

Growth of $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ single crystals by vapor phase gas transport method

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Abstract

$\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ crystals were grown using vapor phase gas transport method (VPGT). The results show that dendritic crystals with grain size up to 3.5 mm can be grown with this technique. X-ray diffraction and Laue back-reflection patterns show that dendritic crystals are single-phase, whose single crystal grains are randomly oriented with respect to the gas-transport axis. Electrical measurements, carried out using Van der Pauw method, show that the as-grown crystals have resistivity of about $10^4 \Omega \text{ cm}$ and n-type conductivity.

Keywords: semiconductors, crystal growth, $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$, vapor phase gas transport

1. Introduction

In the field of wide band gap II-VI semiconductors, CdTe and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ (CZT) have received a lot of attention because of their high potential for many important applications, such as room temperature gamma and X-ray detectors [1], medical imaging spectrometers and laser windows [2, 3].

The theoretical calculations, supported by experimental observations, show that introducing zinc into CdTe structure stabilizes the Cd-Te bond, so that the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals grow with a lower dislocation density [4, 5]. However, growing of large single crystals of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ pseudo-binary compound has several difficulties, due to its inherent physical properties such as: (1) The large lattice mismatch of about 6.4%, between CdTe (6.4810 Å) and ZnTe (6.1037 Å), that may cause strain in the developing lattice; (2) The low stacking-fault energy, that promotes the generation of twins; (3) The significant difference between thermal conductivity (and also, diffusivity) of CdTe and ZnTe that can be the origin of phase segregation, and (4) the large segregation coefficient of zinc ($k = 1.35$) that generally results in variations in zinc concentration along the as-grown crystal [2, 6]. Because of the strong tendency of CZT crystals to develop defects such as sub-grain boundaries and precipitates, considerable efforts are made to grow high quality single crystals, and to reduce defective formation in this compound. Depending on their applications, CZT crystals are prepared using different methods such as: vertical gradient freezing

(VGF) [7], traveling heater method (THM) [5], various modifications of Bridgman method [8], physical vapor transport method (PVT) [9, 10], etc. Melt techniques, especially THM and high pressure Bridgman method (HPB), are currently used as the most convenient methods for growing of large CZT crystals, but they have some shortcomings, such as inhomogeneity in thermal field and thermal stress in grown crystals. Due to low growth temperatures, the crystals grown from the vapor phase have high purity and quality that is required by X-ray and γ -ray detectors [1]. The high purity of CZT crystals grown via vapor phase should be due to low vapor pressure of oxide impurities in comparison to the CZT, so that they don't evaporate during the growth process [11]. However, because of the low vapor pressure of tellurides, it is difficult to grow large CZT crystals from the vapor phase [5].

Several methods of preparing single crystals from the vapor phase have been used for growing CZT crystals, but no report is available on the growth of CZT using inert gas transport of vapor phase method which was used in this work for the first time. Since the optical, electrical, thermal and structural properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ compound are superior for concentrations around $x = 0.04$ [12, 13], we focused our attempt on growing $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ crystals.

2. Experimental procedure

2.1. Growth method

$\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ crystals were prepared using a modified

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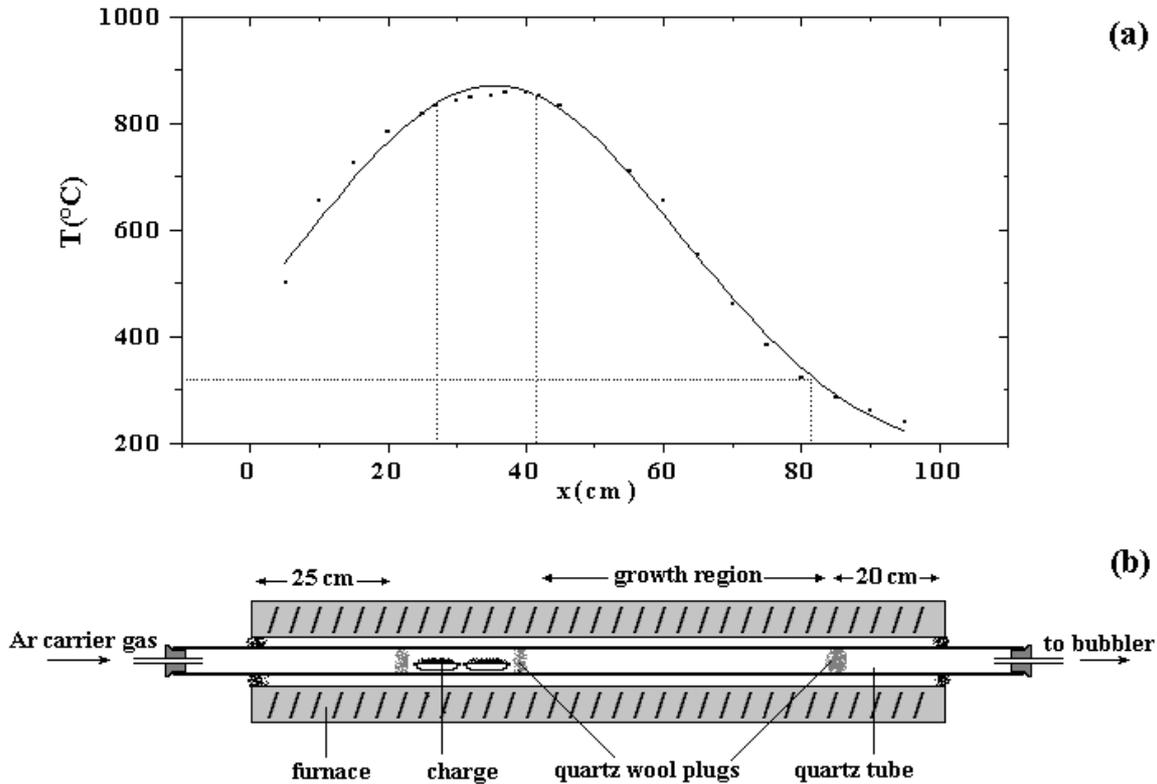


Figure 1. (a) Temperature profile of the furnace, with the growth chamber being present. (b) Configuration of the growth system.

vapor phase gas transport method (VPGT) as described by Lovett [14]. A horizontal tubular (with inner diameter of 6.5 cm) three-zone electric furnace was employed, each zone being about 33 cm long and their temperatures can be individually controlled to the accuracy of $\pm 1^\circ\text{C}$. In this furnace, the desired temperature profile can be deduced by setting the temperature of each zone at different values. A fused silica tube of inner diameter of 2.5 cm and 120 cm length was placed in the furnace as the growth chamber. Quartz is rigid and almost inert at the temperatures used for the CZT growth. The growth took place in this tube in the presence of the argon flow.

In order to obtain the desired temperature profile for growing of CZT crystals, the temperatures of the first and the central zones were preferably kept at 900°C and no power was supplied to the third zone. The temperature profile of the furnace in this situation is shown in Figure 1-a, a uniform temperature of about 850°C is extended over a region of 15 cm long, 25 cm far from the edge of the first zone.

The initial charges, 20 g of synthesized CdTe and ZnTe binary compounds were weighed in accordance to the $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ stoichiometry with excess amount of Te and Cd as required [15]. The charges were loaded into alumina boats and were placed in the region of uniform temperature. In order to enhance homogeneity of the vapor phase, the sides of this region were partly blocked by means of two quartz wool plugs. Also, a third

plug was positioned at the point of about 300°C for producing growth zone. The scheme of growth apparatus is shown in Figure 1-b.

By heating and sublimation of the charges and transporting the vaporized CdTe and ZnTe via continuous flow of argon through the growth chamber, which was entering the tube from the hot side (i.e. the left in the Figure 1-b) with a flow rate of 90 mlit/min., CZT crystals were depositing at the growth zone. The flow rate was chosen by trial and error, so that the vapor phase was transported to the growth zone and then deposited in a minimum length. At low rates, vapor of material would not be transported, and at high rates, the crystallization process would fail and the length of deposition region extends to the cooler end of the growth chamber. The growth process was accomplished within 5 days and these conditions were kept running throughout. In order to prevent generating of dislocation defects and thermal stress in the grown crystals [9], the furnace was switched off and the system was left to cool after cutting off the flow of argon.

2.2. Characterization

In order to determine the composition and crystal structure, some crystals were ground into powder of several microns size, and then they were characterized by X-ray diffraction, using a diffractometer with a resolution of 0.01 degree, operating at 35 kV and 20 mA with Mo-K_α radiation. The diffraction patterns were

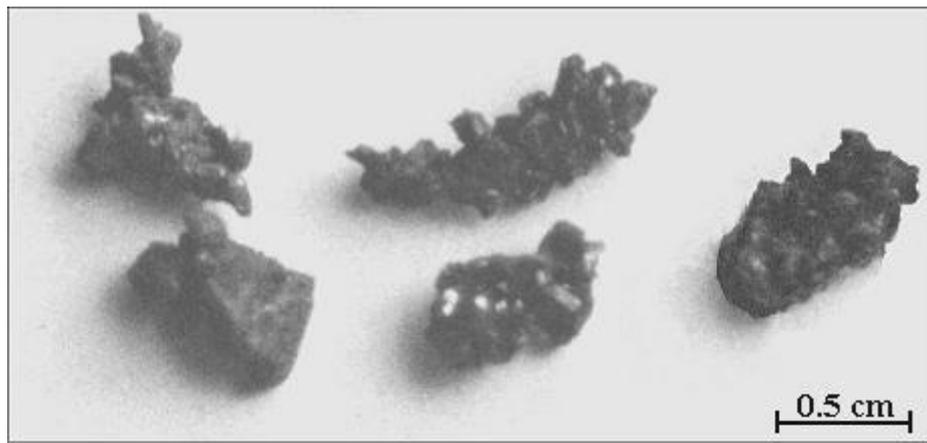


Figure 2. Photograph of some of the as-grown CZT single crystals.

simulated using CELREF software, a product of the LMGP research institute of Grenoble-France. The chemical composition of the final samples was confirmed using an X-ray fluorescence system (XRF, Philips X-UniqueII Model). For determining the orientation of as-grown crystals, and partly their crystallinity, the Laue back-reflection patterns of some crystals were taken, using a collimator of 1 mm diameter. In addition, high quality electron diffraction patterns were obtained from transmission electron microscopy (TEM, Leo 912-AB Model) of the fine edges of crystallites.

The electrical and transport properties of the as-grown crystals were determined using Van der Pauw-Hall measurements. Before carrying out these measurements, and in order to remove the damaged layer, the samples were etched mechano-chemically by 3% $\text{Br}_2\text{-CH}_3\text{OH}$ solution for 3-5 minutes followed by rinsing in dionized water. Many etch-pits have been observed on the etched surface, which indicate the extended presence of grain boundaries in the grown crystals. The good ohmic contacts were made on the etched surface using silver paint.

3. Results and discussion

It was observed that CZT dendrite crystals grow on the inner wall of the growth chamber over a region of about 10 cm. According to the temperature profile of the furnace (Figure 1-a), this region corresponds to the temperature range of $450 < T(^{\circ}\text{C}) < 650$. Although the amount of grown crystals decreased at cooler regions (where $T < 450^{\circ}\text{C}$), but the growth region was extended to about 320°C . The absence of any deposited material in the cooler end of the growth chamber indicates the properly applied temperature profile and the gas flow rate. By measuring the lost weight of the charge during the period of 5 days, the average growth rate was estimated over 0.003 g/min.

The crystals grew in a dendritic form at random angles with respect to the flow direction, due to self-nucleation. Some of the grown crystals are shown in

figure 2. These are composed of single crystallites of the average size up to 3.5 mm. The sharp-edges of the polyhedron form of the crystallites indicate the reasonable quality of as-grown crystals.

The X-ray diffraction pattern of powdered crystals, in the range of $2\theta = 5^{\circ}$ to 50° , is shown in figure 3. Diffraction peaks correspond exactly to $F\bar{4}3m$ space group which implies that the products are of high purity and single phase $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals. The deduced lattice constant was $a = 6.4634 \text{ \AA}$ with accuracy of 0.0001 \AA . The chemical composition of grown crystals (practically, zinc concentration) was estimated by assuming the validity of a linear dependence of the lattice constant and x fraction of zinc in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($a(x) = 6.482 - 0.379x$, Vegard's law [16]). In this manner, the zinc concentration was derived as $x = 0.05$, which is in good agreement with the nominal composition of the initial charges.

The typical electron diffraction and Laue reflection patterns of as-grown crystallites are shown in figure 4. The shape of patterns possessing distinct tissue and sharp spots confirms the products to be single crystals with high crystalline quality and that they are not distorted or twisted crystals.

The measured electrical and transport parameters of grown CZT crystals are shown in Table 1. It is found that the obtained crystals are n-type semiconductors for which the resistivity is about $2 \times 10^4 \Omega\cdot\text{cm}$, the carrier concentration is in the order of 10^{14} cm^{-3} and their mobility is about $12 \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature. These values were compared to the reported data for the crystals of this material grown by other methods in Table 1. Clearly, the electrical resistivity of CZT crystals strongly depends on their growth method.

The low resistivity of as-grown crystals may be of two origins. The higher density of sub-grain boundaries in present samples, usually being Te-rich and having metallic characteristic, is considered as the first cause [17] and the high purity of the grown crystals is regarded as the second one. In fact some impurity and defects, which introduce deep levels and so improve the

Table 1. The electrical and transport properties of the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals grown in this research, compared to the crystals grown by other methods.

Growth method	PVT ^a	PVT ^b [18]	PVT ^c [19]	VB ^d [6]	VB ^e [6]	HPB [3]
Zn concentration (x)	0.05	0	0.05	0.04	0.04	0.1
Contact	Ag	Au	-	-	-	-
Conduction type	n	p	-	p	n	p
Resistivity ($\Omega\cdot\text{cm}$)	2×10^4	1×10^3	8.2×10^8	40-300	< 1	up to 10^{11}
Carrier concentration (cm^{-3})	2.5×10^{14}	8×10^{13}	-	2×10^{14} - 5×10^{15}	1×10^{16}	-
Carrier mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	12	81	-	30-100	680	50

^a This work, ^b Vapor phase growth in semi-closed system by a modified Markov method, ^c Seeded vapor phase growth in semi-closed system, ^d Vertical Bridgman method in sealed quartz ampoule, ^e Vertical Bridgman method in graphite crucible.

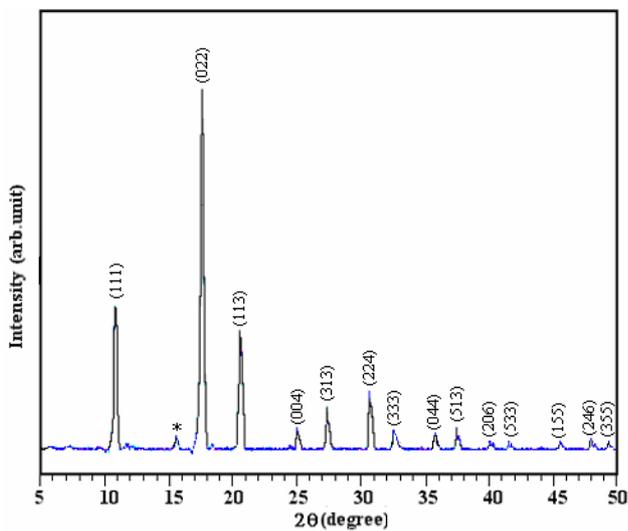


Figure 3. X-ray diffraction pattern of the as-grown $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$ crystals, taken by $\text{Mo-K}\alpha$ line ($\lambda = 0.7093 \text{ \AA}$). Miller indices of the peaks correspond with the space group of cubic structure $F\bar{4}3m$. The peak with an asterisk belongs to the forbidden diffraction of (211) plane, which appears in some compounds with the zincblende structure.

resistivity of CZT crystals [18], seem to be reduced in our crystals due to growth conditions, especially because of the low growth temperature. As the conductivity is proportional to the carrier concentration, one might expect that the resistivity should decrease with the total impurities concentration. However, experimental results indicate that some impurities, such as Al, Mn and Ga, improve the resistivity of CZT crystals, while others, such as Li, Na and Cu, reduce it [8]. In fact, dc-conductivity is proportional to the product of the carrier concentration, N , and the average lifetime of carriers, τ ($\sigma = Nq^2\tau/m^*$) that both can be affected by impurities concentrations. The Al, Mn and Ga impurities are deep donors and form deep levels near the middle of the band gap, which are effective recombination centers for

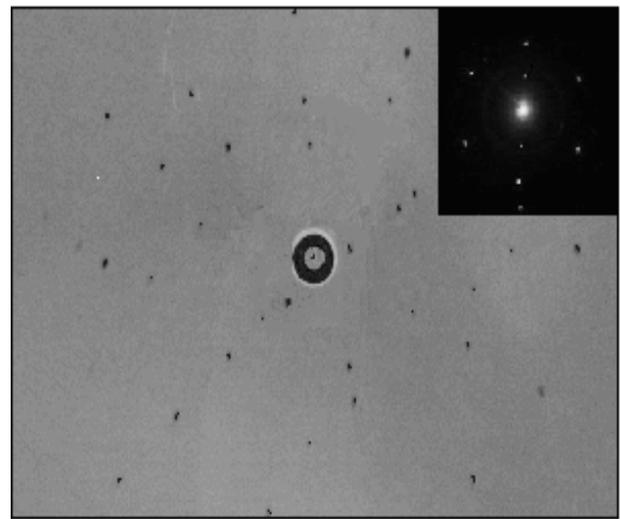


Figure 4. Back-reflection Laue pattern of the as-grown $\text{Cd}_{0.95}\text{Zn}_{0.05}\text{Te}$ single crystals. Inner part is a typical transmission electron diffraction pattern.

carriers, and therefore decrease the lifetime and also the conductivity. While for the Li, Na and Cu impurities increasing in the carrier concentration is dominant, so that the conductivity improves. Hence, the final effect of each impurity on the conductivity of a CZT crystal is determined by the compromise between increasing in the carrier concentration and decreasing of the lifetime. It should be noted that, although some impurities improve the resistivity of CZT crystals, it doesn't mean that they are appropriate for all of the CZT applications, as the decrease of carrier's life-time, caused by them, is harmful for detectors performance. Similarly, the relatively low mobility of the electrons in the as-grown crystals, compared to the reported data in Table 1, can be attributed to the extended presence of sub-grain boundaries which has been visually confirmed by the extended presence of etch-pits. Sub-grains and other extended defects can act as scattering and trapping

centers, and so affect the electrical and transport properties of crystals [9].

4. Summary and conclusions

In this work, the growth of Cd_{0.96}Zn_{0.04}Te single crystals using VPGT method in an open ended quartz tube was reported for the first time. The structural analysis of the as-grown crystals, carried out by X-ray diffraction and Laue back-reflection methods, indicates the relatively

perfect crystallinity of CZT crystals. Comparison of electrical and transport properties of as-grown crystals by other bulk growth methods show that, although the crystalline perfection of CZT crystals is improved using VPGT method, their electrical properties is degraded due to smallness of the crystallites and hence extended presence of sub-grains.

References

1. O Limousin, *Nucl. Instr. and Meth. A* **504** (2003) 24.
2. Shi-fu Zhu, et al., *J. Crystal Growth* **208** (2000) 264.
3. Y Eisen, A Shor, *J. Crystal Growth* **184/185** (1998) 1302.
4. S B Qadri, E F Skelton, A W Webb, J Kennedy, *Appl. Phys. Lett.* **46** (1985) 257.
5. J J Pérez Buenno, et al., *J. Crystal Growth* **209** (2000) 701.
6. Arun Kumar Grag, Meenakshi Srivastava, R C Narula, R K Bagai, Vikram Kumar, *J. Crystal Growth* **260** (2004) 148.
7. T Asahi, O Oda, Y Taniguchi, A Koyama, *J. Crystal Growth* **161** (1996) 20.
8. Guoqiang Li, Wanqi Jie, Tao Wang, Ge Yang, *Nucl. Instr. and Meth. A* **534** (2004) 511.
9. W Palosz, et al., *J. Crystal Growth* **254** (2003) 316.
10. A A Melnikov, et al., *J. Crystal Growth* **197** (1999) 666.
11. M Schieber, et al., *J. Crystal Growth* **231** (2001) 235.
12. M Schieber, et al., *J. Crystal Growth* **237** (2002) 2082.
13. M E Rodríguez, A Gutiérrez, O Zelaya-Angel, C Vázquez, J Giraldo, *J. Crystal Growth* **233** (2001) 275.
14. D R Lovett, *J. Matter. Sci.* **7** (1972) 388.
15. Yu M Ivanov, *J. Crystal Growth* **194** (1998) 309.
16. David K Ferry, "Semiconductors", New York, Macmillan, (1991).
17. T E Schlesinger, et al., *Mater. Sci. Eng.* **32** (2001) 103.
18. T Kunz, M Laasch, J Meinhardt, K W Benz, *J. Crystal Growth* **184/185** (1998)1005.
19. M Fiederle, et al., *Nucl. Instrum. Methods A* **434** (1999) 152.