Chapter 4
Preparation and Characterization of Nanocrystalline CdTe Thin Films by Electron Beam Evaporation

4.1 INTRODUCTION

II-VI compound semiconducting thin films have drawn considerable interest for the past two decades as they find numerous applications in photoconductors, space charge limited diodes, photovoltaic cell, transistors and infra-red (IR) detectors (Entine et al., 1981). Among the different II-VI compound semiconductors, CdTe with a small band gap of 1.45 eV is one of the promising candidates for IR detector, photovoltaic, optoelectronic applications. Several deposition methods such as close spaced sublimation (Britt and Ferekides, 1993; Wu et al., 2001), electro deposition (Miyake et al., 2004), sputtering (Gupta and Compaan, 2003) close spaced vapor transport (Mendoza-Pérez et al., 2005), spray pyrolysis (Vamsi Krishna and Dutta, 2004) metal organic chemical vapor deposition (Hartley et al., 2001; Feng et al., 1996) and vacuum evaporation (Chandramohan et al., 2008) were employed for the preparation of CdTe thin films. Among these methods, electron beam evaporation is more advantageous as impurities can be avoided during the film growth, the tendency to form oxides can be considerably reduced and slow rate of deposition is possible in this technique (Khairnar et al., 2003; Ali and Abd El-Ghanny 2008). The structural and optical properties of the films generally depend on the deposition conditions such as rate of evaporation, substrate temperature and the film thickness etc. Optimization of the deposition conditions is very important to get good quality thin films. This chapter reports the preparation of nanocrystalline CdTe thin films by electron beam evaporation technique and the effect of substrate temperature on structural and optical properties of the CdTe thin films.

4.2 EXPERIMENTAL

4.2.1 PREPARATION OF CdTe THIN FILMS

Pure CdTe thin films were prepared using electron beam evaporation (Hind High Vac 12A4D) technique at different substrate temperatures. Compound CdTe (99.99% purity, M/S Sigma Aldrich) was taken as a source material and loaded into the graphite crucible. Corning 7059 glass substrates were cleaned in ultrasonic bath.
with acetone and then washed with distilled water and subsequently dried in hot air oven prior to deposition and fixed to the substrate holder. CdTe thin films were deposited onto glass substrates at different (T_s) such as 423 K, 573 K, 623 K and 673 K with a rate of deposition 6 - 8 Å/s. A base pressure of about 1x10^{-6} mbar was maintained during deposition. The distance between the source and the substrates was maintained as 10 cm. Thickness of the CdTe thin films was measured using quartz crystal thickness monitor (QTM). A thickness of 400 nm was maintained for all the samples.

4.2.2 CHARACTERIZATION TECHNIQUES EMPLOYED

The crystallographic structure of CdTe thin films was examined by X-ray diffractometer (Bruker D-8 Advance) with a monochromatic CuKα radiation (λ=1.54060 Å). The surface morphology and composition analysis of the films were studied using high resolution scanning electron microscope (FEI Quanta FEG-200) coupled with energy dispersive analysis of X-rays (EDAX). The optical transmittance of the films was recorded using UV-Vis-NIR double beam spectrophotometer (JASCO-V-670) in the wavelength range 200 nm - 2500 nm.

4.3 RESULTS AND DISCUSSION

4.3.1 STRUCTURAL STUDIES

Fig. 4.1 shows the X-ray diffraction patterns of the nanocrystalline CdTe thin films deposited at different substrate temperatures of 423 K, 573 K, 623 K and 673 K. All the films were found to be polycrystalline in nature with a single orientation along (1 1 1) plane reflecting the cubic structure of CdTe. The films formed at 573 K exhibited (2 2 2) and (3 1 1) at a diffraction angles of 39.30° and 46.43°, respectively. The intensity of the diffracted peaks remained constant upto 573 K and increased when the substrate temperature of the films increased from 573 K to 673 K. It may be due to increase in the crystallite size of the deposited films.
Fig. 4.1. X-ray diffraction patterns of the CdTe thin films deposited at different substrate temperatures ($S_1$) 423 K, ($S_2$) 573 K, ($S_3$) 623 K and ($S_4$) 673 K.

Fig. 4.2. Variation of lattice constant and microstrain with substrate temperature ($T_s$).
Fig. 4.2 shows the variation of lattice constant and microstrain at different substrate temperatures from \( S_1 - S_4 \). The lattice constant has been calculated from the prominent diffraction peak \((1 \ 1 \ 1)\) and it increased linearly with the increase of substrate temperature. The lattice constant of the films increased from 6.47 Å to 6.50 Å when the substrate temperature of the films increased from \( S_1 - S_4 \). The microstrain decreased with the increase of substrate temperature.

The increase in the lattice constant with the increase of substrate temperature may be due to internal stress developed in the films. Decrease of microstrain with the increase of substrate temperature may be due to the difference in the temperature coefficient of expansion of the glass substrate and CdTe thin films. The average crystallite size of the films has been calculated using Debye Scherrer formula. It is found that the average crystallite size increases from 35 nm to 116 nm with the increase of substrate temperature. As the substrate temperature increases the ad atom mobility also increases and the FWHM decreases resulting an increase in crystallite size (Sathyamoorthy et al., 2003). Similar behavior was also observed in CdTe thin films prepared by different methods (Abd El-Raheem et al., 2009; Dwivedi et al., 2009; Pandey et al., 2005; Gould and Bowler, 1988; Ghosh et al., 2012). Summary of average crystallite size, lattice constant, microstrain and band gap of the CdTe thin films deposited at different substrate temperatures is given in Table 4.1.

Table 4.1: Summary of average crystallite size, lattice constant, micro strain and band gap of the CdTe thin films deposited at different substrate temperatures \( (T_s) \)

<table>
<thead>
<tr>
<th>Film Name</th>
<th>Substrate Temperature ( T_s ) (K)</th>
<th>2θ (degree)</th>
<th>FWHM</th>
<th>Lattice Constant a (Å)</th>
<th>Average Crystallite Size D (nm) XRD</th>
<th>Average Crystallite Size D (nm) SEM</th>
<th>Micro strain</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_1 )</td>
<td>423</td>
<td>23.78</td>
<td>0.243</td>
<td>6.475</td>
<td>35</td>
<td>31</td>
<td>5.94</td>
<td>2.87</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>573</td>
<td>23.76</td>
<td>0.150</td>
<td>6.496</td>
<td>57</td>
<td>70</td>
<td>3.66</td>
<td>2.47</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>623</td>
<td>23.68</td>
<td>0.088</td>
<td>6.501</td>
<td>96</td>
<td>-</td>
<td>1.78</td>
<td>2.07</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>673</td>
<td>23.66</td>
<td>0.073</td>
<td>6.506</td>
<td>116</td>
<td>108</td>
<td>1.78</td>
<td>2.05</td>
</tr>
</tbody>
</table>
4.3.2 SURFACE MORPHOLOGY AND COMPOSITION ANALYSIS

Fig. 4.3 (a-c) shows the Scanning Electron Microscope (SEM) images of the CdTe thin films deposited at different substrate temperatures. Fig 4.3 (d) shows typical EDAX spectrum of the CdTe thin film deposited at 573 K. From the SEM images, it is clear that the films formed at lower substrate temperature 423 K ($S_1$) exhibited small grains over the entire region of the substrate surface whereas, the films deposited at higher substrate temperatures 673 K ($S_4$) exhibited larger grains. It confirms that the elevated substrate temperature provides sufficient thermal energy for grain growth and hence increased crystallite size. Similar results were observed in CdTe thin films by thermal evaporation. (Chu et al., 1985). From EDAX analysis, the at.% of Cd and Te were found to be as Cd: 46.20% and Te: 53.80% with nearly stoichiometric. But the small difference between atomic ratio is due to the high vapor pressure of Tellurium (Te) when compared to Cadmium (Cd).

![Fig. 4.3 (a-c) HRSEM images of the CdTe thin films deposited at (S$_1$) 423 K, (S$_2$) 573 K and (S$_4$) 673 K respectively (d) Typical EDAX spectrum of the CdTe thin film deposited at (S$_2$) 573 K](image)

Fig.4.3 (a-c) HRSEM images of the CdTe thin films deposited at ($S_1$) 423 K, ($S_2$) 573 K and ($S_4$) 673 K respectively (d) Typical EDAX spectrum of the CdTe thin film deposited at ($S_2$) 573 K
Fig. 4.4 Optical transmittance spectra of the CdTe thin films deposited at different substrate temperatures

Fig. 4.4 shows the optical transmittance spectra of the CdTe thin films deposited at different substrate temperatures. From the transmittance spectra, it is clear that the absorption edge of the films shifted towards the higher wavelengths with increase in substrate temperature. The optical band gap of the films was calculated using the Tauc relation (Tauc 1974),

$$a h \nu = B(h \nu - E_g)^r$$  \hspace{1cm} (4.1)

where $B$ is a constant which is different for different transitions indicated by different values of $r$, $h$ is the Planck’s constant, $\nu$ the frequency of light, $E_g$ the optical band gap and ‘$r’$ a parameter which characterizes the transition process involved. The parameter $r$ takes the values of 2 and 1/2 for the direct allowed transition and for indirect allowed transition, respectively.
From the Fig. 4.5 it is evident that the optical band gap of the CdTe films decreased with increase of substrate temperature. Similar decrease in band gap with the increase of substrate temperature has been reported by vacuum evaporated CdTe films (Pal et al., 1993; Shallan and Muller 1990). The CdTe films coated at low $T_s$ substrate temperature ($423 \text{ K}$) showed optical band gap of $2.87 \text{ eV}$. Whereas a band gap of $2.05 \text{ eV}$ was observed for the film coated at high substrate temperature $673 \text{ K}$. The actual band gap of the CdTe (bulk) is $1.45 \text{ eV}$. In the present study a clear blue shift was observed in nanocrystalline CdTe thin films deposited at different substrate temperatures which is obvious due to the quantum confinement.

Fig.4.6 shows variation of crystallite size and band gap with increase in substrate temperatures. It is obvious from the above plot that an increase in substrate temperature showed an increase in average crystallite size and decrease in band gap. This decrease in band gap may be attributed to an increase in crystallite size with corresponding increase in substrate temperature.
4.4 CONCLUSION

In summary, nanocrystalline CdTe thin films at different $T_s$ were prepared by electron beam evaporation technique. The effect of substrate temperature on the structure, morphology and optical properties of the CdTe films has been studied. The structure of the CdTe thin films was cubic with a preferential orientation of (1 1 1) plane. Microstructural studies revealed an increase in the crystallite size with the increase in substrate temperature from $S_1$ – $S_4$. Optical studies showed decrease of band gap with increase of crystallite size.

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Chapter 5

Preparation and Characterization of Cr Diffused CdTe Nanocrystalline Thin Films

5.1 INTRODUCTION

Currently, thin films of CdTe:Cr are finding much interest due to the potential applications in optoelectronic devices (Chandramohan et al., 2004; Deshmukh et al., 2005). As the difference between melting points of CdTe and Cr is so large, stacked layers of CdTe:Cr were deposited using electron beam evaporation technique and the films were annealed at different temperatures. This chapter reports the systematic study of Cr diffused CdTe thin films prepared using electron beam evaporation technique followed by vacuum annealing. The effect of Cr concentration on structural, morphological and magnetic properties has been discussed.

5.2 EXPERIMENTAL

5.2.1 PREPARATION OF CdTe:Cr THIN FILMS

Cr diffused CdTe thin films were prepared by sequential deposition of CdTe/Cr/CdTe layers using electron beam evaporation technique. Compound CdTe (99.99% purity) and Cr (99.97% purity) procured from Sigma Aldrich were used as starting materials. Prior to the deposition, the glass substrates were ultrasonically cleaned in detergent, acetone and rinsed in deionized water and subsequently dried in hot air oven. A substrate temperature of 373 K and deposition rate of 6-7 Å/s was maintained during the deposition under constant pressure of $10^{-6}$ mbar. The distance between source to substrate was maintained as 10 cm. The thickness of the deposited layers was measured using quartz crystal thickness monitor. Later, all the samples were vacuum annealed for 3 hours at 573 K under a pressure of $2 \times 10^{-5}$ mbar. The source materials were taken in individual graphite crucibles and deposited in the sequence of CdTe/Cr/CdTe. Four sets of Cr diffused CdTe thin films were prepared with Cr layers of different thicknesses. In all the samples, the total thickness of CdTe layers was 1 μm and that of Cr was 25 nm in sample-1 ($S_1$), 50 nm in sample-2 ($S_2$), 75 nm in sample-3 ($S_3$) and 100 nm in sample-4 ($S_4$). Each sample contains five layers of Cr with equal thicknesses sandwiched among six CdTe layers. Fig. 5.1 shows the schematic representation of layers of CdTe:Cr thin films.
5.2.2 CHARACTERIZATION TECHNIQUES EMPLOYED

The structure of the films was studied by the X-ray diffractometer (Bruker D8 Advance) with CuK$_\alpha$ radiation ($\lambda$=1.54060 Å). Surface morphological and chemical composition of the CdTe:Cr thin films were studied with HRSEM equipped with EDAX attachment (FEI Quanta FEG 200). Raman spectra were recorded using Raman Scattering Spectrometer (LABRAM HR 800) with an excitation wavelength of 633 nm at room temperature in backscattering mode. Magnetic measurements were carried out at room temperature using vibrating sample magnetometer (Lakeshore 7410) with an applied field upto 15,000 G.

![Fig.5.1 Schematic representation of Cr diffused CdTe thin films with different Cr thickness](image)

5.3 RESULTS AND DISCUSSION

5.3.1 STRUCTURAL STUDIES

Fig. 5.2 shows the X-ray diffraction patterns of the CdTe/Cr/CdTe thin films deposited at 373 K for different Cr layer thicknesses. It was observed that all the films were polycrystalline and exhibited diffraction peaks corresponding to the (1 1 1), (2 2 0) and (3 1 1) orientations representing the cubic structure CdTe (JCPDS: 89-3053). All the films showed (1 1 1) planes as the dominant orientation, and its intensity increased with increase of film thickness. Other supplementary diffraction peaks related to Cr metal clusters/Cr compounds (tellurides, oxides)/ secondary phases were not observed. It indicates that Cr ions might have diffused into the CdTe host lattices. Further a slight shift in diffraction peak (111) towards lower angles (20) was observed by increasing Cr. The shift in the peak position confirms that the Cr has
substituted Cd atom sites. Fig. 5.3 showed an increase of lattice parameter and crystallite size with increase in Cr thickness. Increase in crystallite size may be due to the columnar grain growth in the film structure and the decrease in the crystallite size at lower Cr content might be due to the strong interaction between the substrate and vapour atoms, which restricts the mobility of ad-atoms. The improved crystallinity of Cr diffused CdTe layers provide an activation energy for the adsorbed atoms to occupy the minimum energy positions, thereby enhancing the recrystallization due to the coalescence of the islands by increasing the volume and surface diffusions (Geetha Vani et al., 2013). Hence, the present result reflects the crystallization approaches more perfect as the film thickness increased. This may be due to decrease of the internal micro-strain in the films and the increase in the crystallite size (Lalitha et al., 2004; El-Kadry et al., 1995). It is seen from the Table.5.1 that the average crystallite size increased with the thickness of the films.

Fig. 5.2 XRD patterns of pure and Cr diffused CdTe thin films
Table 5.1: Summary of 2θ, lattice parameter and average crystallite size of Cr diffused CdTe thin films deposited at 373K

<table>
<thead>
<tr>
<th>Sample name</th>
<th>2θ (111)</th>
<th>Lattice parameters a (Å)</th>
<th>Average Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₀</td>
<td>23.716</td>
<td>6.462</td>
<td>36.9</td>
</tr>
<tr>
<td>S₁</td>
<td>23.799</td>
<td>6.470</td>
<td>35.1</td>
</tr>
<tr>
<td>S₂</td>
<td>23.716</td>
<td>6.492</td>
<td>36.3</td>
</tr>
<tr>
<td>S₃</td>
<td>23.707</td>
<td>6.495</td>
<td>52.1</td>
</tr>
<tr>
<td>S₄</td>
<td>23.676</td>
<td>6.503</td>
<td>61.1</td>
</tr>
</tbody>
</table>

Fig.5.3  Variation of lattice parameter and crystallite size as a function of Cr thickness in CdTe:Cr thin films

5.3.2 SURFACE MORPHOLOGY AND COMPOSITION ANALYSIS

The high resolution scanning electron microscope (HRSEM) image and the cross-sectional view of Cr diffused CdTe thin film of S₁ sample is shown in Fig.5.4 (a) and (b). From Fig. 5.4 (a) it is noticed that the film surface seems to be uniform and the crystallite size of the sample was almost equal to that of crystallite size calculated from XRD.
Fig. 5.4 (a) Surface (b) cross-sectional HRSEM image and (c) the elemental mapping of Cr diffused CdTe thin films of S₁ sample
Fig. 5.5 EDAX spectra of Cr diffused CdTe thin films (a) $S_1$, (b) $S_2$, (c) $S_3$ and (d) $S_4$ samples
The growth pattern of the films has been observed from the cross-sectional image as shown in Fig. 5.4 (b). The CdTe and Cr layers diffused among each other upon annealing and formed as a single layer. Fig.5.4 (c) is the elemental mapping for the S₁ sample revealing uniform distribution of Cd (green), Te (blue), and Cr (red) in the films.

Fig. 5.5 (a) S₁, (b) S₂, (c) S₃ and (d) S₄ shows the EDAX spectra of Cr diffused CdTe thin films. From the EDAX spectra it can be seen that the atomic percent of Cr increased with increase of film thickness with corresponding decrease in Cd and Te. This small difference between Cd and Te atomic percentage may be due to the high vapor pressure and re-evaporation of Te during annealing. In sample S₁ and S₂ same stoichiometry was not maintained among Cd, Cr and Te. Whereas near stoichiometry was maintained only in the sample S₃. Even though as all the samples are chromium rich, at higher content of Cr (S₄) the magnetic moment is decreased as Cr is antiferromagnetic in nature.

5.3.3 RAMAN STUDIES

![Fig. 5.6 Raman Spectra of pure and Cr diffused CdTe thin films](image-url)

Fig. 5.6 Raman Spectra of pure and Cr diffused CdTe thin films
Raman spectra of pure and Cr diffused CdTe films in the wavenumber range of 100 - 200 cm\(^{-1}\) are showed in Fig. 5.5. It is observed from the spectra that the samples S\(_0\) and S\(_1\) showed peak at \(~119\) cm\(^{-1}\), \(~139\) cm\(^{-1}\) and \(~156\) cm\(^{-1}\) which corresponds to A\(_1\),TO and LO modes of CdTe. No additional Raman modes were observed in either Cr or chromium oxides such as CrO\(_2\), Cr\(_2\)O\(_3\). But as the thickness of the Cr is increased from samples S\(_2\) to S\(_4\), the intensity of the Raman peaks diminished. This weakening nature of the Raman modes with increase of Cr content indicates that Cr has successfully replaced the Cd in the CdTe host lattice. As a result, the suppression of Raman modes is observed.

5.3.4 MAGNETIC STUDIES

The magnetic field dependence of the magnetization measurements (M-H curves) of Cr diffused CdTe thin films for various Cr layer thicknesses are shown in Fig. 5.7. It can be seen from Fig. 5.7 for the S\(_1\) to S\(_3\) samples the magnetic moment increased by increasing the Cr content but with further increase of Cr (S\(_4\)) the magnetic moment decreased. In the present work, there exist few possibilities which come to light in order to understand the origin of ferromagnetism in Cr diffused CdTe thin films. Both theoretical and experimental reports are available for Cr doped CdTe in bulk and thin films showing room temperature ferromagnetism. Experimentally room temperature ferromagnetism in Cr doped CdTe crystals, Co doped CdTe powders and Co diffused CdTe thin films were explained in our earlier work (Rigana Begam et al., 2013; Rigana Begam et al., 2014; Rigana Begam et al., 2014) and (Ko and Blamire, 2006; Ko and Blamire, 2006; Kowan-Young Ko 2009). Appearance of ferromagnetism with a Curie temperature of around 395 K was reported in Cr-doped CdTe crystals (Ko and Blamire, 2006). Co diffused CdTe thin films with different annealing temperatures were performed by Alver et al (Alver et al., 2008). In addition to that theoretical calculations also showed half metallic ferromagnetism in Cr and Co doped CdTe (Noor et al., 2011; Saeed et al., 2010; Yao et al., 2005; Zitouni et al., 2014).

As chromium is antiferromagnetic in nature it confirms that the observed ferromagnetism is not due to the presence of metallic chromium clusters, as no sign of metal clusters nor impurity phases were observed in Cr diffused CdTe thin films within the detection limit of the XRD.
On the other hand, of all the oxides of chromium, only CrO₂ is ferromagnetic with bulk magnetic moment of 134 emu/g and Curie temperature of 386 K (Coey and Venkatesan, 2002; Zhang et al., 2008). Cr₂O₃ is antiferromagnetic with Neel temperature of 308 K (Zhang et al., 2008). Since CrO₂ is also ferromagnetic, the question arises whether the observed ferromagnetism in the present samples is intrinsic or due to the presence of CrO₂ phase. If the ferromagnetism is due to CrO₂, the magnetization should be increasing with the increase of chromium thickness. In addition to that, if CrO₂ is present in larger fraction, it can be identified by XRD and Raman analysis. However, from XRD, HRSEM and Raman analysis could not find any signal of Cr clusters or oxide phases of chromium.

Rudermann–Kittel–Kasuya–Yosida (RKKY) and F-center mediated bound magnetic polaron theory (BMP) are the two theories that may explain the mechanism for the observed ferromagnetism in the present system (Calderón and Das Sarma,
RKKY theory is mostly applicable in case of metallic system with large number of delocalized free electrons while BMP theory is applicable in case of semiconducting or insulating system with localized electrons (Calderón and Das Sarma, 2007).

From the XRD patterns the slight shift in the diffraction peak (1 1 1) with Cr diffusion confirms the Cr incorporation into CdTe, which further suggested the arising of ferromagnetism from the exchange interaction between local spin-polarized electrons of Cr\(^{2+}\) ions and conductive electrons according to RKKY mechanism rather than Cr oxide impurities. Hence, it can be concluded that the observed ferromagnetic behavior could be attributed to the substitution of Cr ions (Cr\(^{2+}\)) for Cd ions in the CdTe lattice. This conclusion is in accordance with that of Mn doped CdS (Aksu et al., 2011) and Fe doped ZnO (Xai et al., 2011).

The speculation of low magnetic moment observed at low Cr content is due to the weak coupling of Cr\(^{2+}\) with the host lattice. On comparing among S\(_1\), S\(_2\) and S\(_3\) the Cr content is more in sample S\(_3\). Hence, the ferromagnetic interaction becomes stronger and so the magnetic moment is increased. But, the magnetic moment decreased in the sample S\(_4\), as the Cr content is very high. This decrease of magnetic moment may be due to the direct exchange interaction. These interaction leads to the antiparallel alignment of the spins for small interatomic distances and therefore increase antiferro magnetic interaction. The ultimate result is the effective reduction in magnetic moment.

In connection to the above the decrease of magnetic moment with increase of Cr content might be due to the fact that the excess Cr ions may occupy the interstitial positions as Cr solubility in II-VI semiconductors is very low. This would result in reduction of the ferromagnetic exchange interaction as intrinsic Cr is antiferromagnetic. No previous reports on Cr diffused CdTe thin films are available for comparison. This kind of behavior is analogous to Cr doped ZnTe system in bulk and in thin films (Krishnaiah et al., 2008; Soundararajan et al., 2011).
5.4 CONCLUSION

Cr diffused CdTe thin films with different Cr content were prepared using electron beam evaporation technique onto a glass substrates at a substrate temperature of 373 K followed by vacuum annealing at 573 K. XRD pattern showed a predominant (1 1 1) reflection corresponding to the cubic structure of CdTe. Increase in lattice parameter with increase in Cr content has been observed. The cross-sectional image displayed a columnar grain growth in the films. EDAX data confirmed the presence of Cr, Cd and Te with nearly stoichiometry. The Raman spectra showed peaks corresponding to A1, TO and LO modes of CdTe. Magnetic measurements confirmed that these samples are ferromagnetic at room temperature.

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