices is determined by the concentration of unintentional impurities and defects. At the same time, research into undoped, highly resistive ZnSe, containing a large density of deep centers (DC), is also of interest. This is the subject of our report.

It is known that the intrinsic and impurity stationary photoconductivity (PC) spectral region is the result of a few superimposed bands and does not allow one to obtain the total information about the photosensitive centers position in the semiconductor's band gap. The recording PC stationary signal excludes the possibility to reveal less sensitive, recombination and capture centers. The preliminary excitation can change the state of such levels and leads to their displaying in "flash" phenomenon [3, 4]. These centers, depending on their charge state, can show paramagnetism at different external conditions. In the photosensitivity region of ZnSe with unintentional impurities we have investigated PC "flash" phenomenon, the photocurrent relaxation spectra, photo-EPR and PCCS spectra.

EXPERIMENTAL RESULTS AND DISCUSSION

We have studied highly resistive ($\rho \approx 10^{12} \Omega * cm$) ZnSe crystals with free carrier concentration and mobility of $n \approx 10^{7} cm^{-3}$ and $\mu_n \approx 10 cm^2 / V * s$ respectively. Indium makes an Ohmic contact to ZnSe. One of the contacts was semitransparent.

Mat. Res. Soc. Symp. Proc. Vol. 442 © 1997 Materials Research Society

The PC relaxation spectra and PCCS spectra were measured in the 0.5-1.0μm range at the room temperature. EPR spectra were measured at 20K, 77K with and without optical and X-rays excitation from the fundamental absorption region.

Photocurrent

The "flash" phenomenon of the photocurrent of the investigated ZnSe samples was observed at temperatures of 100-300K. The fall of the photocurrent after "flash" (see Fig.1a, curve 1) from its maximum value I_{PCm} to the stationary signal I_{PCst} (see Fig.1a, curve 2) during illumination with light of the same wavelength, but following preliminary excitation occurred after $10^2 - 10^3 s$ at T=100K and after $10^1 - 10^2 s$ at T=300K. One could distinguish three experimental situations in which this effect was observed: illumination with light from the intrinsic absorption region following preliminary excitation with impurity-absorbed light; illumination with impurity-absorbed light after excitation with light corresponding to the intrinsic absorption region; illumination with impurity-absorption light after excitation with light of a different wavelength within the impurity absorption region.

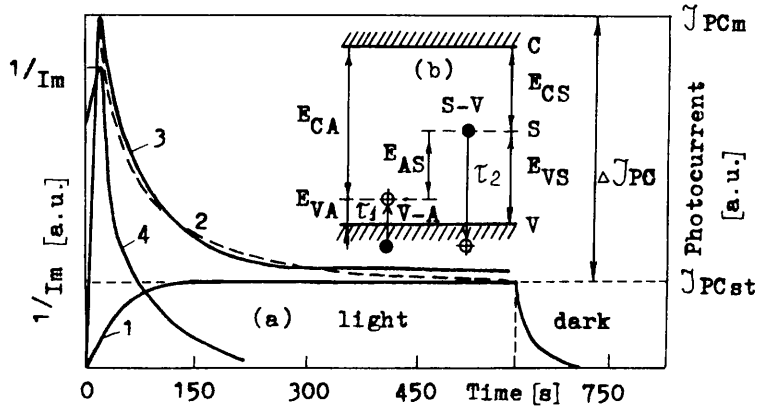

Fig.1. PC decay spectra (a); energy-band diagram of the two-levels model (b).

Figure 2 illustrates typical PC dependence on wavelength without preliminary (curve 1) and with preliminary excitation (curves 2,3), with the wavelength of the PC "flash" (ΔI_{PC}) induced by prior irradiation falling in the 0.46... 0.95 μm range. We measured the spectral dependence of ΔI_{PC} at various wavelengths of prior irradiation, whose "flash" corresponded to energies of 2.05, 2.11, 2.16 and 2.21eV. The dependence of ΔI_{PC} on the wavelength of the prior irradiation measured at a fixed wavelength (Fig.2, curves 2,3) also exhibits a number of peaks. Apparently, nonequilibrium electrons recombine via the above-described local centers, and PC "flash" is probably due to the overcharging of deep centers, which are taken out of equilibrium by prior irradiation in a different frequency range.

A model accounting for the peak of the photoconductivity relaxation curve in the second and third cases was developed by considering the case of a PC "flash" as a result of illumination with light of photon energy E_{CS} after preliminary excitation with light of photon energy E_{CA}. Figure 1b shows the energy band diagram of the two-level model. Levels E_{CS} and E_{CA} are the

energy separation — from the bottom of the conduction band — of a deep level S located near the middle of the band gap and of an acceptor level A. The envelopes of the relaxation curves were obtained by two methods. In the first method we used short light pulses sufficient to reach the quasisteady value of the current (see Fig.3a, curve 1). In the second method we used long light pulses alternating with short intervals in darkness during which the dark value of the current could not be established (see Fig.3a, curve 2). The coincidence of the envelopes of the relaxation curves indicated that relaxation of the nonequilibrium PC after illumination with E_{CS} and the dispersal of the nonequilibrium electrons at the S-level in darkness were both due to the same recombination channel. In other words, dispersal of the charge from the S-centers does not involve the conduction band, in contrary to the model proposed in [5] and [6], and was due to the subsequent illumination of the semiconductor.

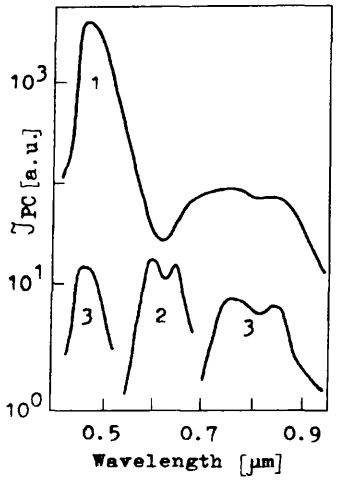

Fig.2. PC spectra without (curv.1) and after preliminary excitation (curv.2) at $\lambda_{exit.}$ = 0.525μm and curv.3 at $\lambda_{regist.}$ = 0.580μm)

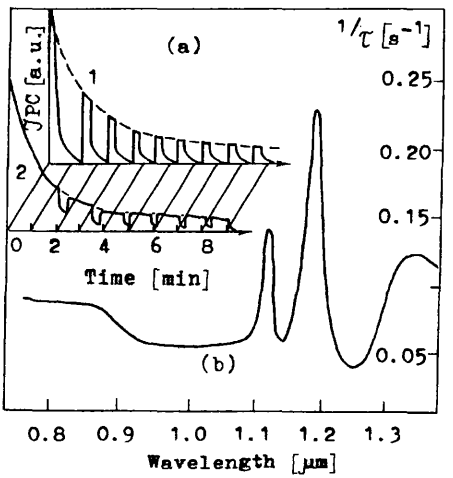

Fig.3. PC decay spectra at $\lambda_{regist.}$ = 0.950μm and $\lambda_{exit.}$ = 0.475μm (a); spectrum after preliminary excitation at $\lambda_{exit.}$ = 0.490μm (b).

We propose that the conditions of optical generation simply transfer electrons to the conduction band and result in repeated trapping on the S-level. We assume that the density of holes in the valence band after a long interval in darkness is zero. This was true if $N_A < N_S$, where N_A and N_S the concentration of the A- and S-centers, respectively. If in such a state the sample was illuminated with light of the photon energy $h\upsilon = E_{CS}$, we should observe the usual relation of the nonequilibrium electron density in the conduction band due to the presence of electrons with a density n_{Sst} at the S-centers. However, if a sample is first illuminated with light of the photon energy $h\upsilon = E_{CA}$, the nonequilibrium electrons from the conduction band were captured by the S-centers and these were only partly emptied. Therefore, after preliminary illumination of a crystal nonequilibrium situation was established in which A-centers were partly emptied and the S-enters were almost filled with electrons. The subsequent illumination of the semiconductor with photons of energy $h\upsilon = E_{CS}$ released electrons from the S-level to the conduction band and this gave a steep rise of the photocurrent above the steady-state value, followed by a fall together

with the density of nonequilibrium electrons at the S-centers. Preliminary illumination with photon of the $h\upsilon = E_{CA} - E_{CS}$ energy did not create a "flash". A change in the electron density at the S-level due to their recombination with holes from the valence band is given by the Bernoulli equation [4]:

$$\frac{dn_S}{dt} + \frac{1}{\tau_2}\frac{n_S}{n_{Sst}} - \frac{n_S}{\tau_2}\left(\frac{n_{Sst}}{n_{Sm}} + e^{-t/\tau_1}\right) = 0 \qquad (1),$$

where n_S is the density of electrons at the S centers at any moment in time t; $n_S\big|_{t=0} = n_{Sm}$ (for ΔI_{PCm}); $n_S\big|_{t=\infty} = n_{Sst}$ (for ΔI_{st}) ; the following characteristic times: $\frac{1}{\tau_1} = \gamma_{Ap} N_A$; $\frac{1}{\tau_2} = \gamma_{Sp} n_{Sm}$. The hole capture coefficient of the S centers is γ_{Sp} and γ_{Ap} is the hole capture coefficient of the A-centers.

Equation (1) has the exact solution :

$$n_S = \frac{n_{Sm} n_{Sst} \exp\left[n_{Sst}/n_{Sm}\tau_2 + \tau_1\left(1 - \exp\left[-t/\tau_1\right]\right)/\tau_2\right]}{n_{Sst} + n_{Sm}\exp\left(\tau_1/\tau_2\right)\left[\exp\left(n_{Sst}t/n_{Sm}\tau_2\right) - 1\right]} \qquad (2).$$

Substitution of the experimentally determined parameters $\tau_1 = 10^{-7} s$, $\tau_2 = 10 s$, $n_{Sm} = 10^7 cm^{-3}$ and $n_{Sst} = 10^6 cm^{-3}$ into eq. (2) ensured satisfactory agreement between the calculated and experimental dependencies (see Fig.1a, curves 2, 3). Taking into account, that $\tau_1 \langle\langle \tau_2$ and $I_{PC} \approx n_S$, we obtained from equation:

$$\frac{1}{\tau} t = \frac{I_{PSm}}{I_{PCst}} \ln\left(\frac{\left(I_{PCst}/I_{PCm}\right) - 1}{I_{PCst}/I_{st}}\right) \qquad (3).$$

Figure 3b illustrates the dependence of $1/\tau$ on wavelength. It is supposed that the peaks at the energies 1.14eV and 1.06eV from the conductivity band bottom correspond to S-centers, which are characterized by high probability of recombination.

Photon-capture cross-section

The independent determination of the A-centers position is carried out from the PCCS (σ_{ph}) spectral dependence. According to ref.7 spectral dependence is determined by the dependence of photon flux intensity (I) on the photon energy: $\sigma_{ph}(h\upsilon) = const/I(h\upsilon)$, at $I_{PC} = const$ on account of the excitation intensity change. The typical PCCS spectra are given in Fig.4a. By bending points the position of photosensitive A-centers with the energy E= 2.05; 2.11; 2.16; 2.21eV there were established. As one can see from Fig.4a satisfactory coincidence of the calculated and experimental curves is observed.

The deep centers PCCS relaxation after the optical recharging reveals "flash" phenomena. It is supposed that preliminary illumination transfers the electrons from A-centers through conductivity band to the centers of "flash" activation (S-centers). The charge state of deep S-center is changing and the average value of photoionization grows ("flash" on Fig.1a, curve 4).

At the recombination of the electrons from S-center with the holes from the valence band PCCS decreases to its stationary value. Thus apparently, PC "flash" phenomena after optical recharging DL is explained by PCCS relaxation on S-centers.

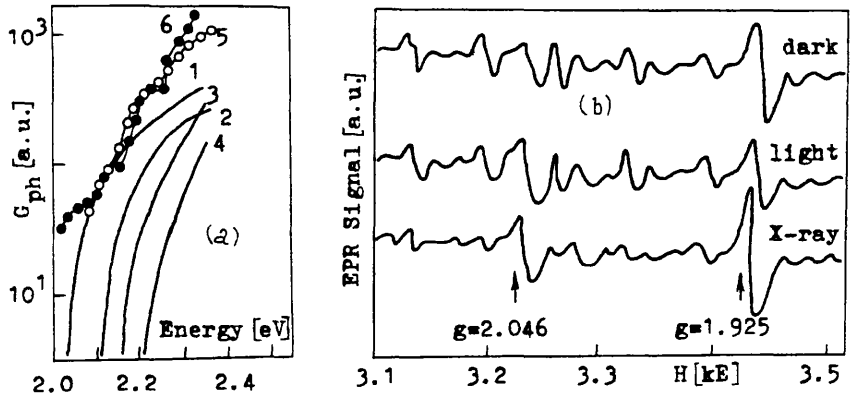

Fig.4. PCCS spectra (curv. for centers 1-E_{CS} = 2.05eV; 2-E_{CS} = 2.11eV; 3-E_{CS} = 2.16eV; 4-E_{CS} = 2.21eV and 5-calculation; 6-experiment) (a); EPR spectra at 77K (b).

Photo-electron paramagnetic resonance

We have studied EPR of unintentionally doped zinc selenide with and without optical and X-ray excitation .

In the EPR spectra of all samples it was observed the Mn^{2+} , consisting from six lines with superfine (HFS) interaction constant A=67.9 Gs, a=9 Gs, g-factor of 2.007 and Fe^{3+} (g=2.046) and lines with g-factor equal to 1.925 at 77K (see Fig.4b) in the dark. The EPR spectra measured at 77K, when magnetic field coincide with the direction of the fundamental symmetry axis H||Z confirms lines structure Mn^{2+} with the intense line with g=2.001. That line is caused by an F-center.

With the illumination of the light corresponding to the fundamental absorption region, the F-center line increases, which can be related to the capture of the electron from neutral selenium vacancy or other impurities or complexes on the double charged vacancy V_{Se}^{2+} destructed by the light. Optical and X-ray excitation intensifies the Fe^{3+} line. The line with g=1.925 also increases with X-ray excitation and decreases with optical excitation. This center may be related to the acceptor center (V_{Zn} -III; V_{Zn} -VII) [8].

Illumination with light from the impurity absorption region, after excitation with the light from the fundamental region, decreases the intensity of lines related to iron up to the level in the dark. It is supposed that this is a result of the destruction of complexes, which consists of the initial inherited defects of the lattice and impurities.

CONCLUSIONS

The properties of unintentionally doped ZnSe using PC spectra, PC relaxation spectra, photon-capture cross-section spectra, EPR and photo-EPR was studied. The results are summarized as follows:

a two-level model involving recombination S-center and an acceptor A has been developed to obtain the relation between the recombination probability and the instantaneous photocurrent value;

the S-centers ionization energies are 1.06eV and 1.14eV from the bottom of the conduction band and charge life times were determined;

the acceptors position are equal to 2.05, 2.11, 2.16 and 2.21eV from bottom of the conduction band;

the photocurrent and PCCS "flash" nature as well as complicated photo-EPR are associated with the relaxation of S-centers attributed to Fe^{3+} ion;

from EPR measurements, F-centers and impurities with g=1.925 (V_{Zn} -III or V_{Zn} -VII) was detected.

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