

# Study of defects in CdTe:Cl by cathodoluminescence microscopy

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Received 3 January 1995; in final form 8 February 1995; accepted 9 February 1995

## Abstract

The effect of Cl doping on the luminescence properties of CdTe is investigated by cathodoluminescence microscopy. Cl enhances the 1.4 eV emission and retards the appearance of the tellurium vacancy related emission band. The behaviour under annealing indicates that doping with substitutional impurities involved in A-centers influences the intensity of the 1.4 eV band.

## 1. Introduction

Some of the luminescence bands often detected in CdTe crystals show a complex behavior as a function of surface treatments, doping and the presence of bulk defects, which is not yet well understood. This fact makes difficult the control of the luminescence properties of this material and the use of luminescence as a characterization technique. In particular, a broad complex band usually termed as the 1.4 eV band has been observed in a wide variety of CdTe samples. Different workers have shown that the 1.4 eV band is related to surface damage as well as to the presence of bulk defects [1–4] as, for instance, the so-called A-centers (cation vacancy–donor pairs) [5,6]. The involvement of cadmium vacancies, through the A-center, can explain the effect of some impurities on the intensity of this band. It has been observed [7] that doping with V quenches the 1.4 eV emission. This can be explained by the location of V on cadmium sites [8] causing the reduction of Cd-vacancy concentration and hence reducing the possibility of luminescent A-center formation. According to this suggestion, doping with atoms occupying Te sites, instead of Cd sites should

not inhibit the appearance of the 1.4 eV band but could affect luminescence bands related to tellurium vacancies, as the 1.10–1.15 eV emission [6,9].

In this work, cathodoluminescence (CL), in the scanning electron microscope, is used to investigate the effect of Cl doping on the luminescence properties of CdTe and in particular on the abovementioned emission bands.

## 2. Experimental method

The crystals used in this work were undoped and Cl-doped CdTe wafers with thickness of about 1000  $\mu\text{m}$  provided by Japan Energy Corporation (formerly Nippon Mining). The resistivities of undoped and doped samples were about 28 and  $> 10^7 \Omega \text{ cm}$  respectively. The samples were observed in a Hitachi S-2500 scanning electron microscope in the emissive and CL modes at temperatures between 80 and 300 K with an accelerating voltage of 25 keV. The experimental setup for spectral and panchromatic CL measurements with a North Coast EO-817 germanium detector has been previously described [10]. Previous results showed that

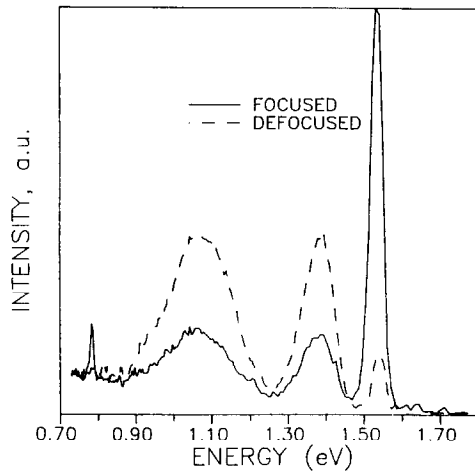


Fig. 1. CL spectra of undoped CdTe at 80 K under focusing (—) and defocusing (---) conditions of electron beam.

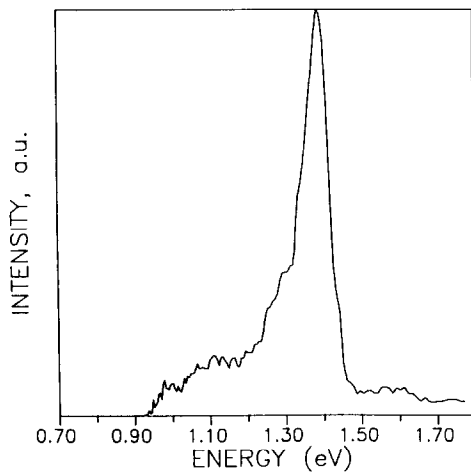


Fig. 2. CL spectrum of CdTe:Cl at 80 K under defocusing conditions of electron beam.

CL spectra of CdTe recorded with focused and with defocused beam are different as a consequence of the presence of radiative centers with a low concentration [4,11]. Usually under defocusing, the intensity of deep level related bands increases. For this reason, CL spectra were recorded under different focusing conditions of the electron beam on the samples. Some samples were annealed under an argon flux at 600°C for 5 h. In some cases, cross-sectional observations of the wafers were performed on fresh cleaved surfaces to eliminate possible annealing-induced surface effects.

### 3. Results

Fig. 1 shows CL spectra at 80 K of an undoped CdTe sample. With focused electron beam, the spectrum shows an intense exciton band and weaker broad emissions at about 1.4 and 1.06 eV. Defocusing causes a decrease of the near band edge emission and an increase of the 1.4 and 1.06 eV emissions. The spectrum of a Cl doped sample, obtained with defocused electron beam is shown in Fig. 2. With focused beam, emission was

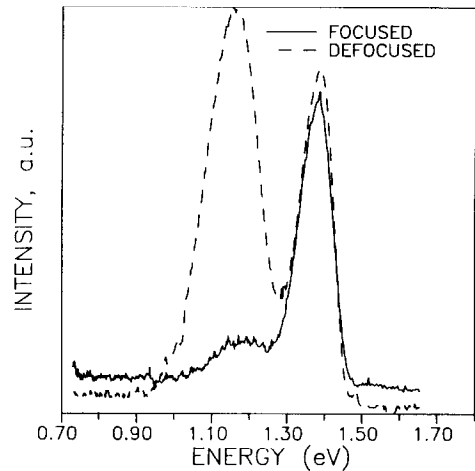


Fig. 3. Focused (—) and defocused (---) CL spectra of undoped CdTe at 80 K after annealing at 600°C for 5 h in an inert atmosphere.

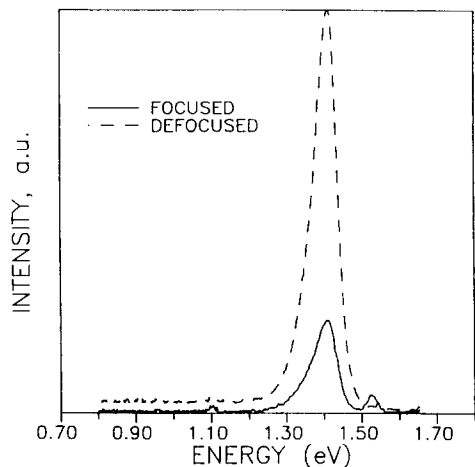


Fig. 4. Focused (—) and defocused (---) CL spectra of CdTe:Cl at 80 K after annealing at 600°C for 5 h in an inert atmosphere.

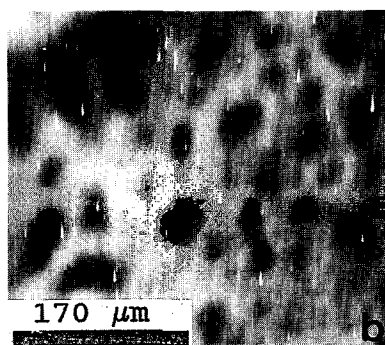
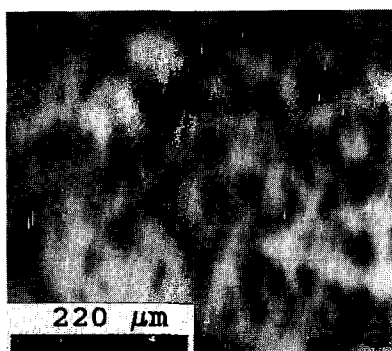


Fig. 5. Panchromatic CL images of undoped CdTe (a) before and (b) after annealing at 600°C for 5 h in an inert atmosphere.

too low to record the spectra with our detection system. In Fig. 2 only the 1.4 eV band is revealed with a shoulder in the 1.15 eV region. The effect of annealing on the CL spectra is shown in Figs. 3 and 4. Annealing the undoped material causes the appearance of an intense band at 1.18 eV in addition to the 1.4 eV (Fig. 3). In the Cl-doped samples, the effect of annealing is the enhancement of the 1.4 eV band while the emission in

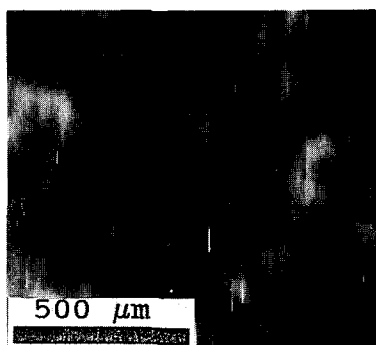


Fig. 6. Panchromatic CL image of unannealed CdTe:Cl.

the range 1.05–1.20 eV is practically absent (Fig. 4).

Panchromatic CL images of undoped samples show inhomogeneous distribution of luminescence intensity (Fig. 5) with dark points in a bright background. Similar qualitative contrast is observed in monochromatic 810 nm images as well as in images recorded with emission above 1000 nm. Annealing causes enhancement of the contrast of dark spots. In Cl-doped samples, CL is inhomogeneous with a diffuse intensity distribution (Fig. 6). The general appearance was not changed after annealing.

#### 4. Discussion

The undoped sample shows near band edge emission, the 1.4 band, a broad band centered at about 1.06 eV and a weak 0.781 eV emission, previously reported by other workers [12]. The latter one will not be discussed here. After annealing, the spectrum is dominated by a band at 1.18 eV probably due to the increase of one component of the broad 1.06 eV band. Emission at about 1.15 eV has been previously observed after annealing in an inert atmosphere [7] and was thought to be the band attributed by Hofmann et al. [6] to tellurium vacancies. In the present work this band appears slightly shifted to higher energies. This is possibly due to a contribution of the 1.22 eV band revealed in some areas of the sample and also previously observed in both doped and undoped CdTe [13]. The spectrum of Fig. 3 was obtained by cross-sectional measurements after cleaving the annealed sample. In the as-annealed sample, the 1.18 eV band is not clearly observed due to intense surface emission related to some components of the 1.4 band.

The presence of Cl inhibits the appearance of the 1.18 eV band and enhances the 1.4 eV emission as shown in Fig. 4. Annealing in inert gas flow at 600°C causes the formation of cadmium and tellurium vacancies and can therefore influence the 1.4 and 1.18 eV luminescence. This influence, however, depends on the impurities present in the sample. In undoped material, the 1.18 eV band related to tellurium vacancies appears after annealing and the 1.40 eV band, which has a component related to cadmium vacancies remains as an intense emission.

Different effects are observed in Cl-doped samples. The annealing-induced vacancies can form complexes

with the Cl donors; i.e. the chlorine A center identified in Ref. [5], and cause enhancement of the 1.4 eV emission. On the other hand, substitutional Cl in Te sites reduce the number of Te vacancies causing a decrease of the 1.18 eV band. This emission, prominent in undoped samples, has a residual character in annealed CdTe:Cl. In a previous work [7], V in cadmium sites was used as impurity in CdTe and an opposite behavior to that of Cl impurities observed here, was found. Due to the decrease of cadmium vacancies by V substitution, the 1.4 eV band was absent and appeared after annealing together with the 1.18 eV band.

Regarding the CL images, the distribution of CL in undoped samples could be related to the existence of dislocations as non-radiative centers. According to the data of dislocation density, revealed by Nakagawa etching and provided by the suppliers (about  $3 \times 10^4 \text{ cm}^{-2}$ ), most of the dark points correspond to dislocations. The fact that the contrast does not change qualitatively in CL images, corresponding to the different spectral regions, shows that the non-radiative centers are competing with both, band edge and deep level, radiative transitions. Annealing enhances the contrast of dark regions but no specific regions related to the 1.18 eV luminescence can be identified. This is partly due to the fact that the intense 1.18 eV emission is observed in defocused conditions. The diffuse (cloudy) appearance of CL images in Cl-doped CdTe indicates a spatial distribution of recombination centers at microscopic scale but this distribution is not related to dislocations or other extended defects which are practically absent in this material.

## 5. Conclusions

Cl doping influences the 1.4 eV and the 1.10–1.20 eV CL bands of CdTe. Cl enhances the 1.4 eV emission and retards the appearance of the tellurium vacancy related emission in the 1.10–1.20 eV region. The

behavior under annealing treatment, as well as a comparison with previous results on CdTe:V, indicates that one way to control the appearance and intensity of the 1.4 eV band is to dope with substitutional impurities influencing the formation of the A-centers involved in the emissions.

## Acknowledgement

UP thanks MEC-DGICYT for a post-doctoral research grant. This work has been supported by DGI-CYT (Project PB-90-1017). Samples were kindly provided by Japan Energy Corporation.

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