

Fabrication and Characterization of $\text{Cd}_{0.4}\text{Sn}_{0.6}\text{Te}$ Thin Films Grown by Hot Wall Evaporation

T. Venkatachalam¹, S. Ganesan²

¹Department of Physics, Coimbatore Institute of Technology, Coimbatore-641014, India

²Department of Physics, Government College of Technology, Coimbatore-641013, India

Received 9 August 2006

Abstract. The cadmium tin telluride compound was prepared by direct reaction of its high purity elemental constituents using rotating furnace. Thin films were fabricated on glass substrates by hot wall vacuum evaporation technique. The X-ray diffraction studies revealed that all the films are face centered cubic structure. The EDAX studies showed the composition as $\text{Cd}_{0.4}\text{Sn}_{0.6}\text{Te}$. The UV-Vis-NIR optical transmittance spectrum of thin films of different thickness and different substrate temperatures were obtained and it was found that the optical band gap decreases with increase in substrate temperature and thickness of films.

PACS number: 68.60.Dv; 78.66.Bz

1 Introduction

Micro and optoelectronic devices, such as light emitting diodes and photo detectors, operating in the spectral regions from visible to far infra red attract much of the current research on the different wide-gap and narrow-band semiconductors and their compounds. In 1962 De Nobel and Kroger listed the possible applications of cadmium telluride (CdTe) and its alloys [1]. In the recent years CdTe and its alloys are principally used in the field of radiation detectors for Infrared rays, X-rays and gamma rays and photo refractive devices for a wide range of applications, including medical imaging, environmental monitoring and nuclear science. There has been a considerable amount of interest in the application of the graded structure such as $\text{CdTe}_{1-x}\text{S}_x$, $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ and $\text{CdS}_x\text{Se}_{1-x}$ in the thin film technology. Tin is well-known to present a semi metallic and thermodynamically stable phase below 285 K with a diamond structure (α -phase)

and to transform into a metallic phase (β -phase) for temperatures above 285 K. Two molecules such as InSb and CdTe are good choices to combine with Sn, since their good lattice parameter matches with α -Sn [2-4]. Thin films of cadmium tin telluride belong to the family of II-IV-VI ternary semi conducting compounds and find wide range of applications in optoelectronics, microelectronics, sensors and solar cells [5,6]. The energy band gap of CdTe and α -Sn are 1.45 eV and 0 eV [7]. As far as the authors knowledge goes not much practical work has been reported on the selected alloy $\text{Cd}_{0.4}\text{Sn}_{0.6}\text{Te}$ and their thin films. Theoretical works in this alloy $\text{Cd}_x\text{Sn}_{1-x}\text{Te}$ with various values of ' x ' (0 to 1) have reported [8-10] such as structure, bonding character of individual valence bands, lattice constants, electronic charge density and bulk moduli. In the mixed system $\text{Cd}_x\text{Sn}_{1-x}\text{Te}$, the transition from a ten-electron ($x = 0$) to an eight-electron system ($x = 1$), a change in the crystal structure from rock salt (SnTe) to zinc blende (CdTe) and the calculated results confirm regard's rule and give a crossover from rock salt to zinc blende. A detailed report on the structural and optical properties of this cadmium tin telluride material is missing so far. This paper investigates the influence of Sn on CdTe by means of structural and optical studies using X-ray diffractograph (XRD), scanning electron microscope (SEM), energy dispersion analysis by X-ray diffraction (EDAX) and spectrophotometer. The energy band gap can be adjusted to any value between 1.45 eV and 0 eV by varying the concentration of tin. This range of values of band gap energy is optimum for fabrication of good quality solar cells, IR sensors and *etc.* These films can be prepared by different processes like vacuum evaporation, chemical bath deposition, electrochemical deposition, molecular beam epitaxy, *etc.* [11-15] The purpose of this investigation is to search for new thin film material, which can be used as an absorption layer of IR sensors and solar cells. We have tried hot wall deposition process [16-19] for the deposition of $\text{Cd}_{0.4}\text{Sn}_{0.6}\text{Te}$ thin films on glass substrate with different substrate temperatures and different thicknesses.

2 Hot Wall Epitaxial System

Epitaxy is a way of depositing thin films maintaining the perfect crystalline order of the substrate. Epitaxial growth of simple crystalline films can be realized with the following method: hot wall epitaxy, vapor phase epitaxy, liquid phase epitaxy, and molecular beam epitaxy. Hot wall epitaxial system is concerned with the fabrication of thin films under conditions close to thermodynamic equilibrium and with the minimum loss of material. Epitaxial growth of II-VI and IV-VI compounds by this technique has been discussed by many authors [20-27]. The substance is placed stationary at the bottom of the quartz tube and substrate is placed on the open end at the top of the hot wall. Three resistive windings serve to heat the substrate, source and wall of the tube independently. The whole apparatus is placed in vacuum as shown in the schematic diagram

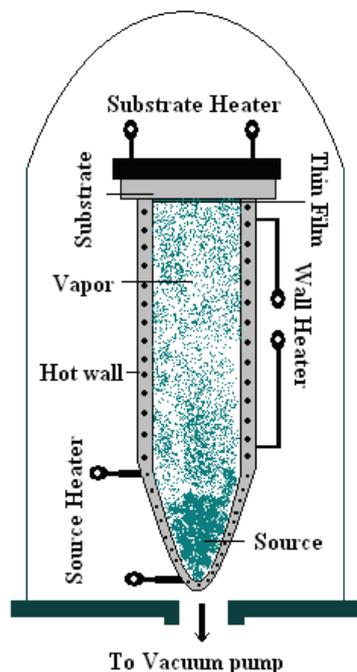


Figure 1. Schematic diagram of hot wall system.

(Figure 1). The main feature of the system is the heated linear quartz tube of diameter 1 cm which serves to enclose and direct the vapor from the source to the substrate, so that the molecular flow in the tube is close to thermodynamic equilibrium.

3 Experiment

The bulk $Cd_{0.4}Sn_{0.6}Te$ alloy is prepared by direct reaction of high purity elemental Cadmium, Tin and Tellurium (99.9999% sigma Aldrich USA). Stoichiometry amounts of the elements (Cd, Sn and Te) are taken in a quartz ampoule, evacuated with the help of vacuum coating unit (Hind Hivac – India) as shown in Figure 1 (Schematic diagram) to a vacuum of 10^{-4} torr and sealed. The sealed quartz ampoule is then placed in a rotating furnace. The ampoule is gradually heated at the rate of 100 K per hour up to 1173 K and then allowed to cool at the same rate to room temperature. During the time of heating and cooling the quartz ampoule is rotated continuously at the rate of 12 rpm to ensure homogeneity in the molten mixture. Thus the $Cd_{0.4}Sn_{0.6}Te$ bulk compound is prepared by direct reaction. A quartz tube of length 8cm and of diameter 1cm is taken. The bottom end of the quartz tube is shaped in such a way that it rests inside

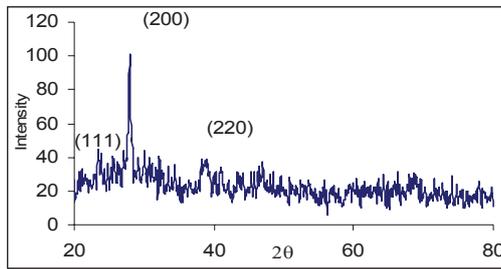


Figure 2. X-ray Diffractogram of $Cd_{0.4}Sn_{0.6}Te$ thin film deposited at 350 K.

the tungsten conical basket (source heater). The wall windings are done using canthal wire of 1mm diameter, which supports the quartz tube also. The canthal wire is wound along the length of the quartz tube to provide uniform temperature. Care is also taken to avoid any cold areas within the reactor tube as this would adversely affect not only the rate of deposition but also the stoichiometry of the deposited films. The quartz tube is charged with $Cd_{0.4}Sn_{0.6}Te$ compound. The substrate is held at a distance less than 1mm exactly above the open end

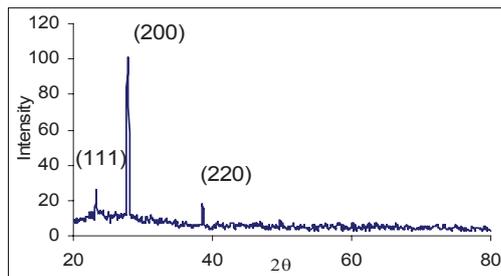


Figure 3. X-ray Diffractogram of $Cd_{0.4}Sn_{0.6}Te$ thin film deposited at 423 K.

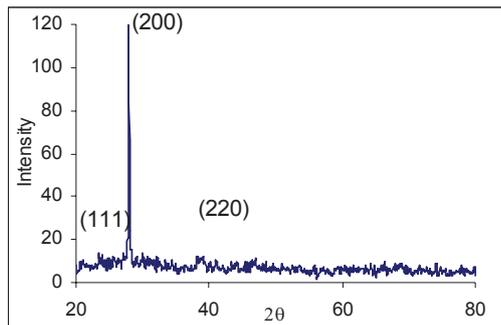


Figure 4. X-ray Diffractogram of $Cd_{0.4}Sn_{0.6}Te$ thin film deposited at 473 K.

Cd_{0.4}Sn_{0.6}Te Thin Films Grown by hot Wall Evaporation

of the quartz tube. The entire hot wall setup is placed inside the vacuum chamber. The pressure inside the vacuum chamber is reduced to 10^{-5} torr. After the wall temperature is stabilized, the source temperature is slowly raised to the required level. Cd_{0.4}Sn_{0.6}Te thin films have been deposited with wall temperature around 700 K and the source temperature around 950 K. Hence, the molecules, which evaporate from the source at the bottom of the tube, hit the substrate and thus describe linear paths inside the tube before reaching the substrate. The temperature has been measured using a Chrome/Alumel thermocouple. Due to radiation from the hot wall of the quartz tube, the substrate temperature raised to 350 K during the deposition. This deposition procedure is repeated by keeping the temperature of substrate as 423 K and 473 K. The thicknesses of the films are measured by using multiple beam interferometer. The structural properties of the thin films are studied by using a X-ray diffractometer (model Bruker D8 Advance). The X-ray diffractograms of thin films deposited at different temperatures are shown in Figures 2–4. The crystallite sizes are calculated using the Debye–Scherrer equation. Microstructural investigations of thin films on glass substrate are carried out using Scanning Electron Micrograph (SEM JOEL – Japan). The specimen is mounted on a stub and a thin layer of gold is sputtered onto it. These stubs are then fixed on the viewing stage of the SEM having XYZ movement as well as rotation and tilt facility. The SEM chamber is evacuated to achieve vacuum $\sim 10^{-5}$ torr before switching on the electron beam. The specimen is scanned thoroughly at a lower magnification in order to see the uniformity of film and then with higher magnification the SEM micrographs are

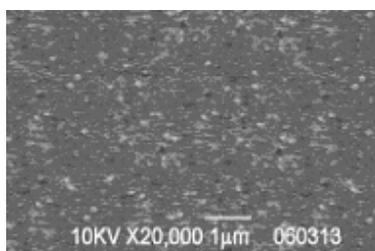


Figure 5. SEM micrographs of Cd_{0.4}Sn_{0.6}Te thin film deposited at 350 K.

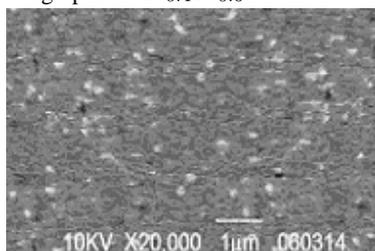


Figure 6. SEM micrographs of Cd_{0.4}Sn_{0.6}Te thin film deposited at 473 K.

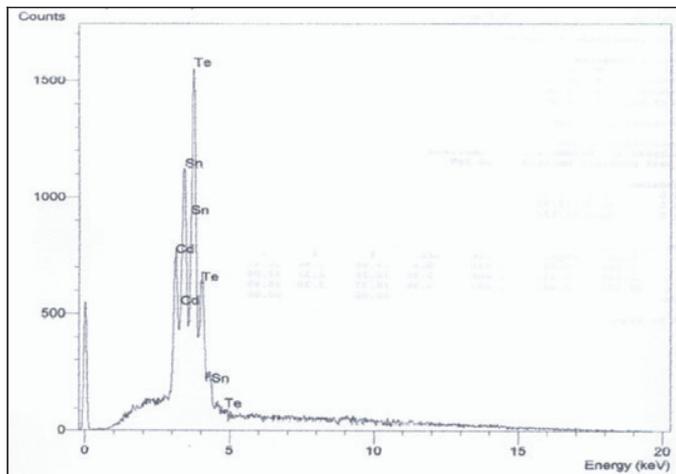


Figure 7. EDAX pattern of $Cd_{0.4}Sn_{0.6}Te$ alloy.

recorded. The SEM micrographs of thin films deposited at temperature 350 K and 473 K are shown in Figures 5 and 6. Composition of the bulk and films are estimated by EDAX measurements and it is found to be 20.49% and 30.06% and 49.45%. The EDAX spectrum is shown in Figure 7. The optical studies are made on the films deposited on glass substrates in the wavelength range from 190 nm to 2500 nm at room temperature by using Spectrophotometer (JASCO-370V). The transmission vs. wavelength was recorded for all the thin films of different thicknesses and different substrate temperatures as shown in Figures 8–10.

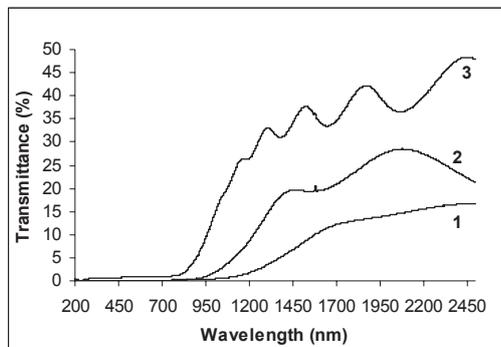


Figure 8. Transmission spectra of thin films deposited at 350 K with different thicknesses: 1 – 652 nm; 2 – 344 nm; 3 – 226 nm.

$Cd_{0.4}Sn_{0.6}Te$ Thin Films Grown by hot Wall Evaporation

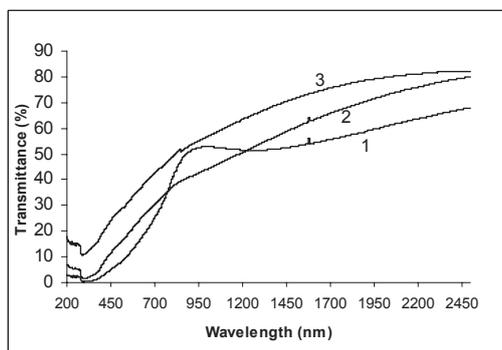


Figure 9. Transmission spectra of thin films deposited at 423 K with different thicknesses: 1 – 329 nm; 2 – 210 nm; 3 – 100 nm.

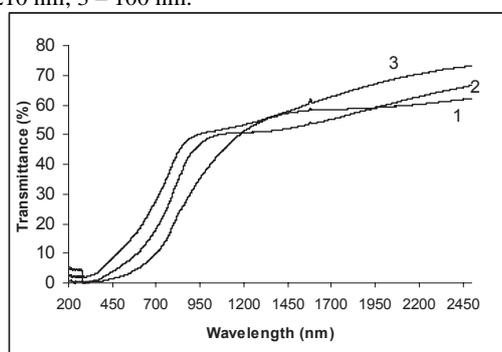


Figure 10. Transmission spectra of thin films deposited at 473 K with different thicknesses: 1 – 172 nm; 2 – 118 nm; 3 – 100 nm.

4 Results and Discussion

All the $Cd_{0.4}Sn_{0.6}Te$ thin films deposited with substrate temperatures 350K, 423 K and 473 K are uniform, smooth and having good adhesion with the glass substrate. From the XRD patterns of the films deposited at different substrate temperatures, exhibited crystalline with (111), (200) and (220) reflection of which the intensity of the (200) orientation is predominant. The XRD patterns of the films deposited at higher temperature clearly show an increase in peak intensity of the (200) peak. The increase in intensity and the decrease in full width half maximum of the (200) peak may be attributed to the improvement of crystallinity on thermal treatment. There is no much variation in the peak intensity of the films deposited at 423 and 473 K, but we can clearly observe the reduction in the intensity of the (111) and (220) peaks. The decrease in intensity of the (111) and (220) and peaks may be due to increase the preferential orientation along (200) direction upon heat treatment. Table 1 gives the lattice parameters and

Table 1.

Substrate temperature (K)	2θ (degree)	$S = h^2 + k^2 + l^2$	$\frac{\sin^2 \theta}{s}$	Lattice parameter a (Å)	Particle size (Å)
350	23.275	3	0.01355	6.617	219.5
	27.812	4	0.01443	6.413	
	38.565	8	0.01362	6.600	
423	23.5	3	0.01381	6.554	415.7
	27.96	4	0.01458	6.380	
	38.25	8	0.0134	6.653	
473	23.06	3	0.0133	6.678	423.4
	27.3	4	0.01391	6.531	
	38.34	8	0.01347	6.638	

particle size of thin films deposited at three different temperatures. It is found that there is an increase in grain size and decrease in dislocation density with the increase in substrate temperature. It shows that there is improved crystallinity with the increase in substrate temperature. The sizes of the particle have length from 0.2 μm to 0.8 μm . Particle sizes are in good agreement with the SEM results. SEM micrographs of the films have shown more or less uniform structure with particles distributed throughout the area scanned. The structure and lattice parameters of these films are in good agreement with the similar compounds CdSnTe_2 and CdSn_3Te_4 as reported in the ASTM index cards [28]. The values of the energy band gap are estimated from the extrapolation to zero absorption in the $(\alpha h\nu)^2$ vs. $h\nu$ plots (where α is the absorption coefficient) and the opti-

Table 2.

Substrate temperature (K)	Thickness of thin films (nm)	Band gap (eV)
350	226	0.750
	344	0.650
	652	0.550
423	100	0.518
	210	0.510
	329	0.500
473	100	0.510
	118	0.505
	172	0.500

Cd_{0.4}Sn_{0.6}Te Thin Films Grown by hot Wall Evaporation

cal band gap values for the films deposited with different substrate temperatures 350, 423 and 473 K are tabulated (Table 2) and it is found to be direct band semiconductor. The decrease in energy band gap is attributed due to variation of stoichiometry and presence of unsaturated defects, which increase the density of localized states in the band gap and consequently decrease the optical energy gap but in the present study the decrease in energy gap is due to the improvement of crystallinity [19].

5 Conclusion

These characterization studies confirm the formation of crystalline cadmium tin telluride films at economical cost for efficient IR detector applications. Cd_{0.4}Sn_{0.6}Te shows a strong (200) orientation of face centered cubic structure. Their band gap energy is found to be from 0.75 eV to 0.5 eV which is suitable for high efficiency IR sensors.

Acknowledgements

We express gratitude to Prof. Dr. C.N.R. Rao (The Indian National Scientist), Dr. Santhosh (IIT Chennai), and The Director STIC Cochin University for their timely help in characterizing the thin films. The authors would like to express their sincere thanks to The Director Dr. S.R.K. Prasad (CIT), Dr. Kulandathivel (Bharthiar University), Dr. Amudha (PSG Tech) for their useful discussions and encouragements during the course of work.

References

- [1] D. De Nobel, F.A. Kroger (1962) US patent No.3, 033, 791 (1962)
- [2] R.F.C. Farrow, D.S. Robertson, G.M. Williams, A.G. Cullis, G.R. Jones, I.M. Young, P.N.J. Dennis (1981) *J. Cryst. Growth* **54** 507.
- [3] W.T. Yuen, W.K. Liu, B.A. Strading (1990) *Semicond. Sci. Technol.* **5** 373.
- [4] H. Calderon, H. Hochst(1984) *Thin Solid Films* **111** 375.
- [5] D. Arivuoli, R.D. Gnanan, P. Ramasamy(1988) *J. Mater. Sci. Lett.* **7** 711.
- [6] E. Magnano, C. Cepek, S. Gardonio, B. Allieri, I. Baek, E. Vescovo, L. Roca, J. Avila, Maria Grazia Betti, C. Mariani, M. Sancrotti (2002) *J. Electron. Spectrosc. Relat. Phenom.* **127** 29-35.
- [7] M. Sgtozern, M. Sterdeur, H. Soboltu, V. Riede (1986) *Phys. Stat. Solidi* **B 138** 259.
- [8] G.H. Grosch, B. Freytag, K.J. Range, U. Rossler (1994) *Int. J. Quantum. Chem.* **52** 919-926.
- [9] B. Freytag, U. Rossler, K. Karch, G.H. Grosch, K.J. Range (1994) *J. Chemi. Phys.* **101** 6782-6789.
- [10] G.H. Grosch, B. Freytag, K.J. Range, U. Rossler (1993) *J. Chemi. Phys.* **99** 6751-6755.
- [11] M. Stolzern, M. Sterdeur, H. Sobottu, V. Riede (1986) *Phys. Stat. Solidi* **B 138** 711.

T. Venkatachalam, S. Ganesan

- [12] H. Noguchi, A. Setiyadi, H. Tanamura, T. Nagutomo, O. Otomo (1994) *Sol. Energy Mater. Sol. Cells* **35** 325.
- [13] P. Prammanek, P.K. Basu, S. Biswas (1987) *Thin Solid Films* **150** 269.
- [14] N.K. Reddy, K.T.R.K. Reddy (1998) *Thin Solid Films* **325** 4.
- [15] S.S. Fouad, A.Y. Morsy, H.S. Soliman, G.A. Ganainy (1994) *J. Mater. Sci. Lett.* **13** 82.
- [16] T. Venkatachalam, S. Ganesan, K. Sakthivel (2006) *J. Appl. Phys. D* **39** 1650-1657.
- [17] S. Agilan, D. Mangalaraj, Sa. K. Narayanadass, Mohan G. Rao (2005) *Physica B* **365** 91-101.
- [18] S. Velumani, X. Mathew, P.J. Sebastian, Sa.K. Narayandass, D. Mangalaraj (2003) *J. Mater. Sci. Lett.* **22** 25.
- [19] S. Velumani, X. Mathew, P.J. Sebastian, Sa.K. Narayandass, D. Mangalaraj (2003) *Sol. Energy Mater. Sol. Cells* **76** 347.
- [20] A. Lopez-Otero, W. Huber (1978) *J. Cryst. Growth* **45** 214-217.
- [21] D. Schikora, H. Sitter, J. Humenberger, K. Lischka (1986) *Appl. Phys. Lett.* **48** 12.
- [22] S. Chaudhuri, S.K. Das, A.K. Pal (1987) *Thin Solid Films* **147** 9-16.
- [23] H. Sitter, K. Lischka, W. Faschinger, J. Wolfrum, H. Pascher (1988) *J. Cryst. Growth* **86** 377-381.
- [24] R. Korenstein, B. MacLeod (1988) *J. Cryst. Growth* **86** 382-385.
- [25] K. Lischka, E.J. Fantner, T.W. Ryan, H. Sitter (1989) *Appl. Phys. Lett.* **55** 1309.
- [26] J. Vaitkus, R. Thomasiunas, J. Kutra, M. Petreuskas, R. Rinkunas, A. Zindulis (1990) *J. Cryst. Growth* **101** 826-827.
- [27] H. Tatsuoka, H. Kuwabara, Y.Nakanishi, H. Fujiyasu (1990) *J. Appl. Phys.* **67** 6860.
- [28] R. Marx, K.J. Rang (1989) *J. Less-Common Met.* **155** 49.