



Te PRECIPITATES AND IMPURITY GETTERING EFFECT IN CdZnTe (Zn ~ 4%) CRYSTALS

Kulkarni Gururaj Anand

S.D.M.C.E.T., Dharwad, Karnataka, India

ABSTRACT

It is well known that HgCdTe (MCT) is an important infrared (IR) detector material to which CdZnTe (Zn ~ 4 %) is a lattice-matched substrate, for the MCT epitaxial growth. But the as grown CdZnTe crystals suffer from Te precipitates, cadmium vacancies and impurities. While Te precipitates reduce IR transmission in the 3 to 5 μm range, free carrier absorption plays the major role beyond 6 μm towards the longer wavelength region. In this connection Te precipitates have been studied in the as grown CdZnTe (Zn ~ 4 %) crystals using Fourier Transform mid-Infrared (FTIR) spectroscopy, micro - Raman spectroscopy and Differential Scanning Calorimetry (DSC) for their qualification, quantification and understanding their nature. Strong absorption around 2661 cm^{-1} in the FTIR spectrum (which corresponds to the band gap of Te) at 300K confirms the presence of Te precipitates. This is further substantiated by the presence of Raman modes of Te in the micro-Raman spectrum of CdZnTe. Low temperature IR transmission measurements have been carried out to resolve the features observed at room temperature, which show two more absorption lines at 3262 and 2294 cm^{-1} . These are correlated with the impurity related absorptions. Differential Scanning Calorimetry has been used to quantify the tellurium precipitates. The thermograms of CdTe, CdZnTe crystals show endothermic peaks at 440.6, 446.7 $^{\circ}\text{C}$ respectively, a deviation from the melting point of elemental tellurium. This has been attributed to the possible diffusion and hence gettering effect of impurities around Te precipitates during the growth process. To further understand the above results, Energy Dispersive X-ray Analysis (EDAX) was performed to check for the composition of these materials and point EDAX around Te precipitates to quantify the impurities and the preliminary results are reported.

KEYWORDS CdZnTe, HgCdTe, Te precipitates, EDAX, FTIR, DSC etc.

INTRODUCTION

CdTe and CdZnTe crystals are being intensively studied for their fundamental importance and the technological applications such as x - ray, γ - ray detectors, electro-optic modulators and laser windows.¹ $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ ternary crystals are the principle substrates for growing $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epitaxial layers due to their chemical and crystallographic compatibility with $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayers², subsequently on which infrared (IR) sensors are fabricated. Basically our focal plane arrays (FPAs) are backside illuminated, with the device connected to underlying silicon multiplexer, using a matrix of indium bumps. Thus the substrate should have high IR transmission to pass the radiation on to the detector for collection. Theoretically estimated value of IR transmission is about ~ 66% in these materials.³ To practically realize this, CdZnTe substrate should have high crystalline quality. However the as grown CdZnTe crystals suffer from cadmium vacancies, tellurium precipitates and impurities due to high growth temperature and phase diagram limitations.⁴ Single crystals of CdTe have a low absorption coefficient, $\alpha = 0.0002 \text{ cm}^{-1}$, in the 0.85 – 30 μm region of the IR spectrum.⁵ Extrinsic factors affecting α are (i) impurities (ii) free carriers (iii) scattering by precipitates. Although vertical Bridgman method usually results in undoped crystals, CdTe and CdZnTe crystals exhibit p-type conductivity with a high carrier concentration and the presence of tellurium inclusions/precipitates due to retrograde solid solubility curve in the phase diagram.

Although extensive efforts have been made in the area of purification of the CdZnTe crystals by using 7N pure starting materials, still impurity pick up during the crystal growth due to high temperature melt growth affects α . In the earlier studies tellurium precipitates were identified by Auger spectroscopy and x-ray diffraction studies.⁶ Although annealing studies have been carried out to minimize or eliminate the Te precipitates, most of the times it has failed to yield stoichiometrically good crystals. Thus understanding of the exact nature of tellurium precipitates is mandatory to improve the quality of CdZnTe crystals and their yield. In this connection CdZnTe crystals have been studied for the quantification of Te precipitates and understanding their nature by various physical characterization techniques.

EXPERIMENTAL PROCEDURE

Undoped bulk CdTe and $\text{Cd}_{0.96}\text{Zn}_{0.04}\text{Te}$ crystals were grown by Asymmetrical Bridgman growth method using evacuated, sealed carbon-coated quartz ampoules, in three-zone furnace. The details of the growth are depicted elsewhere.⁷ Samples polished to mirror finishing and having tellurium precipitates were used in the present study for understanding the nature of Te precipitates and impurity related absorptions. Fourier transform infrared (FTIR) absorption spectra were recorded over 400 – 4500 cm^{-1} range using BRUKER's (IFS) 66V/s spectrometer at a resolution of 4 cm^{-1} . Micro-Raman scattering measurements were carried out in the backscattering

geometry with the 514.5 nm line of an argon ion laser at a power level of ~ 50 mW. The spectra were recorded using DILOR XY Spectrometer equipped with a liquid nitrogen cooled CCD. Differential Scanning Calorimeter (DSC) measurements were performed on a 2920 MDSC V2.6A (TA Instruments) with sample of about 18 mg sealed in an aluminum pan under nitrogen atmosphere.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR transmission spectra of CdZnTe crystal (B) and that of elemental tellurium (C) measured at 300 K. Strong absorption around 3.76 μm corresponding to the band gap of tellurium (0.33 eV) indicates the presence of tellurium precipitates.⁴ Clearly this falls in the

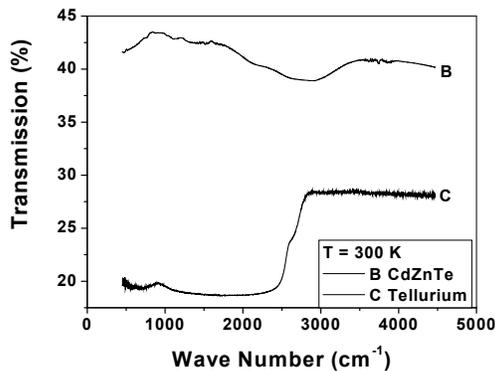


Figure 1: FTIR transmission spectra of CdZnTe and elemental tellurium at 300K

Micro-Raman spectroscopy was carried out to confirm the presence of Te precipitates and identify their symmetry. Both CdTe and CdZnTe samples showed two strong Raman modes centered around 121(A_1) and 141(E) cm^{-1}

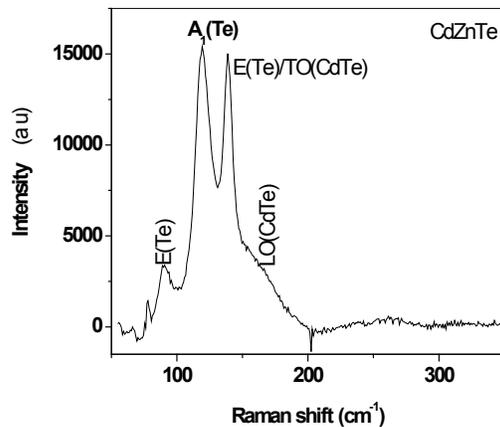


Figure 3: Micro Raman spectrum of CdZnTe

Figure 4 shows the FTIR transmission spectra of CdZnTe collected at 80 K (B) and 300 K (C) respectively. In addition to the room temperature features, there are two more absorption lines at 3262 and 2294 cm^{-1} . The absorption at 2294 cm^{-1} can be attributed to $\text{Fe}(\text{d}^6)$ impurity in CdZnTe. This assignment is in comparison with the respective values of the main absorption lines

3 to 5 μm range atmospheric window, thus deteriorating the MCT device performance.⁸

Figure 2 shows the FTIR transmission spectra of CdTe at 300K. Here monotonic decrease in transmission is to be seen with decreasing wave number. Such a behavior is due to the presence of Cd vacancies, thus indicating p-type behavior. The trend can be explained using the intervalence band transition i.e. an electron in the light hole band can be excited to the heavy hole band by absorbing a photon. Obviously the presence of Cd vacancies leads to the formation of tellurium precipitates confirming their presence.⁹

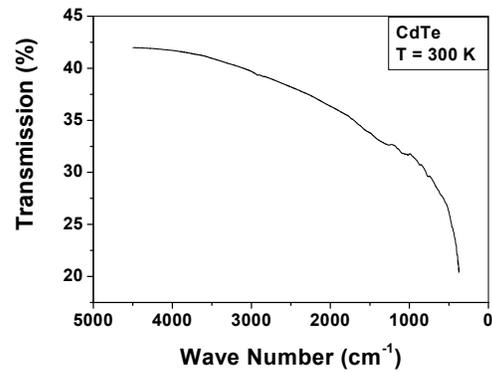


Figure 2: FTIR transmission spectra of CdTe at 300K

and a weak mode around 92(E) cm^{-1} indicating the presence of trigonal lattice of Te, along with Raman modes of CdTe at 141 (TO) and 168 (LO) cm^{-1} as shown in **Figure 3**.⁴

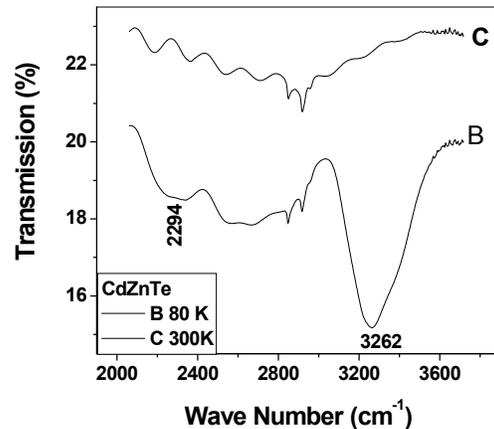


Figure 4: FTIR transmission spectra of CdZnTe collected at 80 K (B) and 300 K (C)

reported for $\text{Fe}(\text{d}^6)$ in CdTe, ZnTe and taking the shift of the energy position of the main absorption line, while moving from CdTe to ZnTe solid solutions.¹⁰ The absorption at 3262 cm^{-1} may be attributed to singly ionized cadmium vacancies.¹¹

Figure 5(A) shows the Differential Scanning Calorimeter endothermic peak at 440.6 $^{\circ}\text{C}$ in case of CdTe. An

endothermic peak is also observed in CdZnTe at 446.7 °C as shown in **Figure 5(B)**. Clearly this is a deviation from the melting point of Te, which is reported to be at 449.5 °C.¹² This may be attributed to diffusion and hence gettering effect of impurities at Te precipitates during the growth process.⁷ Thus DSC is very useful in understanding the nature of Te precipitates. Using the integrated area under the curve (melting peak) and the value, $\Delta H_f = 25.3$ cal/g for the enthalpy of fusion of Te,

the concentration of Te precipitates can be estimated.¹³ The values are 0.041, 0.048 wt. % for CdTe and CdZnTe respectively. Energy Dispersive X-ray Analysis (EDAX) was carried out to check for the composition of the materials. The results are shown in **Table I**. Since the resolution of EDAX is poor, quantification of impurities needs to be cross-checked with other high-resolution measurements.

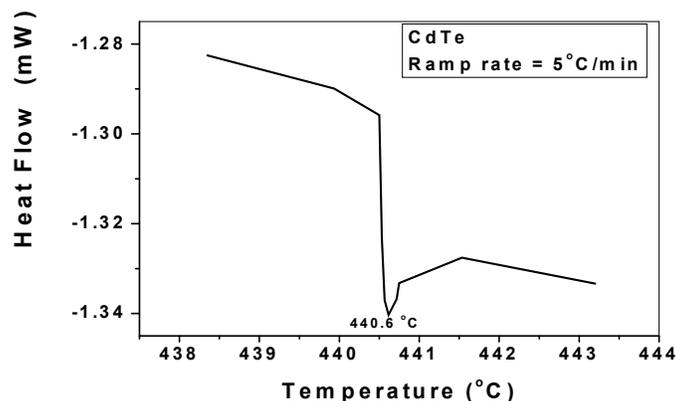


Figure 5(A): DSC thermogram of CdTe

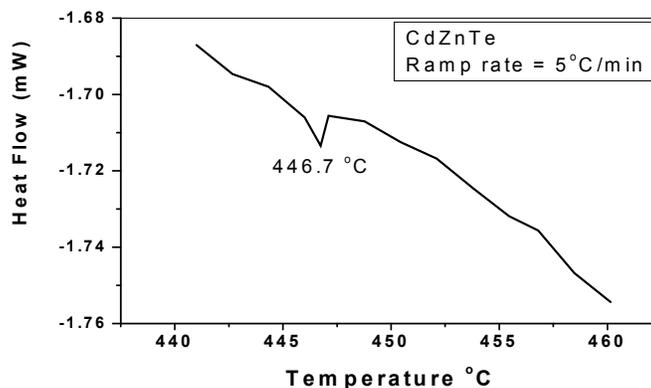


Figure 5(B): DSC thermogram of CdZnTe

Table I

Element	Composition in Wt %	
	CdZnTe	CdTe
O K	0.92	0.68
Si K	0.89	0.43
Cd L	43.45	44.95
Te L	50.86	52.58
Fe K	0.93	1.35
Cu K	0.51	0.00
Zn K	2.44	-
Total	100.00	100.00

CONCLUSIONS

CdZnTe crystals have been studied for the quantification of Te precipitates and understanding their nature by various physical characterization techniques. Strong absorption around 2661 cm^{-1} in the FTIR spectrum at

300K confirms the presence of Te precipitates. The presence of Te precipitates was further substantiated by the appearance of the micro-Raman modes of Te in CdZnTe crystals. Low temperature IR transmission measurements have been carried out to resolve the features

observed at room temperature. In addition to the room temperature features, there are two more absorption lines at 3262 and 2294 cm^{-1} . These are correlated with the impurity related absorptions. DSC is able to reveal about the possible impurity gettering effect around tellurium precipitates. Although EDAX is able to quantify the impurities, however because of its poor resolution, the impurities need to be probed by other high-resolution measurements.

ACKNOWLEDGEMENT

We acknowledge DST national FTIR facility and DSC central facility of I.I.Sc., Bangalore for conducting the experiments and SSPL, Delhi for the samples.

REFERENCES

- 1 K. Zanio, Semiconductors and Semimetals, edited by R.K. Willardson and A.C. Beer (Academic, New York, 1978), Vol. **13**
- 2 A.A. Khan, W.P. Allred, B. Dean, S. Hooper, J.E. Hawkey and C.J. Johnson, J. Electron. Mater. **15**, 181 (1986)
- 3 S. Sen, D. R. Rhiger, C. R. Curtis, M. H. Kalisher, H. L. Hettich, and M. C. Currie, J. Electron. Mater. **30**, 611 (2001)
- 4 G.A.Kulkarni, V.G. Sathe, K.S.R.K. Rao, D.V.S. Muthu and R.K. Sharma, J. Appl. Phys. **105**, 063512 (2009).
- 5 T.F. Deutsch, J. Electron. Mater. **4**, 663 (1975)
- 6 S.H.Shin, J. Bajaj, L.A. Moudy and D.T. Cheung, Appl. Phys. Lett. **43**, 68 (1983)
- 7 A.K. Garg, M. Srivastava, R.C. Narula, R.K. Bagai, V. Kumar, J. of Crystal Growth **260**, pp.148 – 158 (2004)
- 8 R.K. Bagai and W.N. Borle, J. Crystal Growth, 94(2), pp. 561-564 (1989)
- 9 S.Sen, D.R. Rhiger, C.R. Curtis, M.H. Kalisher, H.L. Hettich, M.C. Currie, J. Electron. Mater., 30(6), pp. 611- 618 (2001)
- 10 J.M. Baranowski, J.W. Allen and G.L. Pearson, Physical Review 160(3), pp. 627 - 632 (1967)
- 11 P. Emanuelsson, P. Omling, .B.K. Meyer, M. Wienecke, M. Schenk, Physical Review B, **47(23)**, pp. 15578-15580 (1993)
- 12 D.R. Lide, “CRC Hand book of Chemistry and Physics”, 79th Edn., CRC Press, Boca Raton, pp. 4 – 122 (1998 – 1999)
- 13 J. Zhu, X. Zhang, B. Li, J. Chu, Infrared Physics and Technology **40**, pp. 411- 415 (1999)