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Structural and optical characterization of hot wall deposited $\text{CdSe}_x\text{Te}_{1-x}$ films

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Abstract

$\text{CdSe}_{0.3}\text{Te}_{0.7}$ alloy was prepared from the individual components and its composition and structural analysis were done. Films were prepared by hot wall deposition technique using 0.15 m length tube under a vacuum of 5×10^{-5} Torr on well cleaned glass substrates. The composition, structural, morphological, and optical properties of hot wall deposited films were investigated. The XRD analysis revealed that the films are like amorphous in nature for lower thicknesses but with increasing thickness a more preferred orientation along (101) direction was observed. The crystallite size (D), dislocation density (δ) and strain (ϵ) were evaluated. From the EDX composition analysis, the individual concentrations of Se and Te in the films were estimated. An analysis of optical measurements shows that all the films have fairly good transparency above 850 nm. The optical band gap was found to be around 1.55 eV and decreases with increasing thickness. Also comparison of band gap with corresponding values for CdSe and CdTe are made.

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Keywords: $\text{CdSe}_x\text{Te}_{1-x}$; Thin films; Hot wall deposition; Optical properties; Structural properties

1. Introduction

Binary and ternary chalcogenide alloys, especially CdSe and CdTe present semiconducting properties, which are well suitable for the conversion of solar energy in photo voltaic or photo electrochemical devices. $\text{CdSe}_x\text{Te}_{1-x}$ ternary thin films, alloy of either CdSe and CdTe or Cd, Se and Te find extensive application in photo electrochemical solar cells [1], transistors [2], photoconductors [3], solar control

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applications [4], etc. They can also be used for the photo-assisted decomposition of water. Obtaining a stable film is one of the prime concerns of any device application of a particular material. In the case of $\text{CdSe}_x\text{Te}_{1-x}$, the crystal structure and the band gap can be tailored by changing the concentration of Se and Te, so that the visible solar energy can be suitably harnessed for maximum conversion to electrical energy. Amorphous semiconductors, in particular selenium alloys exhibit the unique property of reversible transformations, which is useful in optical memory devices.

In the past, thin films of cadmium chalcogenide alloys have been studied by several researchers, depositing the films using techniques such as thermal evaporation [5], electroplating [6], slurry painting [7], two source evaporation [8] of CdSe and CdTe, three source elemental evaporation [9], electron beam evaporation [10], etc. Among the various techniques available for the preparation of thin films, recently hot wall deposition has gained importance, because of its simplicity and its economic viability. Schikora et al. [11] have claimed that hot wall deposited CdTe films on GaAs substrates show superior luminescence properties when compared to molecular beam epitaxy (MBE) and metal-oxide chemical-vapor deposition (MOCVD) films. Chaudhuri et al. [12] have used the hot wall technique to deposit CdSe thin films onto glass, NaCl and KCl substrates at different substrate temperatures. Pal et al. [13] have fabricated ZnTe/CdSe solar cells by hot wall technique and studied $I-V$, $C-V$ and spectral response.

Even though, lot of research is pursued on this ternary compound and reports are available on structural, optical and transport properties, practically there is no report available on hot wall deposited $\text{CdSe}_x\text{Te}_{1-x}$ ternary thin films. The hot wall setup, effect of tube length, as well as effect of many experimental parameters on the structural, optical and other semiconductive characteristics of hot wall deposited CdSe films have been outlined in our earlier paper [14]. In this paper, we present a part of our work which deals with the preparation and characterization of $\text{CdSe}_{0.3}\text{Te}_{0.7}$ bulk material and deposition of thin films using this material by hot wall technique and its structural and optical properties. The interest of choosing this composition lies behind the report by Budyonnaya et al. [15]. Their studies on photo electrical and relaxation properties on sintered films of $\text{CdSe}_x\text{Te}_{1-x}$ show a sharp transition from the properties typical of CdSe to those typical of CdTe in the composition region $x \approx 0.3$.

2. Experimental

The source material $\text{CdSe}_{0.3}\text{Te}_{0.7}$ have been synthesized by direct reaction of high purity (99.999%) elemental Cd, Se and Te (Aldrich chemicals Inc., USA). Stoichiometric amounts of the elements are taken in a pre cleaned quartz ampoule of diameter 10 mm and length 150 mm. This ampoule was evacuated to about 2×10^{-4} Torr for vacuum sealing. The sealed ampoule was kept in a rotating furnace. The ampoule is heated at a rate of 100°C per hour and maintained at 800°C for 5 h and thereafter cooled gradually to room temperature to avoid thermal cracks in the alloy and in the quartz ampoule. The bulk alloy thus obtained was finely powdered

using agate mortar and pestle. This source material is taken in the quartz tube of the hot wall set up which is described elsewhere in detail [14].

The main feature of the hot wall system was the heated linear quartz tube, which served to enclose and direct the vapor from the source to the substrate. The source and wall were heated independently. Films were deposited using 0.15 m length quartz tube having a diameter of 0.01 m on to well-cleaned glass substrates. All the depositions were made at room temperature. The structure of the bulk as well as the films were analyzed using an X-ray diffractometer (Rigaku RINT 2100 attached with AFC-7 R-Axis rapid type X-ray generator, using $\text{Cu K}\alpha$ radiation with $\lambda = 0.15418$ nm). The composition analysis (EDX) has been done using JSM 6400 JEOL model SEM attached with NORAN, EDX detector. The thickness of the films are measured using surfometer (Tencor alpha step100).

The crystallite sizes (D) were calculated using the Scherrer formula [16] from the full-width half-maximum (FWHM) (β). The strain (ε) was calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$ plot using the relation

$$\beta = \frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta. \quad (1)$$

The dislocation density (δ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the formula [17]

$$\delta = \frac{1}{D^2}. \quad (2)$$

The optical transmittance spectra were recorded from 400 to 2500 nm wavelength using Shimadzu UV–VIS–NIR double beam spectrophotometer (model 365) at room temperature with unpolarized radiation. The measurements were made on films of various thicknesses deposited on glass substrates. The substrate absorption was corrected by introducing an uncoated cleaned glass in the reference beam.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of $\text{CdSe}_{0.3}\text{Te}_{0.7}$ powder. Different major peaks are indexed and the values of interplanar spacing d are evaluated and compared with standard d values from ASTM file. The calculated values and their corresponding indices are given in Table 1. The EDX pattern of the prepared ternary alloy is shown in Fig. 2, which yield 70% tellurium and 30% selenium.

The source material of composition $\text{CdSe}_{0.3}\text{Te}_{0.7}$ is taken in a quartz tube of length 0.15 m. The source and wall temperatures were maintained around 800 and 700 K, respectively. Even though the source material contains 70% tellurium and 30% selenium, we got tellurium rich films. This variation in stoichiometry may be due to the small distance maintained between the wall and the substrate which paves way for the escape of selenium. Generally, II–VI group compounds undergo complete dissociation during evaporation and the films are grown by allowing the constituent vapors to react with each other at the substrate at elevated temperatures [4]. Normally, by hot wall deposition technique this dissociation can be avoided by

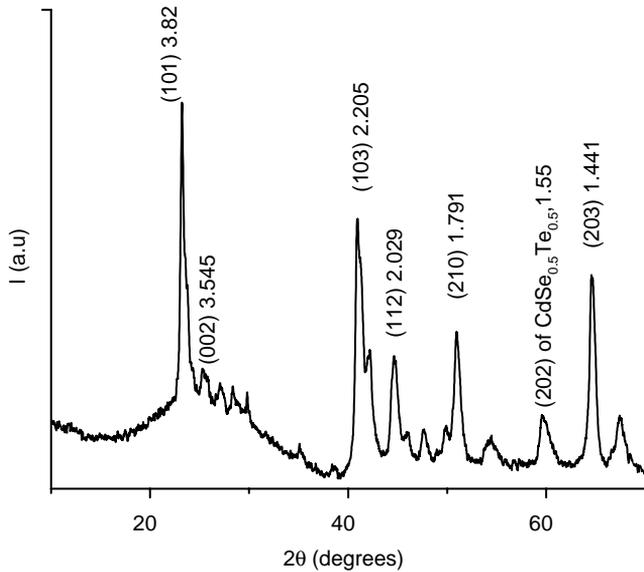


Fig. 1. X-ray diffraction pattern of $\text{CdSe}_{0.3}\text{Te}_{0.7}$ powder.

Table 1

A comparison of calculated d values with standard values of $\text{CdSe}_{0.3}\text{Te}_{0.7}$

Angle (2θ)	d -Observed (\AA)	d -Standard (\AA)	hkl
23.220	3.8275	3.8487	101
25.320	3.5146	3.5603	002
40.900	2.2046	2.2210	103
44.620	2.029	2.0136	112
50.960	1.7905	1.7233	210
64.620	1.4411	1.4985	203

Table 1

A comparison of calculated d values with standard values of $\text{CdSe}_{0.3}\text{Te}_{0.7}$

suitably adjusting the wall and source temperatures. Since selenium is the element of the lowest melting point of the three, the resulting film will always be selenium deficient. In CdSe and CdS this leads to excess cadmium in the film. However, in $\text{CdSe}_x\text{Te}_{1-x}$ films the vapor pressures of the elements are such that at high deposition temperatures and deposition rates the films will be rich in tellurium. The sticking coefficients of the elements also contribute to this state of affairs. They are in the order $S_{\text{Te}} > S_{\text{Cd}} > S_{\text{Se}}$, where the S are the sticking coefficient [4]. Efforts are on to control the wall temperature and the tube length to vary the selenium and tellurium compounds in the films.

The X-ray analysis revealed that the films of lower thicknesses appear to be amorphous in nature without well-defined peaks and as the thickness increases polycrystalline films are obtained. Fayek and Sayed [18] have obtained amorphous

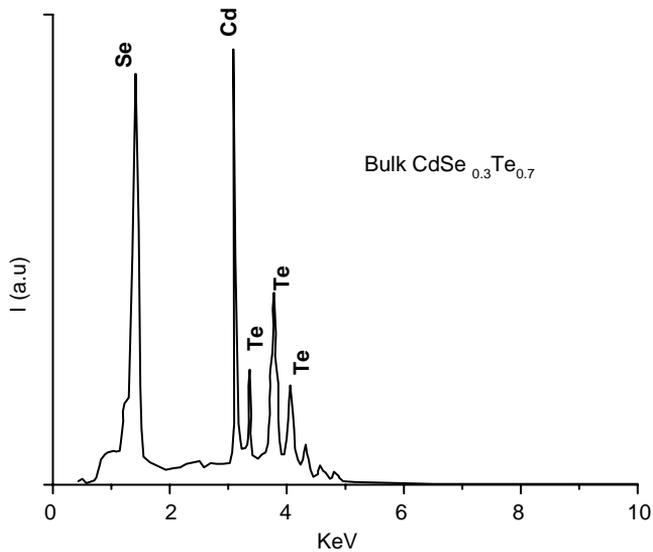


Fig. 2. EDX pattern of $\text{CdSe}_{0.3}\text{Te}_{0.7}$ powder.

films of CdSeTe of thickness 200 nm by vacuum evaporation. At higher thicknesses films are found to be polycrystalline in nature with hexagonal structure and strong preferential orientation along (101) direction as shown in Fig. 3. This result is in agreement with the previous reports [4,19,20]. It can be seen that the film thickness strongly affects the X-ray diffraction pattern. This means that, at the initial stage of film formation, i.e., during the atomistic condensation of the film formation, the deposited atoms are at random orientation.

Fig. 4 shows the EDX pattern of a representative film of thickness 1560 nm. It is found that the film is slightly rich in tellurium having 82% tellurium and 18% selenium. Table 2 show a comparative look of the crystallite size (D), dislocation density (δ), strain (ϵ) and composition of the films of different thicknesses on glass substrates. The composition is found to vary from 76% to 82% tellurium in the thin films. It is observed that the crystallite size increases but the dislocation density and strain decrease with the increase of film thickness. Similar trend of increase in crystallite size with the increase of thickness has been reported by Sebastian et al. [4] for $\text{CdSe}_{0.2}\text{Te}_{0.8}$ films deposited by physical vapor deposition. Since the dislocation density and strain are the manifestation of dislocation network in the films, the decrease in the strain and dislocation density indicates the formation of high quality films. Improvement in quality of the films based on FWHM for the films deposited on glass substrates is reported for CdSe films [14]. A similar trend is observed for the $\text{CdSe}_x\text{Te}_{1-x}$ films on glass substrates, that is when the thickness increases the grain size increases and hence higher the quality of the films. Fig. 5 shows the SEM micrographs of a representative $\text{CdSe}_{0.18}\text{Te}_{0.82}$ film of thickness 1560 nm which reveals the crystalline nature of the film.

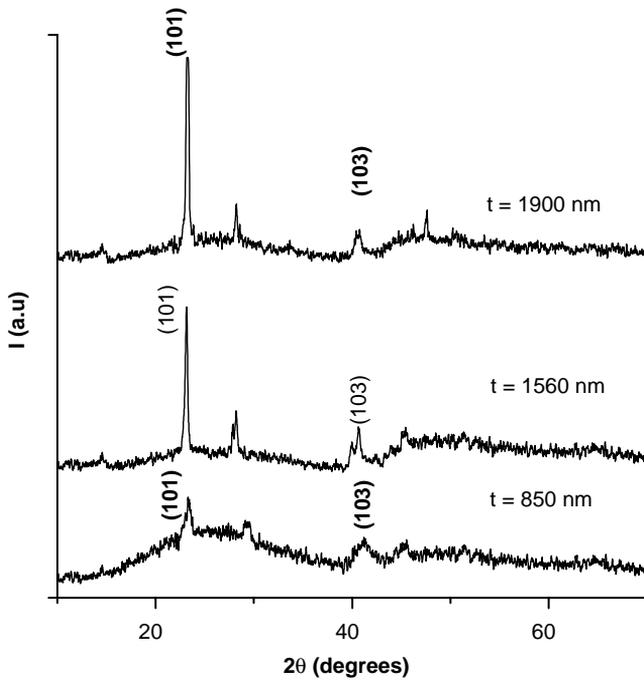


Fig. 3. X-ray diffraction pattern of CdSe_xTe_{1-x} films of various thicknesses.

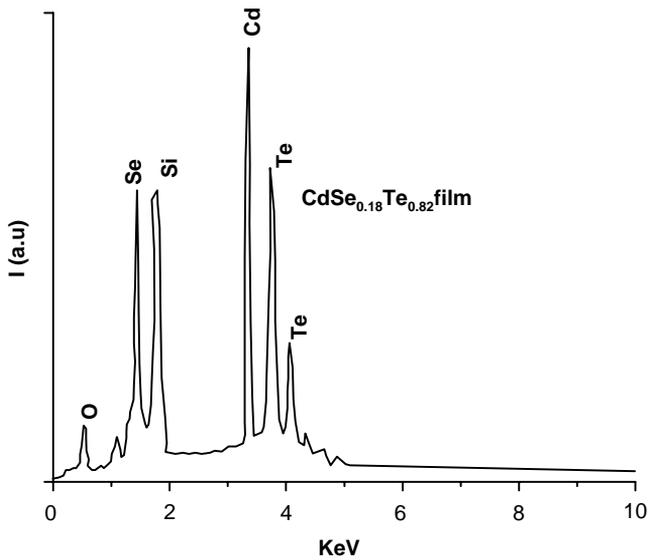


Fig. 4. EDX pattern of a representative CdSe_{0.18}Te_{0.82} film of thickness 1560 nm.

Table 2

Micro-structural and optical parameters of CdSe_xTe_{1-x} films of various thickness deposited on glass substrates

Thickness (nm)	Crystallite size (nm)	δ ($10^{12} \text{ lin m}^{-2}$)	ε (10^{-4})	Composition (Te–Se)	E_g (eV)
250	—	—	—	76–24	1.62
570	—	—	—	76–24	1.61
850	251	15.87	11.98	79–21	1.56
1560	390	6.575	11.25	82–18	1.54
1900	418	5.723	11.25	78–22	1.52

Table 2

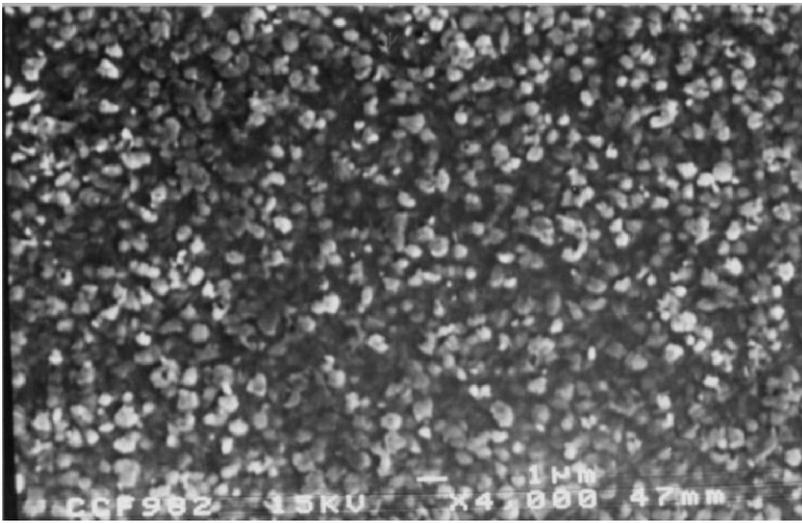


Fig. 5. SEM micrograph of a representative CdSe_{0.18}Te_{0.82} film of thickness 1560 nm.

In general, all the films showed fairly good transparency above 850 nm. The optical transmittance spectra are analyzed using the relations

$$\alpha hv = A_2(hv - E_g^d)^{1/2}, \quad (3)$$

$$\alpha hv = A_2(hv - E_g^i)^2, \quad (4)$$

for allowed direct and indirect transitions, respectively. Where A_1 and A_2 are two constants, α is the absorption coefficient, hv is the photon energy and E_g^d and E_g^i are the direct and indirect band gaps, respectively. From the graphs of $(\alpha hv)^{1/2}$ versus (hv) and $(\alpha hv)^2$ versus (hv) plots it is found that $(\alpha hv)^{1/2}$ versus (hv) did not lead to straight lines over any part of the optical spectrum, thus supporting the interpretation of direct band gap rather than an indirect band gap for all the hot wall deposited CdSe_xTe_{1-x} films. $(\alpha hv)^2$ versus (hv) plots for all the CdSe_xTe_{1-x} films deposited on glass substrates were plotted and the straight line portion is

extrapolated to cut the x -axis which gives the energy gap. Fig. 6 shows a representative plot of $(\alpha hv)^2$ versus (hv) for a film of thickness 1560 nm on glass substrate and it clearly reveals the linear increase in $(\alpha hv)^2$ versus (hv) beyond a

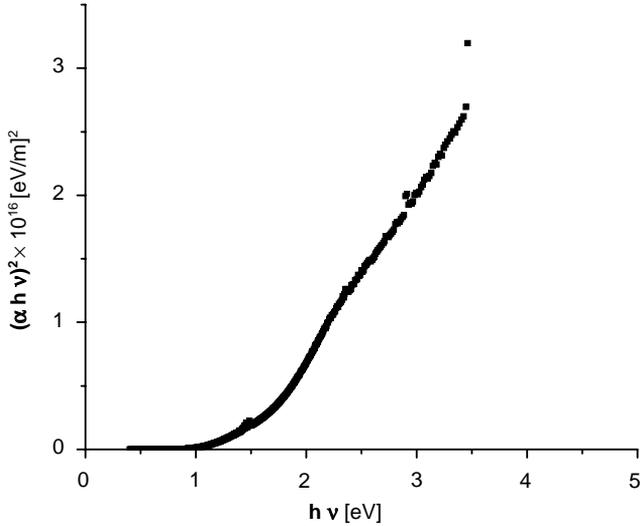


Fig. 6. $(\alpha hv)^2$ versus (hv) plot for a representative $CdSe_{0.18}Te_{0.82}$ film of thickness 1560 nm.

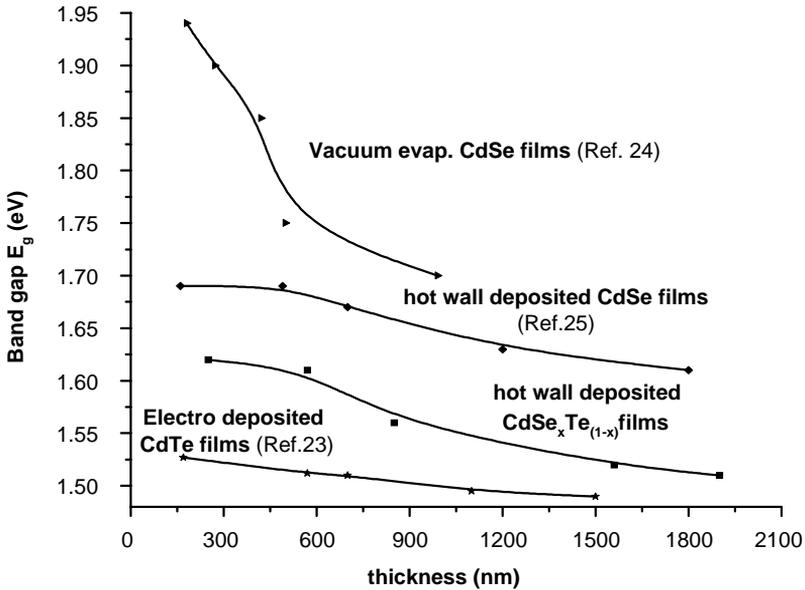


Fig. 7. A comparative plot of variation in band gap with thickness for hot wall deposited CdSe, $CdSe_xTe_{1-x}$ and electrodeposited CdTe films.

certain photon energy. A comparative look of E_g values with the micro-structural parameters for films of various thicknesses is given in Table 2. It is observed that the band gap (E_g) decreases with increase of film thickness. Islam et al. [21] and Sebastian et al. [4] have reported a band gap of 1.5 and 1.47 eV for CdSe_{0.2}Te_{0.8} films deposited by electron beam evaporation and by physical vapor deposition which compares very well with the present value. The decrease of band gap with the increase of thickness may be attributed to the increase of crystallite size and decrease in strain and dislocation density, as reported for other semiconducting films [22].

Analysis of the optical transmittance /absorption spectra is one of the most productive tools for understanding and developing the band structure and energy gap of both crystalline and amorphous systems. Fig. 7 shows a comparative plot of the variation of band gap with thickness for CdTe [23] and CdSe films deposited by various authors [24,25]. The band gap of electrodeposited CdTe films are found to vary from 1.49 to 1.53 eV and for CdSe it varies from 1.9 to 1.7 eV. The band gap of the ternary CdSe_xTe_{1-x} lies between these two values proving the maneuverability of band gap by varying the Se and Te components.

4. Conclusion

CdSe_{0.3}Te_{0.7} compound material was prepared from its individual components and its composition and X-ray pattern are analyzed. Hot wall deposition of this material yielded Te rich films. Films of various thicknesses are deposited onto well-cleaned glass substrates using quartz tube length of 0.15 m. The thickness of the film have profound effect on the structure of the film. From the optical studies the band gap was found to decrease with increase of thickness. A comparison of the optical parameters with those of CdSe and CdTe throws light on the application of this material in solar cells for effectively harnessing the solar energy.

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