Photoluminescence from deep acceptor–deep donor complexes in CdTe

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Abstract

The deep donor–deep acceptor defect model is proposed for the 0.7 and 1.1 eV PL bands in CdTe. It is shown that the interstitial defects with different symmetry are involved in these DA pairs.

Keywords: Luminescence; Deep DA pairs; Semiconductors; CdTe

The donor–acceptor pair (DAP) luminescence in compound semiconductors is usually related to relatively shallow donor and acceptor levels. Although there is a wealth of experimental and theoretical studies of shallow DA pairs, the deep DA pairs have been studied much less.

In order to study these questions experimentally, CdTe appears to be one of the most promising candidate with its relatively large band gap of 1.6 eV. Both deep donor and acceptor defects with $E_{D,A} > 0.5$ eV have been found to be present in CdTe. In the present paper we propose a model of deep donor–deep acceptor complexes for the 0.7 eV and the 1.1 eV PL bands.

We prepared two series of CdTe samples. For the first series (series A) CdTe:Cu:Cl powder was used. After the high-temperature firing treatment, samples were quenched to room temperature. For the second series of samples (series B) CdTe:Cl powder was used. A thermal treatment under Te vapour pressure followed by slow cooling was undertaken. A detailed description of the sample preparation and the PL measurement is given in Ref. [2].

Fig. 1 shows the PL spectra of two CdTe samples in the deep spectral region. Both spectra have a non-symmetrical shape and are obviously composed of two sub-bands, see Fig. 1.

From Fig. 1 several conclusions can be drawn:

1. For both of the samples, the intensity of the higher-energy sub-band 1 exceeds the intensity of the lower-energy sub-band 2.

2. The separation in energy between peak positions of sub-bands 1 and of sub-band 2 is 0.085 and 0.083 eV for samples A and B, respectively.

3. The half-widths of these sub-bands, i.e. for the 0.7 eV band and for the 1.1 eV band, are quite differently and, in fact, oppositely interrelated.

Important complementary information was obtained from an analysis of the temperature

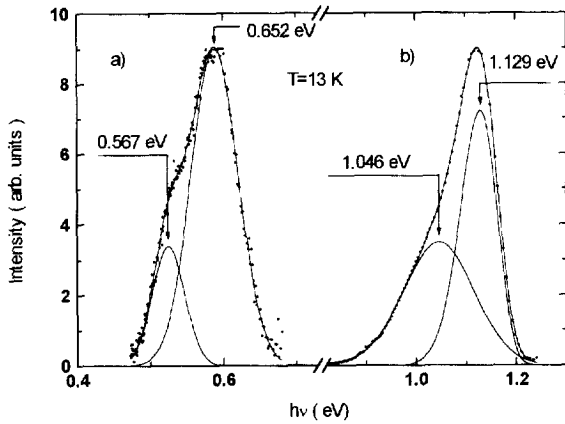* Corresponding author. Fax: +(372) 2474 441; e-mail: jyri@opto.ttu.ee.

Fig. 1. PL spectra of CdTe samples A (a) and B (b) and the fitting results.

Table 1
Calculated approximate energy separation ΔE for different DA pair locations

DA location A D	r_1 (Å)	r_2 (Å)	ΔE (eV)	Interstitial positions types at r_1 and r_2
(a) Cd–Te	2.806	5.373	0.345299	—
(b) Cd–Cd	4.583	6.482	0.12964	—
(c) Cd–i	2.8067	3.241	0.096825	i_2, i_1
(d) i–Te	2.8067	3.241	0.096825	i_1, i_2

dependences of the intensity of these PL bands. The major thermal quenching of these bands starts at a temperature of $T \approx 100$ K with activation energies $E_T = 174 \pm 7$ meV and $E_T = 113 \pm 5$ meV for the 1.046 eV and the 1.129 eV PL bands, respectively. The difference between activation energies $\Delta E_T = 61$ meV is somewhat less than the difference in the peak positions 83 meV, since the 1.046 eV band is wider than the 1.129 eV band (cf. Fig. 1). This is consistent with the idea that these PL bands originate in transitions between localized levels. The temperature dependence of the 0.7 eV PL bands was not measured due to rather weak intensity of this emission, but in Ref. [3] an activation energy $E_T = 440 \pm 20$ meV was obtained for the PL band corresponding to the 0.652 eV PL band in the present paper. We also observe that the peak positions of the 1.046 and 1.129 eV PL bands remain nearly constant over the temperature range $T = 10$–110 K. This is a very direct evidence that the conduction or valence band states are not involved in these recombination processes at low temperatures. For the 0.652 eV emission, involvement of the band states can be detected at temperatures $T > 200$ K [3]. All the aforementioned facts fit nicely the DA-pair model with a deep donor and a deep acceptor.

In CdTe, DA pairs can have different locations: (a) an acceptor at Cd site and a donor at Te site; (b) an acceptor at Cd site and a donor at Cd site;

(c) an acceptor at Cd site and a donor as an interstitial; (d) a donor at Te site and an acceptor as an interstitial. Taking the lattice parameter in CdTe as $a = 6.482$ Å [1] and the dielectric constant $\varepsilon(\infty) = 7.1$ [1], it is possible to calculate the approximate energy separations between pairs of the nearest or the next nearest neighbours: $\Delta E = e^2/\varepsilon^* r_1 - e^2/\varepsilon^* r_2$. Results of these calculation are given in Table 1. It is obvious that this calculation gives only a very rough value for ΔE. For a very short distance between donor and acceptor defects, the dielectric constant $\varepsilon(\infty)$ may not be well defined and some correction should be taken into account.

It is apparent, that cases (a) and (b) of Table 1 are not consistent with the experimentally observed energy separation between the two sub-bands, $\Delta E \approx 85$ meV. According to Fig. 1 the half-widths of sub-bands for both samples are different. A possible reason for this difference in the half-width may be the different surroundings of DA pairs in the first and second coordination spheres. In case (b), both the DA pairs have the same surroundings but in cases (c) and (d) there are differences. In a CdTe cubic lattice there are 3 types of interstitial positions. First two types (i_1 and i_2) have nearest surroundings of tetrahedral symmetry. In type i_1, the interstitial position have 4 tellurium atoms as nearest neighbours and 6 cadmium atoms at the next coordination sphere. Type i_2 has the same symmetry, except that it has 4 cadmium atoms as nearest neighbours. The third type i_3 has octahedral surroundings with 3 cadmium and 3 tellurium atoms as the closest neighbours. It is obvious that the i_3-type interstitial position is quite unstable for

the extrinsic atom, because it is not symmetric due to different atoms in its neighbourhood. Therefore, it seems reasonable to assume that only i_1 and i_2 interstitials can hold extrinsic atoms. The closest interstitial for an acceptor at Cd site has an i_2 symmetry type and the second closest interstitial has an i_1-type symmetry. The closest interstitial for a donor at the Te site has an i_1-type symmetry and the second closest interstitial has an i_2-type symmetry. We believe, that these differences cause the difference in the half-width.

Our CdTe-materials were prepared under low vapour pressure of tellurium. Therefore, the majority of defects are probably formed in the Cd sublattice. The dominating defect in this region is believed to be V_{Cd}. We may also assume that, in the first approximation, an interstitial atom is affected only by the nearest neighbours. So the fluctuations of the V_{Cd} concentration in the near vicinity of the interstitial atom is the reason for the significant widening of the 0.652 and 1.046 eV PL bands. This is why we must assume that for the 1.1 eV PL bands the closest DA pair is formed with the interstitial atom of i_1 type and the second closest DA pair with the interstitial atom of i_2 type, i.e. case (d) above. One possible model for this kind of DA pair is

$V_{Te} - Te_i$ complex, where V_{Te} is acting as a donor and Te_i as an acceptor. For the 0.7 eV PL bands the closest DA pair is then formed with the interstitial atom i_2 type and the second closest DA pair with the interstitial atom of i_1 type, i.e. case (c) above.

Any PL emission in the 0.7 eV spectral region was detected only in Cu-doped CdTe samples after rapid cooling to room temperature. The rapid cooling promotes a formation of defects, which are commonly absent in a slowly cooled material. One of these defects is an interstitial copper – Cu_i. We assume that it is a deep donor and that it forms a DA pair with a deep acceptor on the Cd site. These DA pairs are responsible for the PL emission in the 0.7 eV spectral region.

References

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