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Physica B 337 (2003) 369–374
PHYSICA B
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Photoluminescence studies of heavily doped $CuInTe_2$ crystals

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Received 7 May 2003; received in revised form 2 June 2003; accepted 22 June 2003

Abstract

The photoluminescence spectra of heavily doped $CuInTe_2$ and their dependence on the temperature and excitation power were measured. At 10 K an asymmetric broad peak at 0.98 eV was observed. The PL peak position did not depend on the excitation power, but had a characteristic dependence on the sample temperature. Our computer simulations proved that this behaviour is in good compliance with the Shklovskij/Efros model of heavily doped semiconductors with spatially varying potential fluctuations. Therefore, the PL band was attributed to the band-to-impurity type recombination and the corresponding level to the single acceptor at 70 meV, which is most probably caused by copper vacancy.

PACS: 78.55.Hx; 71.55.Ht; 61.72.Ji

Keywords: Photoluminescence; Chalcopyrite ternary crystals; $CuInTe_2$; Point defects

1. Introduction

$CuInTe_2$ (CIT) is a direct band gap chalcopyrite ternary semiconductor that has the energy gap in the vicinity of 1 eV, being very close to the optimum for solar energy conversion. This makes CIT attractive for solar cell applications.

Photoluminescence (PL) is a very effective and a relatively easy-to-use tool for studying the defect structure of semiconductors. The advantage is its high sensitivity to small changes in the compound structure. Nevertheless, it is not the ultimate tool because some defect states that do not give radiative recombination remain undetected. Moreover, a broad and indistinct experimental spectrum can sometimes be very tedious to interpret. Yet, using an adequate theoretical model, many characteristic phenomena of PL spectra can be explained.

PL measurements have been conducted on CIT by Rincón et al. [1,2]. They report the excitonic and edge emission that refer to relatively regular crystals.

This paper describes the experimental PL spectra of heavily doped $CuInTe_2$ crystals. By heavily doped we mean crystals that have a large concentration of intrinsic defects rather then a high concentration of impurity atoms. In fact, CIT

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doi:10.1016/S0921-4526(03)00429-0

is a compound that tends to have a large concentration of native defects.

Our experimental results are interpreted using the theory of heavily doped semiconductors developed by Shklovskij, Efros, Levanyuk and Osipov in the early 1970s. A detailed theoretical idea is given in Refs. [3–5]. A similar interpretation has been published on heavily doped $CuIn_{1-x}Ga_xSe_2$ in Refs. [6,7], which report band-to-band recombination and in Ref. [8], which observes band-to-impurity emission in this material. To our knowledge, this theory has not been applied to CIT yet.

2. Theory

The main concept in the theory of the PL of heavily doped semiconductors is the spatial potential fluctuation. According to the definition, in heavily doped semiconductors the main distance between defects is smaller than the Bohr radius of the defect state

$$1/N < r_b^3, \tag{1}$$

where N is defect concentration.

The wave functions of closely situated defects tend to overlap, giving rise to energy zones instead of distinct defect levels. In turn, those zones can reach the edges of the energy gap and evoke the so-called "energy tails". If Eq. (1) is satisfied, the kinetic energy of the electron that is localised in the range $r \approx N^{1/3}$ exceeds the Coulomb potential that binds it with a donor. Thus, it is theoretically impossible to observe excitons or the excitonic PL in heavily doped semiconductors. Nevertheless, the complex structure of fluctuating band edges initiates various radiative recombination processes that cannot be observed in moderately or weakly doped semiconductors. Due to potential fluctuations, the energy level from which holes can be considered as free (E_v) is lower than in the undisturbed case (E_{v0}). γ_h marks the difference (see Fig. 1). Here, we mind that the energy of the holes increases towards the bottom of Fig. 1 and the energy of the electrons increases in the opposite direction. From the energy level $E_{v0} - \gamma_h$ and below holes occupy localised acceptor states. Due to their small effective mass in heavily doped CIT ($m_e^* \approx 0.16\, m_e$ [1]), almost all electrons are free. Thus, the radiative recombination can arise from three different channels (see Fig. 1). Firstly, it can comprise a free electron and a hole that is localised in the valence band tail (BT-band). Secondly, it can involve a free electron and a free hole (BB-band). Thirdly, it can occur through the acceptor state (BI-band) that is deep enough not to overlap with the valence band tail.

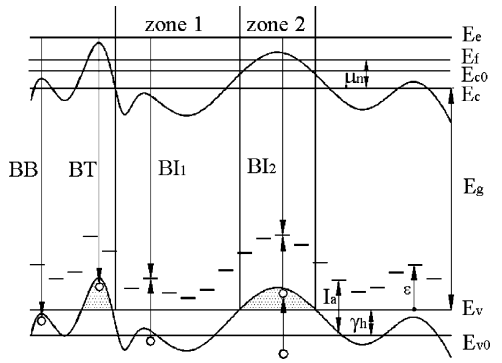

Fig. 1. Zone diagram of heavily doped semiconductors according to the theory of potential fluctuation. Holes that recombine through zone 1 are free, and holes through zone 2 are localised. Because of potential fluctuations the ideal edges of band gap approach ($E_{c0} \to E_c$, and $E_{v0} \to E_v$). Accordingly, the energy gap of heavily doped semiconductors is somewhat smaller than it would be in the case of a perfect crystal. The acceptor level I_a is "smeared" in the energy scale, therefore, we cannot talk about single acceptor level but about the distribution of acceptor states. BI, BB and BT denote band-to-impurity, band-to-band and band-to-tail recombination, respectively.

Here, we describe in detail the latter process, because we have a strong reason to believe that our spectra are dominated by the BI-band. We justify it in the results and discussion section.

The BI-band can be observed if $\gamma < I_a$, where γ is the mean-square fluctuation of the potential energy of a hole and I_a is the ionisation energy of the acceptor state (Fig. 1). The theoretical PL spectrum of this band is defined by the following expression [3]:

$$I(h\nu) = h\nu \iint W(E_e, E_h)\rho_c(E_e)f_e(E_e) \times \rho_a(E_h)q_a(E_h)\delta(E_e - E_h - h\nu)\, dE_e\, dE_h, \tag{2}$$

where $W(E_e, E_h)$ is the recombination probability of a free electron and a localised hole with energies E_e and E_h, respectively, ρ_c is the electron density of states in the conduction band, f_e is the Fermi function, ρ_a is the hole density of states, and q_a is the filling probability of the hole states. As compared to other quantities, W depends very weakly on the electron and hole energies [3,5], thus it will be treated as a constant.

According to the hole capture kinetics, two recombination neighbourhoods can be distinguished. They generate two types of transitions (BI_1 and BI_2), respectively. The first involves the holes whose energy level is above $E_v = E_{v0} - \gamma_h$, from which they can be considered as free. The filling probability of the impurity states in this zone is as follows [3]:

$$q_a^{BI_1} = \frac{N_0}{N_a} = \frac{p(\varepsilon)}{p(\varepsilon) + \Theta n + N_V \exp(-I_a/kT)} = \frac{p}{p + \Theta n \exp[(I_a - \varepsilon)/kT] + N_V \exp(-\varepsilon/kT)}, \quad (3)$$

where N_0 is the concentration of neutral acceptors, N_a is the total concentration of acceptors, $p(\varepsilon) = p\exp[(\varepsilon - I_a)/kT]$ is the Bolzmann distribution of free holes, p is the initial hole concentration, ε is the independent energy variable that has the origin at E_v, $\Theta = W_n/W_p$ is the ratio of electron and hole capture probabilities, n is electron concentration, and N_v is the effective number of valence band states.

The capture of the hole by the impurity state in the second zone is a cascade process in which a free hole is localised on the energy tail and then captured by a neutral acceptor. The capture probability in this process is [3]

$$q_a^{BI_2} = \frac{p}{p + \Theta n + N_V \exp(-\varepsilon/kT)}. \quad (4)$$

Ref. [9] states that in the case of heavily doped semiconductors, the hole density of states has its maximum at the acceptor's activation energy and has a Gaussian shape: $\rho_a(E_h) = (N_a/\sqrt{2\pi\gamma})\exp[-(E_h - E_v^0 - I_a)/2\gamma^2]$. According to the free electron model, the electron density of states is $\rho_c(E_e) = (1/2\pi^2)(2m_e^*/\hbar)^{3/2}\sqrt{E_e - E_c}$, where E_c is the energy from which electrons can be considered as free.

Taking into account that the BI-band is the sum of BI_1- and BI_2-band we substitute all distribution functions into Eq. (2) and obtain an expression for the theoretical PL spectrum of the BI-band that can be used for numerical simulations:

$$I(h\nu) \propto h\nu \int_{Eg-h\nu}^{+\infty} \frac{\sqrt{h\nu - E_g + \varepsilon}\exp\left(-\dfrac{(\gamma_h - I_a + \varepsilon)^2}{2\gamma^2}\right)}{\left(1 + \exp\left(\dfrac{h\nu - \mu_n - E_g + \varepsilon}{kT}\right)\right)\left(p + \Theta n\eta(\varepsilon) + N_V \exp(-\varepsilon/kT)\right)} d\varepsilon, \quad (5)$$

where

$$\eta(\varepsilon) = \begin{cases} 1 & \text{if } \varepsilon > I_a, \\ \exp((I_a - \varepsilon)/kT) & \text{if } \varepsilon < I_a \end{cases}$$

and $\mu_n = E_f - E_c$ is the difference between the Fermi level and E_c.

3. Experimental details

Single crystals of CIT have been grown by the vertical Bridgman technique, which is also used to fabricate $CuInSe_2$ and other chalcopyrite ternary compounds. The pseudobinary phase diagram of CIT was first reported by Palatnik and Rogacheva [10]. A close to stoichiometrical mixture of high (99.999%) purity Cu, In and Te was sealed in vacuum in a thick wall quartz ampoule of 20 mm internal diameter. The mixture was prereacted at about 1000°C for 2 h in a rocking furnace and solidified in the horizontal position. Then the ampoule was introduced into the upper (hot) zone of a two-zone vertical furnace. In this position, the prereacted material was melted again and held at 1000°C for 6 h. Then the temperature of the higher zone was reduced to 850°C, which is above the melting point $T_m =$ 789°C [10]. The lower zone temperature was held

at 750°C. For solidification, the furnace was slowly moved up, translating the ampoule into the lower zone at a speed of 2 cm a day. After solidification the ampoule was slowly cooled at two rates: 1°C/h from 750°C to 600°C and 5°C/h from 600°C to 20°C.

X-ray fluorescence (EDX) measurements coupled with X-ray diffraction analysis on the grown ingot indicated the presence of the single CIT chalcopyrite phase. The samples prepared were measured by the hot-point probe, revealing p-type conductivity. Several samples were analysed using the 2 MeV He^+ Rutherford Backscattering Spectrometry in the Channeling mode (RBS/C) [11]. The normalised minimum-yield $\chi_{min} = Y_a/Y_r$ (where Y_a and Y_r are aligned and random yields of backscattered He^+) along the $\langle 2\,2\,1 \rangle$ axis was about 6% and quite uniform across the surface. This can be taken as an evidence of good and uniform structural quality of the lattice. The RBS/C probes across the surface revealed that the samples are single crystals with homogeneous structural quality.

The sample was cooled inside the closed-cycle He cryostat ($T = 10-300$ K) and excited with 441 nm He–Cd laser, which has the maximum output power of 40 mW. The PL signal was recorded from a freshly cleaved surface, using a standard lock-in technique, computer-controlled SPM-2 grating monochromator ($f = 40$ cm) and an InGaAs detector. The signal detected was corrected in conformity with the grating efficiency and detector sensitivity spectra. The PL spectra dependencies on the variations of the temperature and excitation power were recorded.

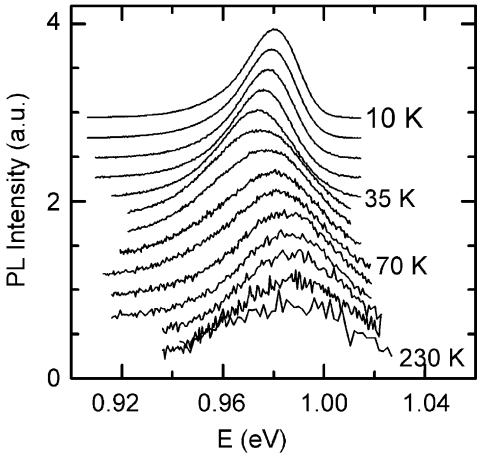

Fig. 2. Normalised PL spectra of $CuInTe_2$ sample measured at different temperatures.

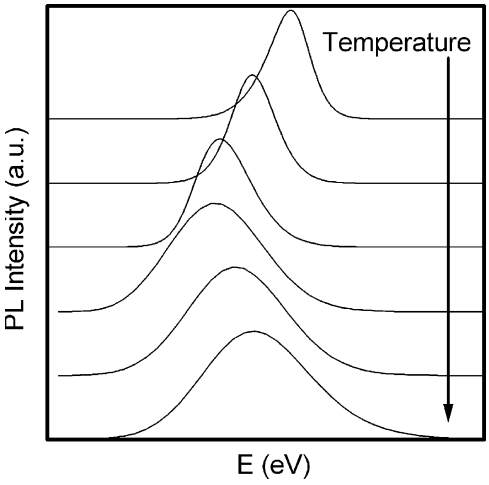

Fig. 3. Calculated PL spectra at various temperatures using Eq. (5). Compared to experimental results (Fig. 2), the simulated spectra have the same kind of asymmetric shape. Also, it features a characteristic shift along the energy scale and broadening as it was observed in our experiments.

4. Results and discussion

A typical shape of the PL spectrum in heavily doped CIT is asymmetric. It has an exponential slope on the low-energy side and a steeper Gaussian incline on the high-energy side (Fig. 2). At low temperature (10 K), its maximum is located at 0.98 eV.

The temperature dependence of the band possesses an interesting quality (Figs. 2 and 4). At low temperatures, the peak position energy of the spectrum decreases with increasing temperature, at some temperature T^*, the PL peak shifts towards higher energy again until it reaches a saturation level. The measured PL spectra were fitted and compared with computer simulations, which proved that Eq. (5) indicates the same behaviour (Figs. 3 and 5). The depth of the vale and its position depend on the carriers'

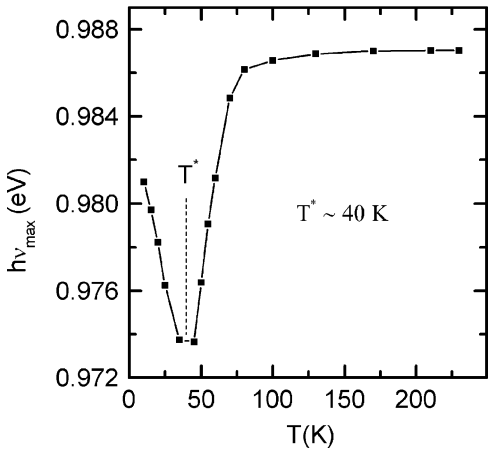

Fig. 4. The shift of $CuInTe_2$ PL peak position versus temperature.

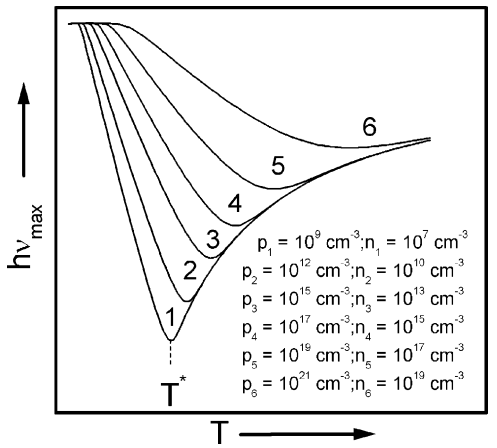

Fig. 5. The dependence of the BI-band peak position on temperature, resulting from computer simulations of Eq. (5). Larger curve numbers correspond to higher carrier densities. The position of T^* is also very sensitive to parameter γ, which characterises the amplitude of potential fluctuations. If the carrier concentrations are fixed, T^* shifts towards higher temperatures with a higher value of γ. This is coherent with the theory, because in the case of deeper energy tails the holes become more difficult to thermalise.

concentrations, i.e. on the excitation power. Smaller carrier concentrations correspond to steeper inclines.

Such a behaviour of $h\nu_{max}$ can be explained as follows: the transition BI_2 has a maximum probability at temperature T^* after which the thermal activation process starts to dominate and thermalise localised holes into zone 1 (see Fig. 1). Accordingly, the PL band maximum shifts towards higher energies. The saturation takes place when all localised holes become thermalised. The BI_2 radiation vanishes and all the recombination goes through BI_1.

A comparison of Figs. 2 and 3 shows that the dependence of the measured PL spectra on the sample temperature is in good conformity with Eq. (5). They both indicate the same type of shift and change in the half-width of the spectra, which widens with the increasing temperature.

The theory of heavily doped semiconductors [3] and our simulations prove that at low temperatures the BI-band's maximum is located at $h\nu_{max} = E_g - I_a$. Whereas the energy gap at 10 K in CIT is in the range $E_g = 1.06-1.02$ eV [12] and the maximum of our spectrum at 10 K is approximately 0.98 eV, I_a must lie between 40 and 80 meV. According to [13], where the defect levels were calculated theoretically, it can be attributed to the singe acceptor level $I_a = 70$ meV, whose possible origins are copper vacancy V_{Cu} or antisite point defects Te_{In} and Cu_{Te}. Though, it is believed that the former has much higher formation probability, the antisite defects must not be totally disregarded.

To endorse the idea of recombination through the acceptor level, the PL band with a similar activation energy appeared also in not so highly defective CIT crystal [14], where the phonon structure of the PL spectra was detected.

The acceptor's activation energy I_a could not be calculated from the traditional Arrhenius plot because in the case of potential fluctuations, the relation Ln(I) versus $1000/T$ generates no straight line at high temperatures. Indeed, because of potential fluctuations we do not have a single acceptor level but the distribution of the acceptor states around I_a.

The shape of the measured PL spectra remained unchanged in regard to various excitation powers (Fig. 6). Also, no shifts along the energy scale were observed. It means that the shape of the BI-band does not depend on the carrier densities. This implies that the filling probability of the acceptor states is close to uniformity. Again, our computer

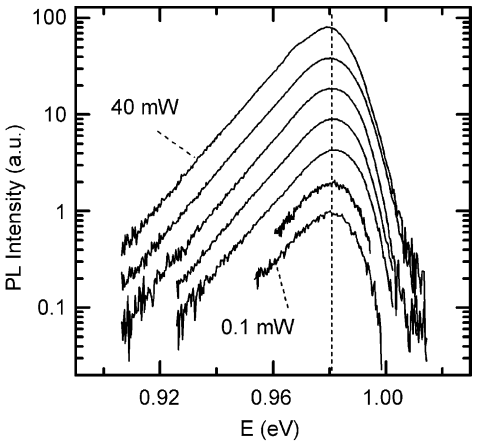

Fig. 6. Normalised PL spectra of $CuInTe_2$ sample measured at different laser excitation power.

simulations of Eq. (5) confirmed that the PL spectra do not depend on the excitation power.

The PL spectra of heavily doped semiconductors are distinctive because of their characteristic asymmetric shape. This distinguishes them from other recombination models. However, the shape of the BT-band is similar to the shape of the BI-band. Thus, it should be carefully considered before attributing the emission to one or the other. Whilst working with other CIT samples, we have seen both bands on the same spectra [15]. The BI-band appeared exactly in the same position (0.98 eV) and the BT-band had its maximum at about 1.01–1.02 eV.

5. Conclusion

The spectrum of the BI recombination in heavily doped semiconductors has a characteristic asymmetric shape. Also, it features a unique behaviour with regard to excitation powers and temperature variations. Our experimental results are in good agreement with the theory of heavily doped semiconductors. Thus, based on the features of the theory, we suggest that the broad band in our spectra was generated by the BI recombination. We attribute the recombination to free electrons with holes that are localised on the acceptor level at 70 meV that is most probably caused by the copper vacancy.

Acknowledgements

This work was supported by the Estonian Science Foundation, Grant No. 5149.

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