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1.4 eV photoluminescence in chlorine-doped polycrystalline CdTe with a high density of defects

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The 1.4 eV photoluminescence (PL) band in a polycrystalline CdTe:Cl with a high density of defects was studied as a function of the chlorine dopant concentration and temperature. For a material with a high density of defects this band has a smooth, non-symmetrical shape without any apparent phonon structure. The energy of the intensity maximum of the 1.4 eV band depends on the concentration of chlorine and varies from 1.389 to 1.408 eV. The temperature quenching of the PL intensity for all samples was measured and the activation energy (E_T) was found. Minimum and maximum values of the E_T were 0.10 and 0.20 eV, respectively. A configurational–coordinate model is proposed for the 1.4 eV PL band in which the excited state of the recombination centre lies within the conduction band. In this model the temperature quenching of the PL is pictured as being essentially due to an electronic transition from the excited state directly to the ground state (the internal mechanism).

1. Introduction

The 1.4 eV photoluminescence (PL) band is the most commonly observed band in CdTe [1–15]. This emission is seen in CdTe samples prepared in a wide variety of ways and with wide ranging properties. Since the 1.4 eV luminescence is more prominent in donor-doped material it is believed that donors play a definite part in the underlying physical mechanism responsible for this emission, but the exact nature of this mechanism remains obscure. The donor's role is confirmed also by observing how the energy of the intensity maximum depends on the nature of the donor dopant. Agrinskaya *et al.* [6] found that for chlorine-doped CdTe the energy of the intensity maximum is 0.02 eV higher than for indium-doped CdTe. Chlorine in CdTe usually acts as a hydrogenic shallow donor substituting at a Te site. However, it is known that Cl also acts as an acceptor by creating a complex centre $V_{Cd}Cl_{Te}$ [16]. High chlorine concentration must also increase the probability of creating more complicated defects such as $V_{Cd}(Cl_{Te})_2$ [17]. These kinds of defect usually act as non-radiative recombination centres in other II–VI materials [18]. According to Norris and Barnes [5] the peak energy of the 1.4 eV band has been found between 1.39 and 1.49 eV. This wide variation of the energy of the band peak position is also one of the unresolved problems. It is generally known that this broad band has a non-symmetrical shape, which does not seem to be caused by a superposition of two or three Gaussian bands. In many cases the 1.4 eV band has a very well-resolved LO-phonon structure [1, 6–8]. In these cases, the band shape is often closely approximated by the well known Pekarian shape, with a Poisson-distributed amplitude for the successive component lines. If analysed in detail, however, the Pekarian shape is not pure, but seems to contain some disturbances. Up to now there is no clear understanding of the processes causing such a variation of the shape of this emission band. The most probable explanation is connected with the assumption that, in fact, several recombination processes are involved in the 1.4 eV band [5]. Cotal *et al.* [13] found recently two closely overlapping components peaking at 1.47 and 1.49 eV in high-resistivity p-type CdTe single crystals. These two components have a different temperature quenching activation energy. Because of this a variation in the 1.4 eV band shape as a function of temperature was clearly observed. This model of overlapping components, due to different recombination processes, was emphasized also by Hofmann *et al.* [15]. Some progress on resolving the nature of defects responsible for the 1.4 eV luminescence band in CdTe has been achieved in the latest studies of ODMR [14, 15]. It appears obvious that the so-called A-centre plays a key role in the 1.4 eV band. The chemical nature of this centre in chlorine-doped CdTe is believed to be $V_{Cd}Cl_{Te}$. In a certain sense it resembles an SA-centre in other II–VI compounds, especially in ZnS [19]. However, as pointed out by Biernacki *et al.* [14] the

A-centre has a more complicated structure and the 1.4 eV luminescence is related to an electronic transition from the donor state of an isolated substitutional halogen atom to the vacancy t_2 level split by the nearest-neighbour halogen atom. The role of the donor–acceptor pairs (DAP) recombination in the 1.4 eV luminescence is still a matter of controversy. Although many experimental data can be found in the literature that are difficult to explain with the other models, there are also observations that contradict the DAP model [13]. The localized transition within a compact defect complex is also suggested to be responsible for the 1.4 eV PL band [3]. In order to clear out this discrepancy, additional experimental information is required. One possible way to determine the structure of the corresponding defect and thus the recombination mechanism is to study the behaviour of the luminescence upon the concentration of the donor. These kinds of studies have proved to be very successful in resolving the nature of deep-centre luminescence in several II–VI materials [20–22]. On the other hand, the investigation of the chlorine doping is also attractive for the reason that $CdCl_2$-heat treatment is often used to improve the properties of CdTe thin films and thus conspicuous numbers of chlorine atoms may be incorporated in the CdTe lattice.

In this paper we present the results of chlorine doping on the 1.4 eV luminescence band in polycrystalline CdTe with a high density of defects. Polycrystalline CdTe is a typical starting material in the screen-printing method to prepare thin solid films. This method is proven to be a very successful in producing low-cost solar cells [17].

2. Experimental details

The initial material used was a CdTe powder subjected to vacuum sublimation at 873 K for 3 h. The chlorine doping was carried out using $CdCl_2$ aqueous solution ($N_{Cl} = 10^{17}$–$10^{19}\ cm^{-3}$). The diffusion of chlorine into CdTe took place at 1073 K applied for 20 h in evacuated quartz ampoules. After the high-temperature firing treatment the powder samples were rapidly cooled to room temperature in order to freeze in the high-temperature atomic defect concentrations. The total chlorine content was determined by potentiometric titration. The powder was glued onto copper plates with a non-luminous glue.

For the photoluminescence (PL) measurements, a 10 mW Ar-ion laser beam with a wavelength of 488 nm was used for excitation. The laser light was chopped at 277 Hz. The samples were mounted in a closed cycle He cryostat capable of cooling down to 12 K. A computer controlled SPEX 1870 0.5 m grating monochromator with a spectral slit of 0.5 nm was used. The chopped signal was detected with a R-632 photomultiplier using the conventional lock-in technique. The emission spectra was corrected for grating efficiency variations and for the spectral response of the photomultiplier. The standard tungsten lamp was used to calibrate the set-up. To measure the temperature quenching of the luminescence intensity, the temperature of the samples was carefully controlled by a heater in connection with a precision temperature controller.

3. Results and discussion

Fig. 1 shows the 1.4 eV PL band spectra at 14 K in CdTe:Cl with different concentrations of chlorine. All these spectra have a non-symmetrical shape with no phonon structure. The shape is well represented as a sum of several individual gaussians, separated by a LO-phonon energy (21.2 meV [14]). The intensity distribution of these individual component emission lines can be described by a Poisson distribution,

$$I(n) = I_0 \exp(-S) \frac{S^n}{n!} \qquad (1)$$

with the Huang–Rhys coupling parameter S and a constant factor I_0.

All spectra were fitted using Equation 1. The fitting of nearly 100 spectra revealed that there exists an additional weak band peaking at the high energy side of the 1.4 eV band. The peak position of this additional band approximately coincides with the peak position of the first ($n = 1$) phonon replica of the 1.4 eV band. The relative importance of this band increases at higher temperatures but it still does not have a significant effect on the overall shape of the 1.4 eV band.

The peak energy of the 1.4 eV band depends on the concentration of chlorine and varies in our measurements from 1.389 to 1.408 eV. These values are lower than those usually observed ones in the chlorine-doped CdTe. Using a polycrystalline powder with a large density of defects is a possible reason for this and also for the fact, that no phonon structure was detected even at 13 K and with a spectral slit of 0.5 nm. No trace of optical emission was detected in the usual exciton spectral region either. This fact indicates that the concentration of intrinsic defects in our materials must be extremely high.

The temperature quenching of the luminescence emission is often used to find out the position of the corresponding energy levels of the recombination centre. The quenching behaviour of the integrated intensity $I(T)$ of the 1.4 eV band is described by the

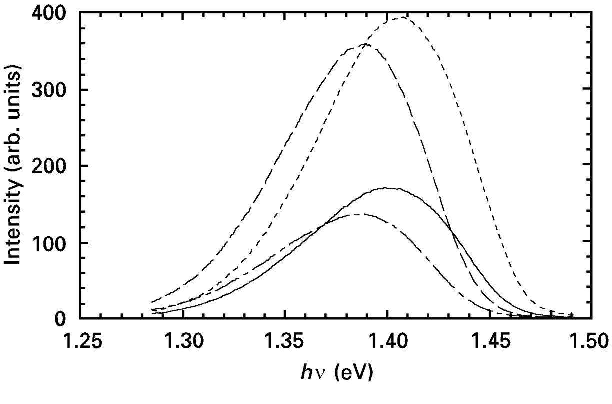

Figure 1 Photoluminescence spectra of CdTe:Cl at T = 14 K. Key: $N_{Cl}(cm^{-3})$: —— 10^{17}; ---- 5×10^{17}; —— 2×10^{18}; ——— 10^{19}.

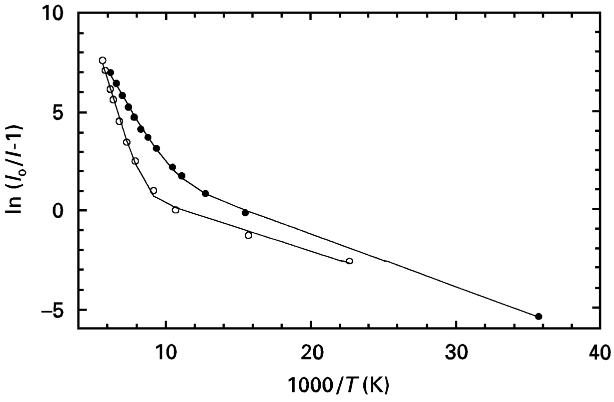

Figure 2 The temperature dependence of the 1.4 eV PL band intensity and the fitting to Equation 2. Key: —— theory; ○ $N_{Cl} = 5 \times 10^{17}$ cm^{-3}; ● $N_{Cl} = 2 \times 10^{18}$.

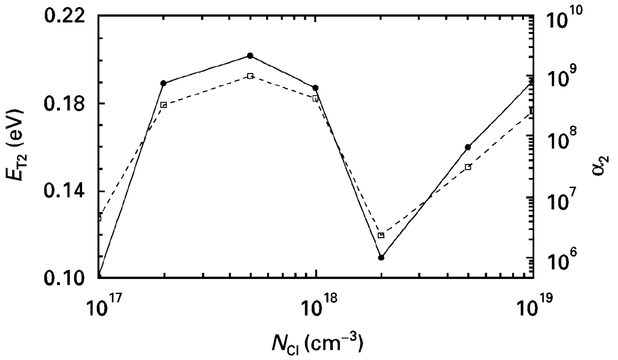

Figure 3 Chlorine concentration dependence of the quenching activation energies E_{T2} and the parameter α_2. Key: —●— E_{T2}; --□-- α_2.

expression

$$I(T) = \frac{I_0}{1 + \alpha_1 \exp\left(-\frac{E_{T1}}{kT}\right) + \alpha_2 \exp\left(-\frac{E_{T2}}{kT}\right)} \quad (2)$$

with parameters α_1 and α_2 and two activation energies E_{T1} and E_{T2}. An attempt to model the experimental data with one activation energy only failed. Here E_{T1} and α_1 belong to the low-temperature quenching region and E_{T2} and α_2 to the high-temperature region. The temperature dependence of the 1.4 eV band of chlorine-doped CdTe and the fitting to Equation 2 for two samples are presented in Fig. 2. Fig. 3 shows the experimentally determined dependencies of E_{T2} and α_2 on the chlorine concentration. Minimum and maximum values of the E_{T2} are 0.10 eV and 0.20 eV, respectively. It is notable that these values would not be consistent with the 1.4 eV band peak position in a model where the luminescence originates from an electronic c-band–acceptor level transition and where the temperature quenching of the PL band is caused by the thermal release of trapped holes from this acceptor level, i.e. in our measurement the minimum value of E_T corresponds to the minimum value of the peak position and vice versa. The same situation was also detected by Norris [3]. He concluded that the 1.4 eV luminescence transition cannot originate at a band edge.

The quenching in the low-temperature region is characterized by very low values of α_1 and E_{T1}. Both parameters show a tendency of increasing with chlorine concentration within values $\alpha_1 = 7$–50 and $E_{T1} = 10$–25 meV. Unfortunately there was too little experimental data in this region to determine a precise dependence upon chlorine concentration.

Analysis of the PL spectra reveals that a phonon-broadening of the 1.4 eV band also takes place when temperature increases. The low-temperature half-width W of individual sub-bands is nearly independent of the chlorine concentration and has a value ≈ 30 meV. Although a fully unambiguous fitting, with all the parameters as free variables, of high-temperature PL bands was difficult, the analysis of the temperature dependence of W showed that acoustic phonons are responsible for the broadening of the sub-bands. This strong interaction with acoustic phonons may be one reason for the absence of a well-resolved LO-phonon structure in the 1.4 eV PL band, in our powder samples. The second possible reason is the widening of the acceptor level due to fluctuations of the concentration of charged defects [20].

It is known that the dimensionless Huang–Rhys factor S depends on the lattice relaxation around the defect site [25]. Therefore, the variable concentration of chlorine must affect the value of the Huang–Rhys factor. As can be seen from Fig. 4 there is a certain dependence of S on N_{Cl}.

Fig. 5 presents the temperature dependence of the energy of the intensity maximum of the 1.4 eV PL band. As it can be seen, the peak position exactly follows the temperature dependence of the gap energy E_g. According to Fig. 5, one must conclude that band states are involved in the recombination process.

Low temperature half-width $W_{1/2}$ and the peak position E_{max} are presented together in Fig. 6. As can be seen from Fig. 6, the highest value of E_{max} corresponds to the lowest value of $W_{1/2}$ and vice versa. In the donor–acceptor pair recombination model the relationship between E_{max} and $W_{1/2}$ would be quite the opposite, because the high E_{max} have pairs with the closest separation. These pairs give the widest luminescence band because of coulombic broadening. The donor–acceptor pair model may also be ruled out because of the observed temperature dependence of the peak position, see Fig. 5. Thus some other model should be applied to explain our experimental data.

On the other hand it is difficult to interpret such a big variation of the temperature quenching activation energy without a comparable variation of the peak position of the PL band if the quenching is interpreted as the thermal release of the trapped holes from the acceptor level into the valence band. It seems reasonable to surmise that all these effects are related to the simultaneous presence of two or more PL bands with slightly different shapes. According to our results these PL bands must have a temperature quenching activation energy range from 0.10 to 0.20 eV. Such a big range of E_T must have an effect also on the

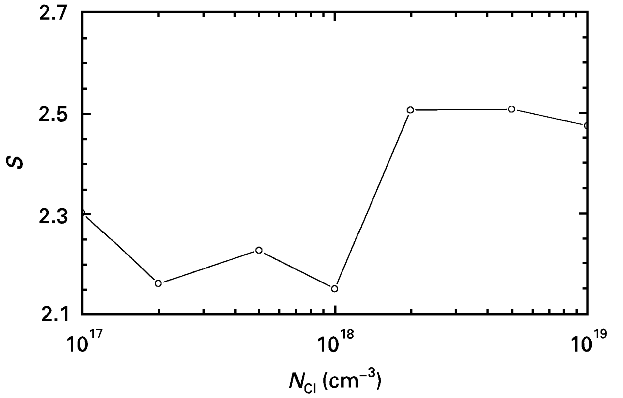

Figure 4 The Huang–Rhys factor S as a function of chlorine concentration.

temperature dependence of the band shape. In [13] the variation in the shape of the 1.4 eV band as a function of temperature was clearly detected. Two overlapping components were found although they were separated in energy only by 0.02 eV and the difference in E_T was 0.02 eV. Despite our efforts, however, our samples did not show any remarkable variation in the shape with temperature. We thus believe that in our samples only one single band, which is basically Pekarian, exists and that the model of overlapping component bands must be refused at least at low temperatures.

Difficulties arise also from attempts to apply the localized transition model within a compact defect complex. It is troublesome to comprehend the experimentally obvious connection between the temperature dependence of the peak position of the PL band and the energy gap $E_g(T)$, see Fig. 5. To overcome these difficulties we propose a configurational–coordinate model in which the excited state of the recombination centre lies within the conduction band close to its bottom, see Fig. 7. It is known that in materials with high numbers of charged defects the shape of the edge of both conduction and valence bands essentially changes and the localization of electrons in the

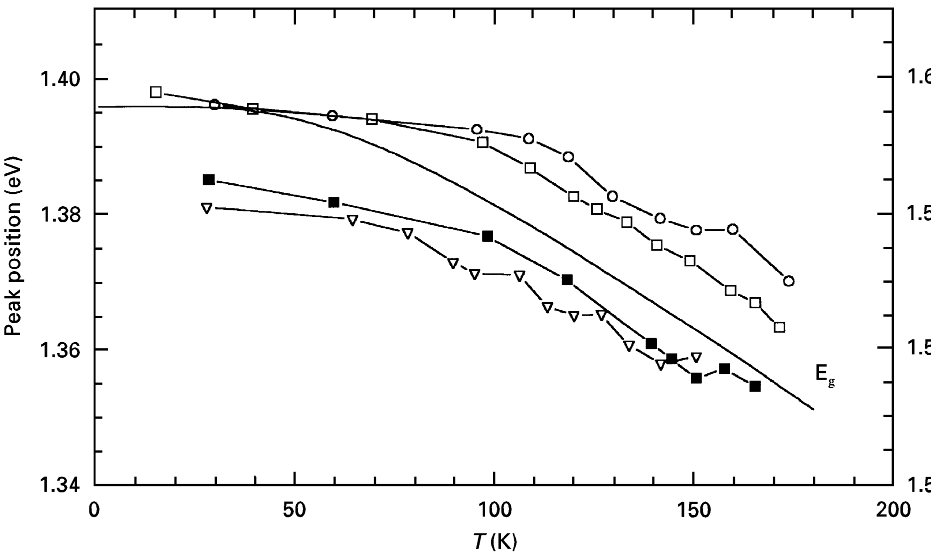

Figure 5 The temperature dependence of the peak position of the CdTe:Cl 1.4 eV PL band with different concentrations of chlorine and E_g versus T [26]. Key: N_{Cl} (cm^{-3}): —○— 2×10^{17}; —□— 10^{18}; —▽— 2×10^{18}; —■— 5×10^{18}.

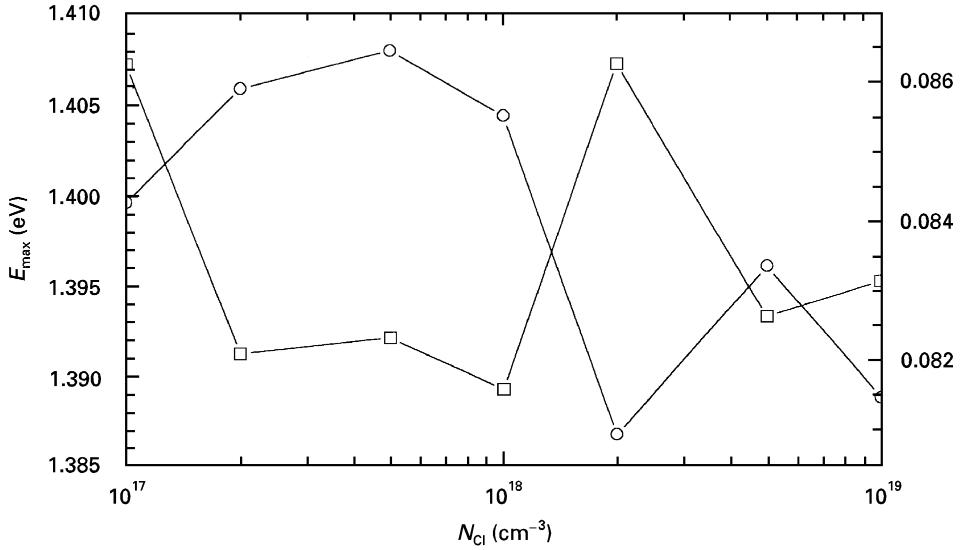

Figure 6 Effect of the chlorine concentration on the peak position E_{max}(○) and the half-width $W_{1/2}$ (□) of the 1.4 eV PL band at $T = 14$ K.

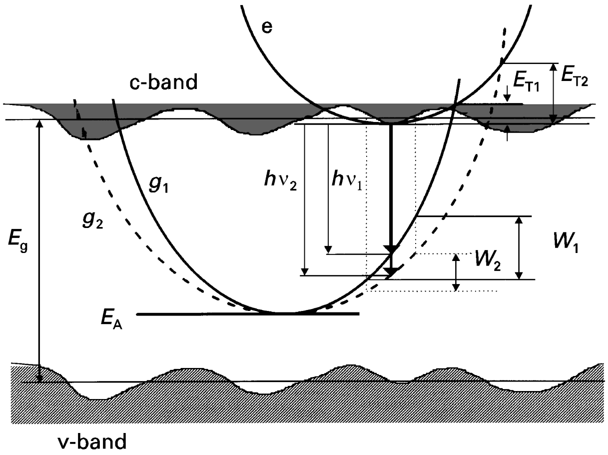

Figure 7 The configuration coordinate model for the 1.4 eV PL band in CdTe:Cl.

conduction band becomes possible. The ground state is connected with a defect level E_A. A similar model was proposed for CdSe [24]. In this model the temperature quenching of the PL intensity is due to electron transition from the excited state directly to the ground state (the internal mechanism). The temperature quenching activation energy E_T is then related to the energetic distance between the bottom of the excited state curve and the crossover point of the potential energy curves for the ground state and for the excited state, as depicted in Fig. 7. The potential curve of the ground state is essentially affected by neighbouring defects. According to our results the excited state remains comparatively unaffected by a local defect field. The widening of the potential energy curve of the ground state causes an increase in the temperature activation energy E_T and in the peak position E_{max}. At the same time the half-width of the PL band and the "effective" Huang–Rhys factor decrease, see Figs 4 and 7. In this model the temperature dependence of the peak position should more or less follow the energy gap. This is exactly what we observe in our experiments. It is clear that the temperature quenching of PL may partly be caused also by the thermal release of holes from the defect level, i.e. by the external mechanism. Such a process becomes essential if the parameter α_2 in Equation 2 has a value bigger than for the internal quenching mechanism. As was shown in [23], the high-temperature parameter α_2 for the 1.4 eV PL band in good quality CdTe single crystals typically has a value 1.5×10^6. The physical significance of the α parameter is different for these two quenching mechanisms. In the case of holes release, the parameter α depends on the ratio of hole and electron capture cross-sections at the recombination centre and the electron concentration which are all affected by the donor concentration [21, 24]. In CdS:Ag:Cl the dependence of α on N_{Cl}^{-3} was experimentally detected [21]. It is apparent that in the present samples the parameter α is too small to account for the thermal release of holes. This gives additional support to our postulate that the quenching can safely be assumed to be due to the internal mechanism.

4. Conclusion

It seems likely that the 1.4 eV PL band in CdTe may be caused by several recombination mechanisms depending on the preparation and quality of the material. The model, where the 1.4 eV PL is produced by transitions between localized levels of a compact centre, was proposed by Norris [3]. Later this model received valid criticism [13] since it can not be fully supported by available experimental data. In the present paper we look at this problem from a slightly different point of view and propose an improved configurational coordinate model in which the excited state of the recombination centre is located within the conduction band and the temperature quenching of the luminescence is caused by internal transition of an electron directly from the excited state to the ground state of the recombination centre. All observed experimental dependencies appear to be in conformity with this model. It is obvious that the model presented here presumes an electron localization near the recombination centre. Difficulties arise if we try to explain such a localization in a pure CdTe. In our polycrystalline samples, where the concentration of defects is extremely high, it is possible that potential fluctuations caused by charged defects affect the shape of the edge of the conduction band and some kind of localized states may be formed.

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