



ELSEVIER

Journal of Crystal Growth 159 (1996) 171–174

JOURNAL OF
**CRYSTAL
GROWTH**

Preparation and photoluminescence study of high purity CdTe single crystals

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Abstract

CdTe single crystals were grown by vertical Bridgman (VB) and physical vapor transport (PVT) methods. The photoluminescence was measured at 4.2 K to evaluate the crystals and to examine the behavior of residual impurities and the effect of Cd purity. The segregation of dominant residual impurities was confirmed in VB as-grown crystals. The purification effect of PVT was also confirmed. The dominant emission line (A_0, X) at 1.5896 eV in the PL spectrum, related to Cu_{Cd} or V_{Cd} , has been found to have a doublet structure shared by two origins, though a complete understanding is still lacking.

1. Introduction

Recent research on CdTe single crystal growth has mostly been focused on the preparation of bulk crystals of applicable size and on epitaxial fields. However, control of the electrical properties of this materials has not yet been achieved. This is due to the behavior of native defects and impurities. Their interaction has not been fully clarified. For example, the instability of elements with a single valance electron, the compensation of V_{Cd} to shallow donors [1,2], and the existence and electrical activation of native defects, are still under discussion [3–5].

Although photoluminescence measurement is a

useful method for studying the behavior of residual impurities and native defects, there have been several unsolved problems about the photoluminescence of CdTe. For example, there are several proposals, such as Cu_{Cd} , V_{Cd} , $V_{Cd}-D$ [3,4,6,7] for the origin of the dominant (A_0, X) emission line at 1.5896 eV commonly observed as the most intense one in as-grown crystals. No single model can interpret the behavior of this line regarding annealing and Cu-doping.

The broadening of emission lines caused by residual impurities makes analysis difficult in lower purity crystals. Therefore, the purity of the crystal is one of the key factors in clarifying the behavior of residual impurities and their interaction with native defects by photoluminescence measurements. In this work, high purity CdTe single crystals were obtained by the combination of the VB and PVT methods, and the effect of the purity of the raw materials on as-grown crystals has been shown. We tried to identify the origin of the dominant (A_0, X) emission line.

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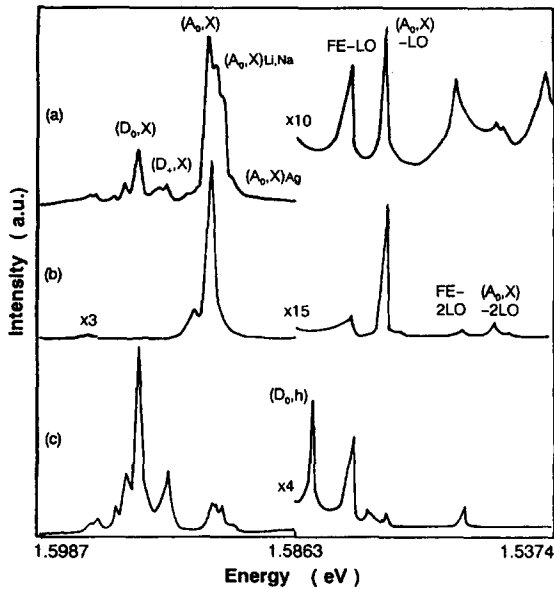


Fig. 1. Typical photoluminescence spectra of CdTe single crystals grown by vertical Bridgman method. (a) Samples as-grown from 6N Cd. (b) Samples as-grown from high purity Cd. (c) Annealed samples grown from high purity Cd.

2. Experiments

In order to examine the effect of the purity of raw materials on the purity of grown CdTe crystals, extremely pure Te and Cd with two different purity levels, were used. We employed commercial 6N Cd with an RRR (Residual Resistivity Ratio) of 10000 and high purity Cd with an RRR of 20000 prepared by the overlap-zone-melting method [8].

CdTe crystals grown by the conventional VB method, were further purified by the sublimation method prior to the growth of high quality single crystals by the physical vapor transport method. We used a Cd reservoir to control the stoichiometry. After cleaning, the quartz tubes were vacuum-baked at 1373 K for over 20 h. This was followed by carbon-coating and then we baked them again using the same method. A slight Te excess of no more than 0.01 at% was used in VB growth.

A growth rate of 3.2 mm/h and a temperature gradient of 12 K/cm were adopted for VB growth, and a ΔT of 3 K and a growth temperature of 1093 K were used for PVT growth.

PL measurements with a resolution better than

0.04 nm were performed at 4.2 K on the cleaved surfaces without any surface treatment.

3. Results and discussions

A typical PL spectrum of crystals VB-grown from commercial 6N Cd is shown in Fig. 1a. They show characteristic emission lines with (D_0,X) , (A_0,X) at 1.5896 eV, $(A_0,X)Li,Na$ and the LO-phonon replicas.

In Fig. 2 the dependence of their PL emission intensities on the solidified fraction of crystals VB-grown from 6N Cd is plotted, in intensity ratios of bound excitons to the first LO-phonon replica of a free exciton (FE). This graph shows a pronounced increase in the relative intensity of solidified fraction (g) for all the acceptor bound exciton lines. This has been generally observed before [9,10]. These increases are mainly due to segregation effects of these Cd-site substitutional Ag, Li and Na impurities with a segregation coefficient smaller than unity [11].

The segregation also exists in the case of substitutional donor impurities such as In, Al, Ga. These are the usual dominant residual impurities in CdTe. However, the g -dependence plot of the relative intensity ratio of the (D_0,X) emission is flat owing to

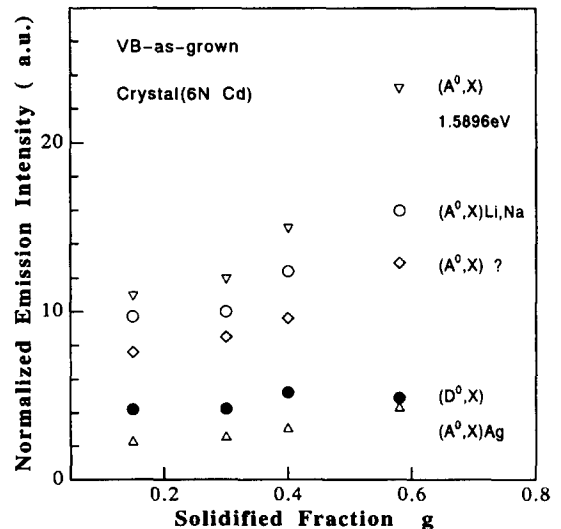


Fig. 2. Solidified fraction dependence of the luminescence intensity ratios of bound excitons to FE-LO. Solid symbols: donor bound exciton; open symbols: acceptor bound exciton.

the association of donor impurities with V_{Cd} by forming complexes. It is different from the decreasing trend with g reported by Zimmermann et al. [10].

On the contrary, in the case of crystals grown from high purity Cd as shown in Fig. 1b, no other emission lines, except for the dominant (A_0, X) line at 1.5896 eV, are observed. Comparing the PL spectra of the crystals as-grown from 6N Cd to high purity Cd ones demonstrates that the purity of the crystals mostly depends on the original materials.

PVT growth was carried out using a VB crystal as the source material. Its PL spectrum corresponds to that in Fig. 1a. The PL spectrum of the PVT crystal is shown in Fig. 3. The purification effect during PVT growth is clearly seen in Fig. 3. Only the dominant (A_0, X) line at 1.5896 eV is observed against a very low background. It can be expected that a pure crystal can be grown by the PVT method using VB growth from the purer Cd as source material.

Fig. 1c shows the annealing effect on the behavior of the residual impurities. After Cd-saturated annealing at 873 K for 70 h, the emission intensities of FE-LO and (D_0, X) increase sharply and the latter becomes the most intense emission. Similarity has also been observed in Zn-dipped ZnSe [12]. A new line appears at 1.5826 eV, attributed to (D_0, h) , a transition from neutral donor to valance band.

On the other hand, the extremely intense (A_0, X) emission at 1.5896 eV observed in as-grown crystals, decreases drastically and shows almost the same

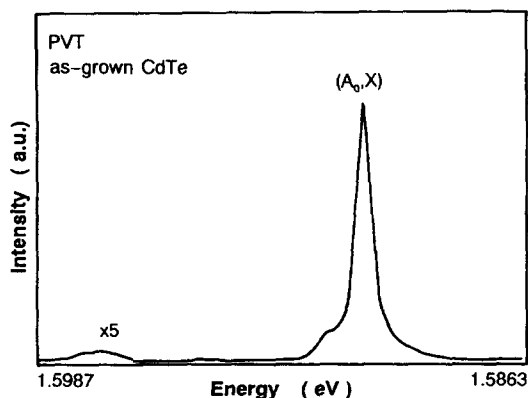


Fig. 3. Photoluminescence spectrum of high quality crystals grown by physical vapor transportation.

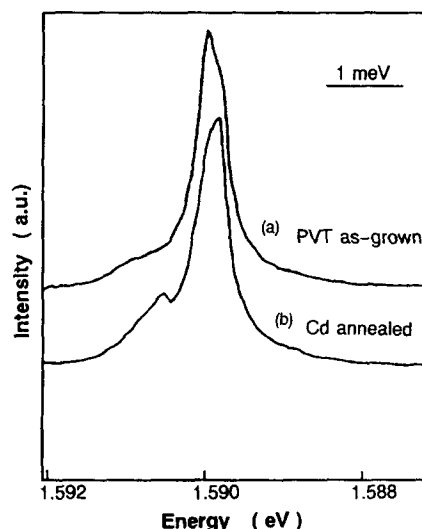


Fig. 4. Feature view of dominant (A_0, X) line at 1.5896 eV.

intensity as other (A_0, X) lines related to Ag, Li and Na. This is in contrast to their extremely large intensity ratios before annealing. As a matter of fact, the other (A_0, X) emissions are almost unidentifiable in as-grown crystals because of the strong emission of (A_0, X) at 1.5896 eV. This behavior cannot be explained by the assignment of the (A_0, X) origin to Cu_{Cd} , because no purification is expected during the isothermal annealing process. This phenomenon suggests that this extremely intense emission is attributed to an other defect related to V_{Cd} .

Much effort has been devoted to the identification of the origin of the dominant (A_0, X) line. This is actually complicated by the interaction of native defects and impurities. Therefore, a high quality crystal is essential for solving this problem. Fig. 4 shows the change of the dominate (A_0, X) line caused by Cd annealing for 24 h measured on one of the PVT crystals grown from less pure Cd. The sample and reservoir temperature of the Cd annealing are 873 and 793 K, respectively. The shape of the peak probably resembles a doublet structure in correlation with a Cu_{Cd} and $V_{Cd}-D$ complex. Detailed observation is needed, because the separation of these two sub-lines within this peak is extremely small.

We are now growing purer crystals by the PVT method from zone refined Cd. Doping experiments using purer crystals will make clear the situation as reported in ZnSe [13].

4. Summary

In this work, segregation of residual impurities is observed, and the effect of the purity of the starting materials is confirmed. High quality crystals are obtained by the combination of purification of the raw materials and growth using VB and PVT. The emission line of (A_0, X) at 1.5896 eV is found to have two origins, related to V_{Cd} and Cu.

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