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Determination of trap density in CdSe thin films from thermally stimulated conductivity spectra

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The trap density N_t and mobility-lifetime product $\mu\tau$ in CdSe thin films are investigated combining data from thermally stimulated conductivity and photoconductivity measurements. A method of simultaneous fitting of thermally stimulated conductivity spectra is applied and four peaks at 193, 213, 230 and 258 K are resolved in the temperature range 80-270 K. Temperature dependences of the steady-state photoconductivity under excitation with strongly absorbed light (525 and 630 nm) are measured at photon fluxes of $5x10^{13}$ - $5x10^{15}$ $cm^{-2}.s^{-1}$ and temperature dependences of the exponent γ in the intensity dependence of the photoconductivity are obtained. The $\mu\tau$ products and trap densities N_t are calculated for both kinds of light excitation. It is shown that they depend on the wavelength of the exciting light, being 2-3 times larger for excitation with λ=630 nm.

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1. Introduction

Semiconductor thin films with high photosensitivity, such as CdSe and CdS, are suitable for gas sensor applications [1]. Adsorbed gases may change the concentration of electronic defects by introducing donors or acceptors or by surface band-bending through the electrostatic effect of polar molecules [2]. The thermally stimulated conductivity (TSC) technique has been successfully used to study defects in crystalline [3] and amorphous [4,5] semiconductors. In the former case, discrete trap distributions may be observed and the TSC technique enables determination of several trap characteristics, namely, energy depth E, capture cross section S and attempt-to-escape frequency ν. In order to determine the trap density from TSC spectra, one needs the mobility-lifetime product ($\mu\tau$). The $\mu\tau$ values can be obtained from the sample photoconductivity (PC) measured with strongly absorbed excitation, provided the photocurrent is equal to the TSC at peak maximum.

A useful method for determining the density of states in amorphous semiconductors, which have a continuous distribution of localized gap states, has been developed and applied to a-Si:H [6-8]. It is based on a combination of TSC and photoconductivity measurements at various photon fluxes. In this study, a similar approach is applied to determine the trap density in microcrystalline CdSe thin films in which a discrete trap distribution is anticipated. The effect of the excitation wavelength on the trap density obtained is also investigated.

2. Experimental details

CdSe films having a thickness of 280 nm were deposited step-by-step at a rate of 0.5 nm/s by physical vapour deposition (under 2-4 10^{-4} Pa vacuum) on Corning 7059 glass substrates maintained at room temperature. Details of the deposition system and procedure are described in more detail in [9]. The optical band gap of microcrystalline CdSe thin films at 293 K is about 1.75 eV [10].

Contacts of gold (about 1 cm long and spaced 0.15 cm apart), sputtered on top of the layers, were used. Thermally stimulated currents were measured after the samples had been illuminated at 77 K for 5 min with white light from a halogen lamp (50 mW/cm^2) and then kept in the dark for 5 min. During the measurement, samples were heated at a rate of 0.05 K/s. Steady-state photoconductivity (SSPC) measurements were carried out using strongly absorbed monochromatic light from a green (λ = 525 nm) or a red (λ = 630 nm) LED. The photon flux F, incident normally on the layer surface, was varied in the range $5x10^{13}$ - $5x10^{15}$ photons $s^{-1}cm^{-2}$. The TSC and photocurrent were measured by a Keithley 610C electrometer at a bias voltage of 100 V.

3. Results and discussion

A typical TSC spectrum of microcrystalline CdSe thin films and the result of its deconvolution are shown in Fig. 1. Four bands peaked at 193, 213, 230 and 258 K are resolved in the temperature range 80-270 K., using the simultaneous fitting method [11]. In this, assuming slow retrapping [3], each band is generated using equation (1), which describes the TSC of a discrete trap with energy depth E below the conduction band:

$$\sigma_{TSC}(T) \approx A\exp[\theta - B\exp(-\theta)/\theta^2], \qquad (1)$$

where: $\theta=E/kT$, A and B are parameters: $A=e\mu\tau n_0\nu$ (n_0 is the initial density of filled traps) and $B=\nu E/\beta k$ (β and k are the heating rate and Boltzmann's constant, respectively). The fitting procedure is performed by varying the energy E, the temperature of the band maximum T_m and A for each separate band, in order to achieve good coincidence of the complete fitting TSC curve with the experimental one. The constant B for T_m and E, specified in the fitting, is given by the relation [3]: $B=\exp(\theta_m)\theta_m^3/(\theta_m+2)$. When the best fit is achieved, the trap parameters S, ν and n_0 are determined from the following relations: (i) $S=B\beta k/N_c v_{th}E$, where $N_c=2(2\pi m^*kT_m/h^2)^{3/2}$ is the effective density of states in the conduction band, m^* is the effective mass of electrons ($m^*_{CdSe}=0.11e$, e - the free electron mass), h is Planck's constant and $v_{th}=(3kT_m/m^*)^{1/2}$ is the thermal velocity of electrons in the conduction band; (ii) $\nu=N_cSv_{th}$ and (iii) $n_0=A/\mu\tau ev$. It has been observed that the preliminary illumination of films for 5 min ensures a total filling of the traps and, therefore, we accept that for certain trapping states n_{to} is equal to the trap density N_t.

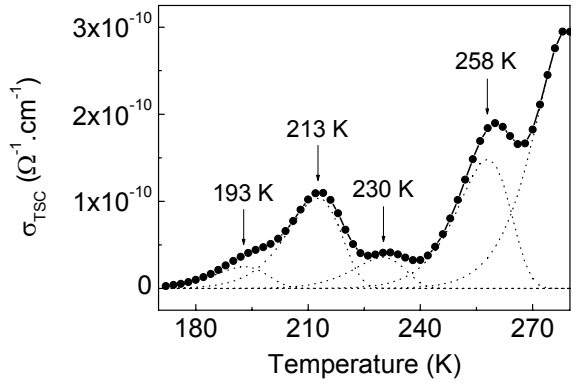

Fig. 1. Experimental TSC spectrum of CdSe thin film (–•–) and TSC bands (–), obtained from a fitting procedure.

As mentioned above, the $\mu\tau$ product is necessary to determine N_t and normally it is obtained from the SSPC relation $\sigma_p=e\mu\tau G$, in which

$$G=\eta F(1-R)[1-\exp(-\alpha d)]/d \qquad (2)$$

is the photocarrier generation rate (d - sample thickness, η - quantum efficiency, F - incident photon flux, R - reflectivity, α - absorption coefficient). Since $\mu\tau$ depends not only on the temperature but also on the position of the quasi-Fermi level, it is necessary that the condition $\sigma_p(T)=\sigma_{TSC}(T)$ is fulfilled [6]. This can be achieved by appropriate adjustment of G at any T. The mobility-lifetime product $(\mu\tau)_{TSC}$, related to σ_{TSC} can be determined using the equation [7]:

$$(\mu\tau)_{TSC}=\left(\frac{\sigma_{TSC}}{\sigma_p}\right)^{(\gamma-1)/\gamma}(\mu\tau)_p, \qquad (3)$$

where $(\mu\tau)_p$ is the mobility-lifetime product, corresponding to σ_p which is produced by a photon flux F and taking into account that $\sigma_p\sim F^{\gamma}$.

In order to obtain $(\mu\tau)_{TSC}$ for the traps resolved in the TSC spectrum, $(\mu\tau)_p$ and the exponent γ have to be determined. Fig. 2 shows the temperature dependences of the SSPC under excitation with $\lambda_{exc}=630$ nm (1.96 eV) at various F. The spectra obtained are typical for chalcogenide materials [12] and consist of three parts: (i) a low temperature part in which σ_p is nearly constant and proportional to G; (ii) a middle part in which $\sigma_p\sim(G)^{1/2}$ rises with T by several orders of magnitude and (iii) a high temperature part where the concentration of thermally generated carriers exceeds that of photocarriers, and $\sigma_p\sim G$ decreases with increasing T. It is seen from Fig. 2 that thermal quenching of σ_p starts at the points where $\sigma_p=\sigma_d$. The temperature dependences of SSPC under excitation with $\lambda_{exc}=525$ nm (2.36 eV) were also measured at the same series of photon fluxes. Similar spectra were observed, but the σ_p values obtained are about three times larger than that measured when exciting with $\lambda_{exc}=630$ nm. Based on Eq. (2) and taking into account that $R_{525\,nm}\approx R_{630\,nm}$, one can assume that the observed difference is due to a difference in the quantum efficiency η at the two λ_{exc}. This can be anticipated keeping in mind that in some chalcogenide materials (amorphous Se, As_2S_3) η strongly depends on the energy of the exciting light and rises up to $\eta=1$ at photon energies significantly greater than their optical band gap E_g [12].

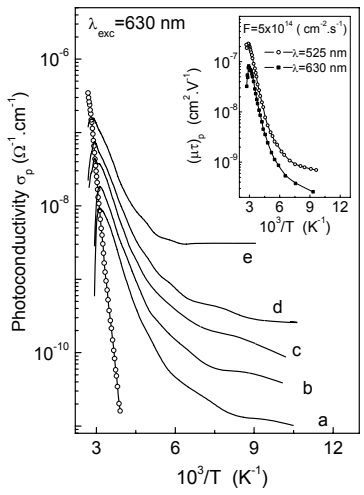

Fig. 2. Dark-(symbols) and photoconductivity (solid lines) spectra measured with $\lambda_{exc}=630$ nm and photon fluxes F: (a)- $5x10^{13}$; (b)- $1x10^{14}$; (c)- $5x10^{14}$; (d)- $1x10^{15}$ and (e) - $5x10^{15}$ s^{-1} cm^{-2}. Inset: $\mu\tau$ product vs $10^3/T$ calculated for excitations with $\lambda=525$ nm and $\lambda=630$ nm; $F=5x10^{14}$ s^{-1} cm^{-2}.

Normally, $(\mu\tau)_p$ is determined by exciting with only *one* wavelength having energy $E>E_g$ and η=1 is assumed. In order to estimate the error introduced by this approximation in the trap density obtained, we have calculated $(\mu\tau)_p$ for the two excitation wavelengths assuming η=1. Using the relation:

$$(\mu\tau)_p=\sigma_p d/e\eta F(1-R)[1-\exp(-\alpha d)] \quad (4)$$

where α=2x10^4 cm^{-1}, $R_{525\,nm}$=0.175 and $R_{630\,nm}$=0.208 [9], the temperature dependences of $(\mu\tau)_p$ have been obtained for λ_{exc} = 525 nm and 630 nm and a photon flux of 5x10^{14} s^{-1} cm^{-2} (see the inset in Fig. 2).

Fig. 3 depicts the temperature dependences of the exponent γ obtained for excitation with 525 nm

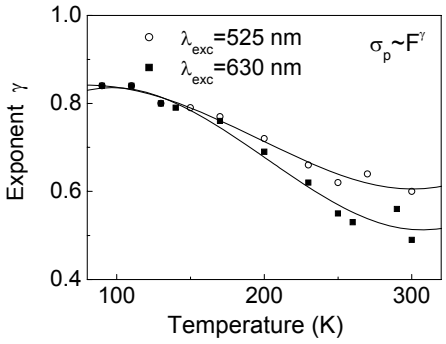

Fig.3 Temperature dependences of the exponent γ in a CdSe thin film determined for λ_{exc} = 525 nm and λ_{exc} = 630 nm; the lines represent the best polynomial fits.

and 630 nm. A value γ =0.84 has been obtained at low temperatures for both λ_{exc}, while at room temperature γ decreases to 0.6 and 0.51 for λ_{exc} = 525 nm and λ_{exc} = 630 nm, respectively. These results are similar to those reported in [13] for a CdSe film of thickness 50 nm.

The mobility-lifetime product $(\mu\tau)_{TSC}$ for all TSC peaks resolved were calculated applying Eq. 3 and using the values of $\sigma_{TSC,}$ σ_p and γ (from the polynomial fit) at the corresponding T_m. The calculations were performed for both $(\mu\tau)_p$ values corresponding to the two λ_{exc} as well as for all different photon fluxes applied. Trap densities N_t were obtained from the relation $N_t=A/(\mu\tau)_{TSC}ev$; the A and v values were obtained in the TSC fitting procedure.

Fig. 4 shows the intensity dependences of the density of traps related to the TSC peak at 193 K. One can see that at the lowest intensity N_t determined for λ_{exc}=630 nm is about two times greater than that for λ_{exc} =525 nm. The observed difference can be connected with the assumption of equal quantum efficiencies η_{525} = η_{630} = 1 which results in incorrect values of $(\mu\tau)_p$. This result implies that such an assumption can cause an error of up to 100% in the N_t values determined from combined TSC and SSPC measurements.

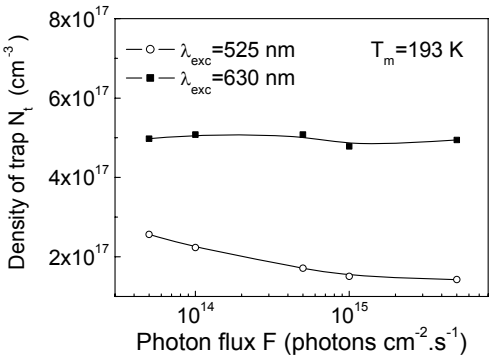

Fig. 4 Intensity dependence of the trap density, related to the TSC band centered at 193 K, obtained for two exciting wavelengths λ_{exc} = 525 nm and λ_{exc} = 630 nm.

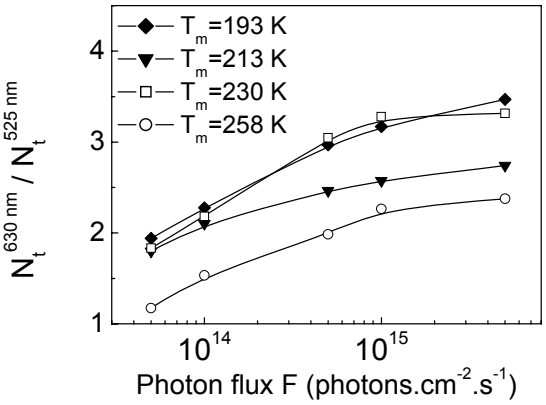

Fig. 5 Intensity dependences of the ratio of the trap densities determined for λ_{exc}=525 nm and λ_{exc}=630 nm.

The intensity dependences of the ratio N_t^{630}/N_t^{525} (which gives an idea about the error in trap density obtained when exciting with different wavelengths) for the four TSC bands resolved are shown in Fig. 5. As expected (Eq. (3)), for all traps this ratio is minimal at the lowest F, where σ_P is close to σ_{TSC}. The observed upward shift in the curve with decreasing T_m can be related to the difference in the temperature dependences of γ (Fig. 3).

It is seen from Fig 4 that N_t does not change significantly when red illumination is used, but for the green one N_t decreases by approximately a factor of two with increasing F. This observation leads to the N_t^{630}/N_t^{525} increase seen in Fig. 5. The N_t^{525} decrease (Fig. 4) can be understood, taking into account that the two multipliers on the right-hand side of Eq. (3) change in different ways with light intensity. The reason for the N_t^{630} constancy is not clear yet. Consideration of Eq. (4) shows that it could be assigned to intensity induced changes in η.

4. Conclusions

The trap density N_t and mobility-lifetime product $\mu\tau$ in CdSe thin films was investigated using data from both thermally stimulated conductivity and photo conductivity measurements carried out under excitation with two strongly absorbed light wavelengths (525 and 630 nm) and photon fluxes between $5x10^{13}$ and $5x10^{15}$ $cm^{-2}.s^{-1}$. Four peaks at 193, 213, 230 and 258 K have been resolved in the temperature range 80-270 K. It has been shown that the trap densities N_t obtained depend on the wavelength of the exciting light; the N_t values are 2-3 times greater when using $\lambda_{exc} = 630$ nm. For all traps, the N_t^{630}/N_t^{525} ratio reaches a minimum at the lowest F, where σ_P is very close to σ_{TSC}.

Acknowledgements

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