TECHNICAL NOTE

DEEP-LEVEL PHOTOLUMINESCENCE OF DOPED CdTe IN THE 0.8 eV REGION

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Abstract—Photoluminescence studies of CdTe:Cu:Cl in the 0.8 eV region were carried out with respect to the influence of partial vapor pressure of Cd or Te. Two PL bands were detected with peak energies 0.72 eV and 0.81 eV. The intensity of both bands abruptly diminishes at high partial pressures of Cd and Te. According to the proposed model these bands are due to close DA pairs and one of them may be related to a portion of the hexagonal phase in the cubic lattice of CdTe.

Keywords: CdTe, photoluminescence, component vapor pressure, DA pairs.

CdTe is a II–VI semiconductor of particular interest, since it can be obtained either with *n*- or *p*-type conductivity. Although numerous studies on photoluminescence (PL) properties of CdTe crystals have been done, there is very little information known about the deep levels related PL in this material. At the same time, the deep levels are responsible for most electrical and optical properties. There are three groups of deep PL-bands generally found in CdTe and located at 0.5 eV, 0.8 eV and 1.0 eV, respectively, each group containing at least two bands [1–3]. Proposed recombination models and also the chemical nature of the corresponding PL-centers are often in conflict with experimental results. Recently some studies on CdS have been done about the influence of chemical preparation conditions on PL properties [4–5]. These studies proved to be very perceptive in understanding both the chemical and physical nature of recombination centers. So in the present paper we use the same method with respect to CdTe and report the behavior of some deep PL bands in CdTe:Cu:Cl, annealed under different partial pressures of Cd or Te. These bands under study belong to the 0.8 eV group of deep PL bands. According to one of the models proposed for these bands, they are due to a radiative transition between bound states [2, 6], while the second model connects these bands with the radiative capture of a free electron by a deep acceptor level [7, 8]. There seems to be no firmly established opinion concerning the mechanism of the 0.8 eV PL bands. Besides, usually only one band was detected in the 0.8 eV region. This is why a further investigation of these PL bands will be useful.

CdTe powder doped with copper ($N_{Cu} = 10^{17}$ cm^{-3}) and chlorine ($N_{Cl} = 2 \times 10^{17}$ cm^{-3}) was used. Annealing was carried out in a sealed two-zone quartz ampoules at 800°C during 1 h. The first temperature zone was used for CdTe:Cu:Cl powder, the second one for producing the component partial pressure by placing there a piece of Cd or Te. The partial pressure of Cd and Te was determined by the temperature of the component zone [9]. Different ampoules with the same CdTe:Cu:Cl powder were used for each value of the partial vapor pressures, yielding 25 different samples. After high-temperature firing treatment the samples were quenched to room temperature, the ampoules opened and the powder put in the quartz tube for PL measurements.

The PL of CdTe:Cu:Cl was excited with $\lambda < 600$ nm from a 250 W high-pressure mercury lamp. All the PL measurements were performed at 77 K. The PL signal was collected into the inlet slit of a SPM-2 monochromator with a spectral slit width of 0.04 eV in the 0.8 eV region and detected by a Ge detector. PL spectra were measured by a conventional lock-in technique. Computer analysis of the measured spectra was carried out by the method of damped least squares to determine the parameters of each PL-band.

Figure 1 shows a typical PL spectrum of CdTe:Cu:Cl in a "deep" region at 77 K. The results of computer analysis are also presented. The PL spectra in Fig. 1 exhibit four emission peaks at 0.72 eV (1.72 μm), 0.81 eV (1.53 μm), 0.96 eV (1.29 μm) and 1.1 eV (1.13 μm). In addition, a well-known 1.38 eV (0.90 μm) band was also present in all samples. As can be seen in Fig. 1, the emission in the 0.8 eV region contains two Gaussian PL bands with a half width of about 0.1 eV. The energy difference between these bands is 0.09 eV. The peak positions and half widths of both bands did not change with the partial vapor pressure of the components. Figure 2 shows the dependence of integral intensities of the 0.72 eV and 0.81 eV bands upon the partial vapor pressure of the components. For comparison, the same dependence for the 1.38 eV band is presented. As can be seen from Fig. 2, the whole range of obtainable component vapor pressures may be divided into four regions. Two of them lie on the Te-side (I, II) and two on the Cd-side (III, IV) of component pressures. The integral intensity of the 0.72 eV and 0.81 eV PL-bands abruptly diminishes in regions I and IV, i.e. at high partial pressures of both Cd and Te. At the same time the integral intensity of the 1.38 eV PL-band does not show any significant changes in these regions (see Fig. 2). This is why the possible role of nonradiative recombination centres in quenching the 0.72 eV and 0.81 eV PL-bands must be excluded. If we suppose that the quenching is due to a decrease of the recombination stream through the PL-centers, then it may be caused by a decrease of the concentration of PL-centers or by a decrease of the recombination cross-section of these centres. The quasichemical theory allows us to calculate the dependence of the concentration of each defect upon the partial vapor pressure of the components [9]. These calculations have shown that the steep decrease of any defect concentration is not possible at the same time on both the Cd and Te sides. Then at least one of these intensity transitions must be connected with a decrease of the recombination cross-section of the PL-centres. It is known that the change in the partial vapor pressure of the components causes a transformation of Fermi level position. At high
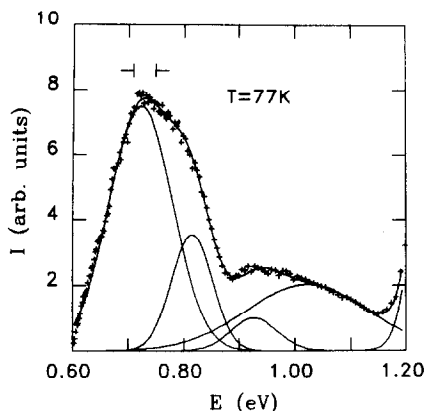
Fig. 1. Photoluminescence spectrum of CdTe:Cu:Cl (pluses) and the results of computer analysis (curves).

Fig. 3. The recombination model for 0.8 eV bands in CdTe.

pressures of Te (I region) the Fermi level would be expected to be close to the valence band while at high Cd pressures (IV region) it shifts near the bottom of the conduction band. It is obvious that such a transformation of the Fermi level position in turn causes recharging of the defects and thus affects the creation of complexes between donors and acceptors at high temperatures. If we suppose that the observed 0.72 eV and 0.81 eV PL bands may be connected with these complexes, then in region I the high temperature Fermi level must be lower than an isolated acceptor level causing a neutralization of the acceptor and as a result a decrease of the coulombic interaction energy between donor and acceptor. The same situation is valid in region IV, where neutralization of donor defects occurs (see Fig. 3). Therefore, the random distribution between donors and acceptors can be expected in regions I and IV whereas in regions II and III the strong pairing is in force. According to [8] there were no j-shifts detected for the 0.8 eV PL bands in CdTe and thus only closest DA pairs may be involved in recombination. Moreover, because of the high treatment temperature ($T = 800°C$) the probability of pair formation with $r > 7$ Å is negligible since the thermal energy exceeds the coulombic interaction energy. In the case of close DA pairs the donors and acceptors must have quite a deep energy level to show a bound to bound transition, as it was found in [2, 6].
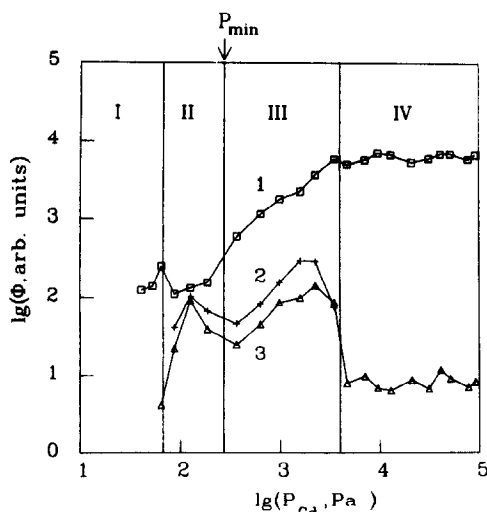
As can be seen in Fig. 2, the behavior of the 0.72 eV and 0.81 eV PL bands is similar. Therefore we suppose that these PL centers have the same chemical nature but a different physical structure. Because of DA complexes, the possible reason for this is the different distance between components. However, our calculations of possible energies of DA pairs in cubic lattice of CdTe did not show any coincidence with the experimentally detected value of 0.09 eV. This is why we assume a portion of the hexagonal phase to be involved in the formation of DA pairs. It is known that the pure hexagonal lattice cannot be achieved in CdTe crystals but a portion of it may be presented [10]. Then at higher treatment temperatures the role of hexagonality would be also higher. We annealed some of the samples at 900°C and the intensity of the 0.81 eV PL band increased compared to the 0.72 eV PL band. It is also known that a great number of PL bands found in ZnS is usually connected with different phases [11]. Further work of course is needed to clarify the chemical nature of these PL centres and to support the proposed model.

Fig. 2. The dependence of integral intensity of PL bands Φ upon component vapor pressure: 1-1.38 eV band; 2-0.72 eV band; 3-0.81 eV band.
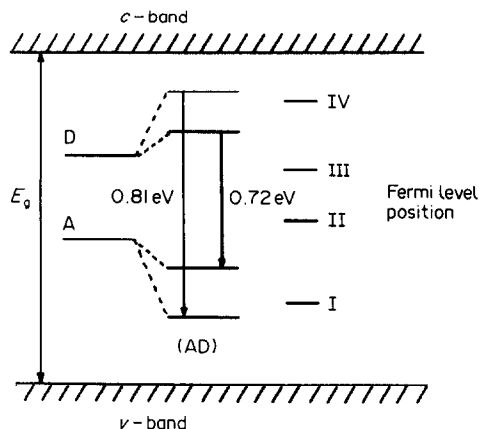
REFERENCES

1. Halstead R. E., Aven M. and Coghill H. D., *J. Electrochem. Soc.* **112**, 177 (1965).
2. Bryant F. J. and Webster E., *Br. J. Appl. Phys. (J. Phys. D.)* **1**, 965 (1968).
3. Panossian J. R., *Trudy Inst. Fiz. Akad. Nauk SSSR* **68**, 147 (1973).
4. Krustok J., Mädasson J., Altosaar M. and Kukk P., *J. Phys. Chem. Solids* **51**, 1013 (1990).
5. Krustok J. and Kukk P., *Mat. Sci.* **15**, 3 (1989).
6. Ermolovich I. B., Sheinkman M. K., Sanitarov V. A., Kalinkin I. P. and Aleksandrova L. A., *Fiz. Tekh. Poluprov.* **17**, 1454 (1983).
7. Kosjachenko L. A. and Mahnij V. P., *Ukr. Fiz. Zh.* **31**, 253 (1986).
8. Han H.-X., Feldman B. J., Wroge M. L., Leopold D. J. and Ballingall J. M., *J. appl. Phys.* **61**, 2670 (1987).
9. Kröger F. A., *The Chemistry of Imperfect Crystals*. North-Holland, Amsterdam (1964).
10. Aven M. and Prener J. S. (Eds), *Physics and Chemistry of II–VI Compounds*. North-Holland, Amsterdam (1967).
11. Krustok J. and Mädasson J., *Trans. Tallinn Tech. Univ.* **587**, 11 (1984).