Growth and characterization of high purity CdTe single crystals

B. Yang [a,*,1], Y. Ishikawa [a], Y. Doumae [b], T. Miki [a], T. Ohyama [c], M. Isshiki [a]

[a] *Institute for Advanced Materials Processing, Tohoku University, Sendai 980, Japan*
[b] *Osaka Asahi Metal MFG, Co. Ltd., Osaka 557, Japan*
[c] *Department of Physics, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan*

Abstract

High purity CdTe single crystals have been grown by improved physical vapor transport (PVT), following the purification by normal freezing using 6N Te and highly purified Cd as starting materials. As-grown single crystals were characterized with photoluminescence and photo-excited cyclotron resonance (CR) at 4.2 K and infrared transmission at room temperature. The improved PVT growth ampoule was confirmed very effective for controlling the growth rate and the reproducibility of a successful growth. Electron cyclotron mobility at 4.2 K is as high as 2.5×10^5 cm^2/V · s and the neutral donor concentration (N_D) obtained from the linewidth of CR is 5×10^{14} cm^{-3}.

1. Introduction

A full understanding of the behavior of some impurities and native defects in CdTe crystal has not been achieved, and a good control of the electrical properties of this material remains quite difficult. For these researches, to improve crystal quality is believed to be the key factor.

Physical vapor transport (PVT) method has been most preferred among various crystal growth techniques when high quality single crystals are pursued [1–3], because impurities can be effectively reduced, and defects are much inhibited. The growth process and the properties of the resulting crystal become more controllable, with a Cd reservoir in the growth to control the vapor composition [4].

Previous works found that the controlling step of the common PVT growth rate was the mass transport but neither the evaporation of source nor the growth of crystal [4–6]. The mass transport is greatly affected by the partial pressures of the components, which are often deteriorated much by the oxidation of source materials and the presence of volatile impurities. Therefore, efficient reduction of the contamination and usage of purer source materials are important for getting a stable mass transport and growing a high purity single crystal.

In this work, high quality CdTe single crystals are grown by the PVT method, following the purification by normal freezing (vertical Bridgman growth), for which highly purified Cd [7] was used as starting material. The PVT growth ampoule is improved, aimed to reduce the contamination during the ampoule-making operation. Grown crystals are charac-

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* Corresponding author. Fax: +81 22 261 0938; E-mail: ishikawa@iamp.tohoku.ac.jp.
[1] Permanent address: Changchun Institute of Physics, Changchun, Jilin 130021, People's Republic of China.

terized by photoluminescence (PL), photo-excited cyclotron resonance (CR) and infrared transmission (IR).

2. Experimental procedure

Nominal 6N Cd was highly purified by overlap zone melting following vacuum distillation. Analytical results of 6N and the purified Cd by glow discharge mass spectrometry are shown in Table 1. CdTe single crystals were firstly grown by vertical Bridgman (VB) using 6N Te and the purified Cd as well as 6N Cd for comparison [8]. The purest part of the high purity VB crystal, verified by PL measurement, was subjected to the source material for PVT growth.

Typical PVT growth conditions are listed in Table 2. The improved PVT growth ampoule is shown in Fig. 1 together with the conventional one. As to the conventional method, after the CdTe source is loaded into the growth ampoule, the two pieces of quartz tubes are burnt into sealing–connection at place A. During this operation, place B is cooled to avoid the oxidation of the source. However, several problems are encountered in this procedure.

Firstly, although the quartz tube is cooled, the oxidation of the source can not be completely prevented, because the source is so close to the place under burning. Secondly, volatile impurities evaporated from the quartz material easily condense on the source and on the inner surface of the cooled growth chamber.

For solving these problems, an extra segment having a capillary hole was put into the growth chamber as shown in Fig. 1. These three pieces were burnt into connection at place C for making the whole growth ampoule, while place D was cooled (step 1). Since the burnt place C is far away from the

Table 1
Glow discharge mass spectrometry analysis results (in mass ppb) for 6N Cd and the Cd highly purified by overlap zone melting (OZM)

Element	Al	Si	Cl	Fe	Ni	Co	Cu	Zn	In	Ti	Pb
6N Cd	1	4	390	17	30	<1	10	12	59	60	<10
CCd (OZM)	1	1	7	6	3	<2	<3	7	56	9	13

Table 2
Growth conditions of physical vapor transport for CdTe single crystals

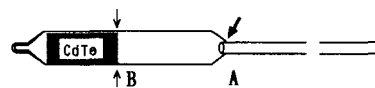|	
Growth temperature	1095 K
Reservoir (Cd) temperature	107 K
ΔT between crystal and source	3–4 K
Temperature gradient near the s–v interface	1–1.2 K/cm
Distance between crystal and source	4–6 cm
Seed	No
Inner diameter of growth ampoule	~ 13 mm
Growth rate	~ 0.25 mm/h

source, the heat transported to the source is much reduced and oxidation of the source is effectively inhibited. The contamination can be reduced extremely because the volatile impurities accumulated at place D under cooling and the path hole of the inner segment is very small.

The ampoule was then evacuated by turbomolecular pump. Under a vacuum of 10^{-3} Pa, the inner and the outer tubes were sealed at place E (step 2). No oxidation of the source could happen no matter how close the source was to the burnt place E. The volatile impurities, if there are any, could be extracted by the vacuum. On the other hand, the impurities, condensed at place D during step 1, had no
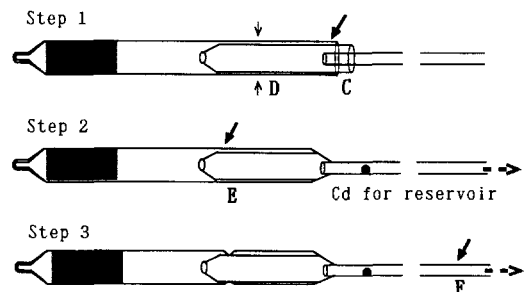

Fig. 1. PVT growth ampoules: (a) the conventional method and (b) the improved one.

ways to access the growth chamber and the source. Finally the ampoule was sealed at place F.

This process allows one chose the length of the growth chamber more freely, depending on the experimental motives or conditions. The whole ampoule-making operation became much easier and safer.

The PL at 4.2 K was measured at the cleaved planes of the crystals, as described previously [8]. CR and IR measurements were performed at 4.2 K and room temperature, respectively. The microwave setup for CR is a nonresonant reflection-type wave guide system working at 35 GHz. The excitation light was provided by a xenon flash lamp with a pulse width of 1 μs. The absorption spectra were obtained with a boxcar averager.

3. Results and discussion

Fig. 2 shows the changes of the PL spectra, measured on the crystals grown by VB using 6N Cd, with the solidification fraction (g). The PL spectra show a variety of emissions, which are assigned after the report by Molva et al. [9].

The dominant donors in the as-grown VB crystals are supposed being contributed by Cl and In, judging from the data in Table 1. However, they are not separable in their (D_0,X) emissions. Similarly, because the emission lines of $(A_0,X)_{Li}$ and $(A_0,X)_{Na}$
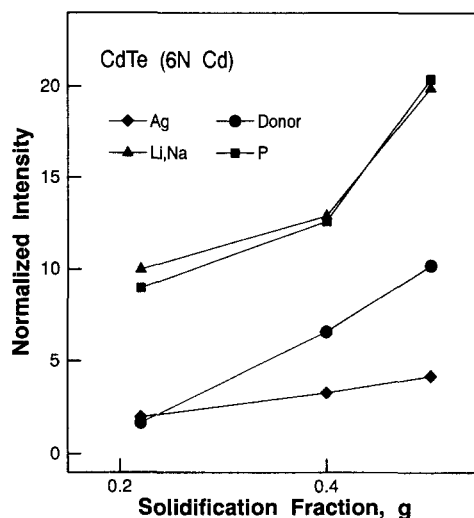

Fig. 3. Solidification fraction dependence of the emissions of some bound excitons normalized to FE-LO.

are very close, we do not assign this line more certainly. The emission of (A_0,X) at 1.5896 eV, commonly one of the dominant emissions in as-grown CdTe crystals, has been found being contributed by two origins [8]. One is Cu_{Cd} and the other is a V_{Cd}-related defect. In the case of the undoped VB crystal, this line is dominantly contributed by the V_{Cd}-related defect. At the low energy emission region, quite strong emissions of DAP and deep centers related to various impurities are observed.
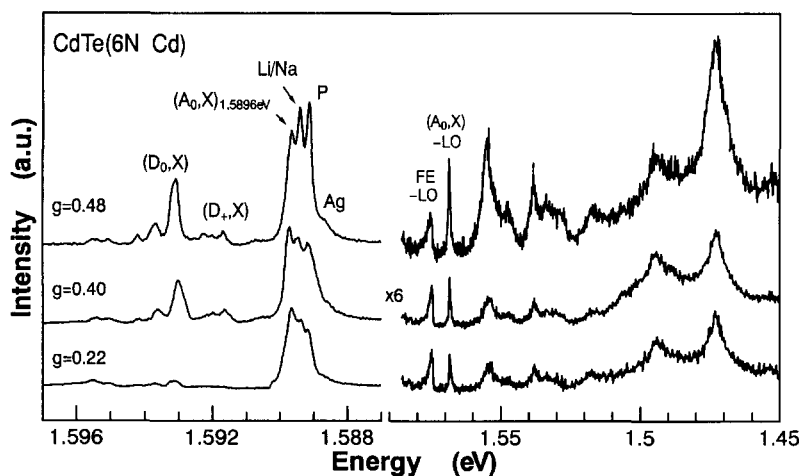

Fig. 2. The PL spectra of CdTe single crystals grown by VB using 6N Cd and Te, at three different solidification fractions (g).
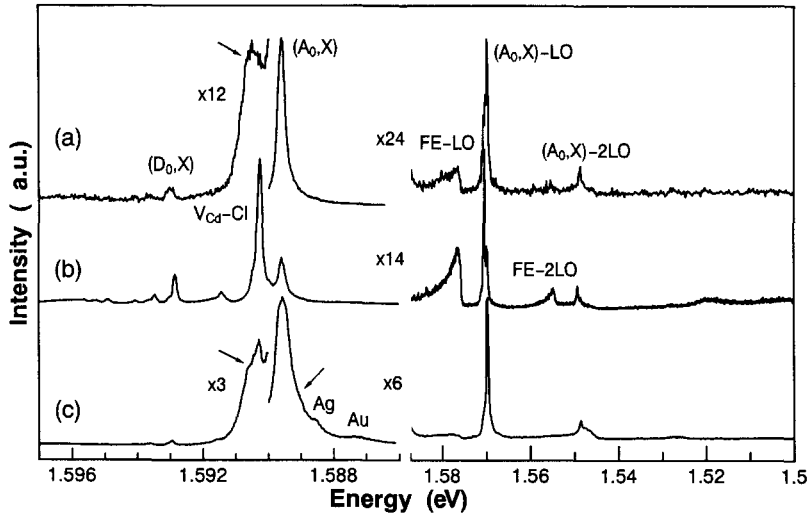
Fig. 4. The PL spectra of CdTe crystals: (a) grown by VB using high purity Cd, (b) grown by PVT using high purity VB crystal and (c) the residue after PVT growth

All emissions increase evidently with the solidification fraction (g). This observation confirms the distribution of most residual impurities due to their segregation behavior. In CdTe, almost all elements have segregation coefficients less than unity. The purest part of the crystal ingot locates in a g-range from 0.1 to 0.4, as seen in Fig. 3.

However, the increase of V_{Cd} concentration with g should not be neglected [10]. The higher $[V_{Cd}]$ provides an easier occupation of the metallic impurities on Cd sites, and consequently contributes to the increase with g of the emissions of (A_0,X), (D_0,X) and DAP. But, the increase with g shown also by $(A_0,X)_p$ indicates that the segregation is the main factor that accounts for this distribution, because a higher $[V_{Cd}]$ has no favor for P atoms to occupy Te sites.

The PL spectrum of the VB crystal grown from highly purified Cd, shown in Fig. 4, is in evident contrast to that of the crystal grown from 6N Cd. Except for FE-LO, only the emission of $(A_0,X)_{1.5896\,eV}$ along with its LO replica is observed in a very low background. The emissions of (D_0,X) and (D_+,X) are reduced to an unidentifiable level. The difference of the purity of the starting material is well exhibited in the resulting crystals. That also demonstrates the contamination level of our VB

growth is below the residual impurity level of 6N grade material.

The typical PL spectra of the single crystal and the residue of PVT growth are also presented in Fig. 4, and the photograph of a typical resulting crystal is shown in Fig. 5. The emissions related to Ag and Au, which are not observed in the VB crystal, appear in the PVT residue. This observation demonstrates the concentrating of the impurities in the residue. On the other hand, in the case of the PVT crystal, the emission of the dominant (A_0,X) is drastically reduced, and so are several unidentified emissions that evidently show in the VB crystal and/or the PVT residue, indicated by arrows in the figure. We attribute this efficient purification effect to the extremely low vapor pressures of these impurities compared with that of Cd and Te. The emission of (A_0,X) related to V_{Cd}–Cl [11] is observed as the
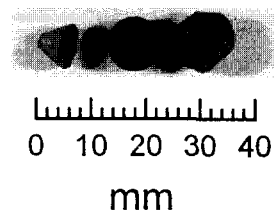

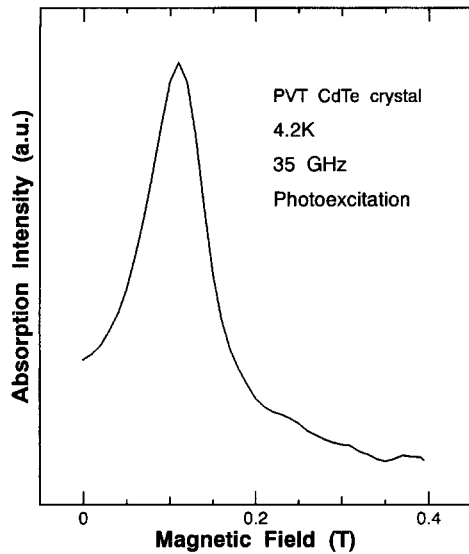Fig. 5. The photograph of a cleft single crystal grown by PVT.

Fig. 6. Cyclotron resonance absorption at 4.2 K.

dominant line. The emission of (D_0,X) is believed also mainly originating from Cl_{Te}. Reduction of Cl concentration can not be efficiently achieved in PVT growth, because Cl has relatively high vapor pressure and present in the vapor in some amount.

The emission line of FE-2LO is observed in a well defined shape and even as intense as (A_0,X)-2LO. The FWHM (full width at half maximum) of the dominant line is only about 0.2 meV, much less than 0.35 meV of the VB crystal. Both these results show the high quality of PVT single crystals.

A typical trace of CR at 4.2 K is shown in Fig. 6. The signal is taken at a delay time of 5 μs after the photopulse. The values of m^* and $1/\tau$ obtained from the signal of the photo-excited cyclotron resonance are $0.092 m_0$ and 7.6×10^{10} s^{-1}, respectively, where τ is the carrier relaxation time, m^* the effective mass of electron and m_0 its vacuum mass. A electron cyclotron mobility of 2.5×10^5 cm^2/V · s is obtained by the relation [12]

$$\mu = e\tau/m^* . \tag{1}$$

To our knowledge, this is the highest reported value, which shows the high perfectness of the crystal. Under photo-excitation, the electron scattering is dominated by neutral donors. The neutral donor concentration, N_D, of the p-type as-grown crystal is

derived to be 5×10^{14} cm^{-3} from the Erginsoy formula [12]

$$1/\tau = 20\hbar\, \alpha_B^* N_D/m^* , \tag{2}$$

where α_B^* is the effective Bohr radius of the shallow donor and we employed $\alpha_B^* \approx 60$ Å for the donor in CdTe.

All the donors are neutralized under photo-excitation; therefore, the obtained concentration of the neutral donors is almost equal to the total concentration of the donors. The direct estimation of the total concentration of donors or acceptors is generally unavailable by electrical methods such as Hall measurement, due to the unavoidable compensation between donor and acceptor.

The value of N_D was estimated in many works on the crystals grown by VB or THM [13]. However, because the shallow donors suffer much from the association with native defects such as V_{Cd}–D, which holds especially serious in the crystals grown by VB and THM, their results can not generally be used as the scale of the purity. The V_{Cd} is much inhibited by the usage of a Cd reservoir in our PVT growth and, consequently, the result is more close to the real value of total concentration of shallow donors.

The m^* was also determined in many works, however, the results were very scattered, ranging from 0.088 to $0.1054 m_0$ [14]. It is believed that the quality is the key factor for a precise determination.
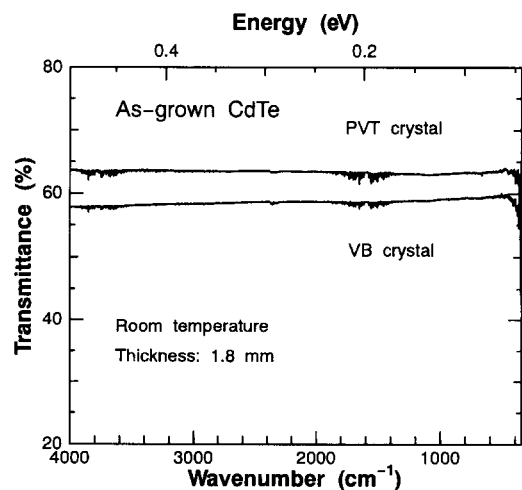

Fig. 7. The IR transmission spectra of CdTe single crystals grown by VB and PVT.

The m^* value, $0.092 m_0$, obtained in this work can be supposed more authentic because of the high perfectness of the crystal sample. Strictly speaking, this is a polaron mass but not a band mass in such a material as CdTe with a large electron–phonon coupling constant, α, of about 0.315 [15].

Fig. 7 shows the IR transmission spectra of the single crystals grown by VB and PVT, respectively. The transmittance of the PVT single crystal is very close to the theoretical maximum, 65%, in the whole energy range under study. The extinction of infrared light is dominated at higher energy by the scattering of precipitates and/or inclusions, and at lower energy by the absorption of free carriers (n-type) or intra-valence transition (p-type) [16]. The high IR transmittance of the PVT single crystal manifests that the precipitates and inclusions are greatly prohibited.

All above results demonstrate that the resulting PVT single crystals are not only extremely chemically pure but also structurally pure.

4. Conclusions

High quality CdTe single crystals are obtained by the improved PVT growth with a Cd reservoir, after refining of CdTe by the normal freezing of VB growth using highly purified Cd as starting material. The neutral donor concentration is 5×10^{14} cm^{-3} and the 4.2 K electron cyclotron mobility is as high as 2.5×10^5 cm^2/V · s, which demonstrates the high purity and high perfectness of the crystal.

The improved PVT growth is expected to be applied for the preparation of high quality CdTe single crystals in an applicable volume.

Acknowledgements

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