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# CdS<sub>x</sub>Te<sub>1-x</sub> films: preparation and properties

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Abstract.  $CdS_x Te_{1-x}$  films (0 < x < 1) were deposited by simultaneous evaporation of CdS and CdTe powders from a vertical two-zone hot wall evaporation jig onto glass substrates. Electrical conductivity, thermoelectric and optical properties along with microstructural properties were studied in order to derive information on the electron transport processes in the films. Raman scattering was also studied for the films.

#### 1. Introduction

Ternary compound semiconductor films based on solid solutions of II-VI compounds have shown promise in various device applications. Besides other applications,  $CdS_x Te_{1-x}$  offers the advantageous property of its use in graded band-gap thin film solar cells [1, 2]. The band gap of the material can be tuned from 1.4-2.4 eV while the lattice parameters can also be adjusted to match the absorber layer. Preparation of  $CdS_xTe_{1-x}$  films by various techniques was reported in earlier publications [1-3] and the main emphasis was to study the variation of optical energy gap of the films with their composition. In this paper we present our studies on  $CdS_{x}Te_{1-x}$ films prepared by simultaneous evaporation of CdS and CdTe powder from a vertical two-zone evaporator and characterized by measuring the electrical, thermoelectric, optical and microstructural properties along with the Raman shift.

#### 2. Experimental procedure

 $CdS_x Te_{1-x}$  films (0 < x < 1) were prepared by co-evaporating CdS and CdTe powder (both 99.999% purity) from a vertical two-zone evaporator [4]. Two distinct temperature zones at 1000 K and 1100 K could be located for simultaneous evaporation of CdTe and CdS powders, respectively, placed inside quartz crucibles. The details of the two-zone evaporation jig are described elsewhere [4]. The films were deposited onto glass substrates kept at 470 K and at a system pressure of  $\approx 10^{-4}$  Pa. The compositions of the films were determined by energy dispersive x-ray detection (EDAX) measurements and the optical traces were recorded by a Hitachi U-3410 spectrophotometer. The x-ray diffraction (XRD) traces were recorded by a Philips PW 1130 diffractometer while the Raman spectra were taken by using an argon ion laser with exciting radiation of 514.5 nm in a near backscatter geometry. Cross-shaped sample geometry [5] was used for measuring the electrical conductivity  $\sigma$  by the four-probe technique [6]. The thermoelectric power (TEP) was measured with samples having length-to-breadth ratio of 16:1.

#### 3. Results and discussion

Figure 1 shows the micrographs obtained from transmission electron microscopy (TEM) and scanning electron microscopy (SEM) for some representative films. Columnar growth as shown in figure 1(b) was obtained in all the films studied here. The grain size increased with increasing CdS content of the films. The diffraction patterns (figure 1(a) and 1(c)) indicated polycrystalline nature with cross-oriented grains. They also indicated wurtzite structure for all the films, with the most intense ring for (002) planes followed by reflections from (102) and (112) planes.

Hot probe measurements were carried out by measuring the thermoelectric power in the above films having a length:breadth ratio of 16:1 to avoid possible perturbation due to heat flow from hot end to cold end and vice versa. The thermo emf (TEMF) was measured with respect to spectroscopically pure copper wire (0.1 mm diameter) by a voltmeter with impedance > 1 G\Omega. The Cd/(S + Te) ratios for all the films were always  $\ge$  1 and the films were p type for x < 0.25, beyond which they were always n type, as has been indicated (figure 2) by hot probe technique. The XRD traces indicate (figure 3) wurtzite structure with the c axis perpendicular to the film surface. The most intense peak is for the (002) plane whose position shifted from  $2\theta = 24.3^{\circ}$  to 25.3° with change in composition



Figure 1. TEM and SEM micrographs of representative films of CdS<sub>x</sub>Te<sub>1-x</sub>. (a), (b), x = 0.18; (c), x = 0.32; (d), x = 0.53; (e), x = 0.62; (f), x = 0.79.

(0.1 < x < 0.8). The values of the lattice parameters a and c were evaluated from the XRD traces and are shown in figure 4. The values of the lattice constants decreased for films with increasing CdS content of the films and could be fitted well to the expressions: a = 4.566 - 0.148x and c = 7.502 - 0.538x.

The Raman spectra (room temperature) of the  $CdS_xTe_{1-x}$  films had two peaks with harmonics indicating two-mode behaviour. The compositional dependence of the Raman lines is shown in figure 5. The LO phonon frequencies of CdS continuously decreased while the TO frequencies increased with increasing concentration of CdTe. These two lines when extrapolated seem to meet at a point  $\approx 236 \text{ cm}^{-1}$  in the region of 100% CdTe and this frequency may be considered as the local mode of S in CdTe. The LO of CdTe, on the other hand, linearly decreased and its TO increased with increasing concentration of CdS. The point of intersection at 157 cm<sup>-1</sup>, which occurs in the region of 100% CdS, may be regarded as the gap mode of Te in CdS.

The absorption coefficient  $\alpha$  was determined by measuring the reflectances R from the film side and  $R_1$  from the substrate side, details of which have been reported elsewhere [7]. Considering light of wavelength  $\lambda$  incident normally on a film of thickness t and bounded



Figure 2. Variation of thermoelectric power S with composition.

by two transparent and nearly non-absorbing media (i.e. air and glass substrate), the reflection coefficient R from the upper surface of the film at the absorption edge can be expressed as [8]:

$$R = \frac{(n_0 - n)^2 + k^2}{(n_0 + n)^2 + k^2}$$
(1)







Figure 4. Variations of the lattice constants with composition.



**Figure 5.** Variation of Raman shift with composition x for CdS<sub>x</sub>Te<sub>1-x</sub>.

and

$$k^{2} = \frac{(n_{0} - n)^{2} - R(n_{0} + n)^{2}}{(R - 1)}$$
(2)

 $n_0$ , n and  $n_1$  are the refractive indices of air, film and substrate (glass) respectively. k is the extinction coefficient of the film.

Again, if the light is incident from air to film through glass, i.e. by reversing the substrate, the corresponding reflectance  $R_1$  reduces to

$$R_{i} = \frac{(n_{1} - n)^{2} + k^{2}}{(n_{1} + n)^{2} + k^{2}}$$
(3)

which gives the value of

$$k^{2} = \frac{(n_{1} - n)^{2} - R_{1}(n_{1} + n)^{2}}{(R_{1} - 1)}.$$
 (4)

Equating expressions (2) and (4) and rearranging for n, one obtains

$$n = \frac{(n_1^2 - n_0^2)(R + R_1 - RR_1 - 1)}{2[(n_1 + n_0)(R - R_1) + (n_1 - n_0)(RR_1 - 1)]}.$$
(5)

Thus equation (5) allows us to determine the value of the refractive index n of the film without knowing the value of the thickness of the film. The expression for the extinction coefficient k may be obtained by substituting the above expression of n in equation (2) or (4) and the absorption coefficient  $\alpha$  may be calculated by using the relation

$$\alpha = \frac{4\pi k}{\lambda}.$$
 (6)

This means that  $\alpha$  may be calculated by using the measured quantities R and  $R_1$  and the standard values of the refractive indices of air and glass (substrate material) only. This method of evaluation of  $\alpha$  differs from that given by Manifacier et al [9] due to the fact that in the latter method one has to use generated and regenerated quantities (i.e. t and n) from transmittance  $T_r - \lambda$  trace. Thus the error in measuring  $T_r$  adds up each time in evaluating  $\alpha$  through the multiple use of  $T_r$  for determining n and t. Hence this method will permit accurate determination of the absorption coefficient of thin films. It may be noted that the relative precision of measurements  $\Delta R/R$  of reflectance R by a Hitachi U-3410 spectrophotometer is  $\approx 1\%$ , which is also to be reflected in the precision of obtaining the refractive index.

The band gap  $E_g$  was determined [7] from plots of  $\ln \alpha$  against  $h\nu$  (figure 6). The variation of  $E_g$  with composition shows a nonlinear behaviour and indicates a bowing phenomenon (figure 7). Figure 7 shows that the band gaps of  $CdS_xTe_{1-x}$  films can be continuously tuned from 1.4 to 2.4 eV by varying the CdS content of the films. It is interesting to note that the band gap reaches a minimum of 1.36 eV at about x = 0.3, which is in agreement with the observations by Radojcic *et al* [1] and Ohata *et al* [2]. However, the values of the minimum band gap and the corresponding composition differed from one another. The band gap E(x) of the CdS<sub>x</sub>Te<sub>1-x</sub> can be fitted with the following expression [10]

$$E(x) = E_2 + (E_1 - E_2 - b)x + bx^2$$
(7)

where  $E_1$  and  $E_2$  are the band gaps of CdS and CdTe films respectively and b is the bowing parameter. The value of b obtained from the fit of the experimental data is 1.7 eV, which compares well with that obtained (b = 2.0 eV) from theoretical considerations [11]. It may be noted that our b value agrees quite well with

1

![](_page_4_Figure_1.jpeg)

**Figure 6.** Plot of  $\ln \alpha$  ( $\alpha$  in cm<sup>-1</sup>) against  $h\nu$ .

![](_page_4_Figure_3.jpeg)

**Figure 7.** Variation of band gap E(x) with composition: O, experimental points; --, theoretical plot with b = 1.7.

those obtained by other workers [1-3]. The films are also characterized by the presence of only direct transition for all compositions. We have also plotted [10, 11]  $\Delta E(x)a^4/(1-x)$  against x to see any possibility of the presence of more than one phase in these films. Here  $\Delta E(x)$  is defined to be equal to  $E_{\text{lin}} - E(x)$ , where  $E_{\text{lin}} = E_2 + (E_1 - E_2)x$ . The straight-line fit (figure 8) for the entire composition range indicates that only one phase, i.e. wurtzite, is present in these films. This is in agreement with the results obtained from the XRD and TEM data. It may be noted that Hill and Richardson [3] observed a structural phase change from zinc blende to wurtzite as x increased, while Goede etal [12] observed a change from sphalerite to wurtzite near compositions close to CdTe. This deviation may be due to the adoption of the improved technique for depositing ternary compounds, as evaporation from a single boat or by electron gun would certainly lead towards fractional distillation of the elements constituting the compound.

Optical constants such as refractive index n and extinction coefficient k were computed by using relations (5) and (2) respectively. The variation of the absorption coefficient  $\alpha$  for  $CdS_xTe_{1-x}$  films with incident photon energy is shown in figure 6. It can be seen that the films having higher CdS content have higher absorption coefficient. The variations of refractive index and extinction coefficient with composition are shown in figure 9.

![](_page_4_Figure_7.jpeg)

Figure 8. Plot of  $\Delta E(x)a^4/(1-x)$  against x.

![](_page_4_Figure_9.jpeg)

Figure 9. Variation of n and k with composition x.

Both the refractive index and the extinction coefficient are seen to fall with x before showing a sharp increase at  $x \approx 0.5$ .

Variation of room-temperature resistivity with composition is shown in figure 10, which indicates a monotonic fall in resistivity values with increasing CdS content of the films. The films are polycrystalline in nature and, as such, grain boundary scattering will play a predominant role in describing the electron transport processes in these films. The films are highly resistive. Thus, accurate measurements of electrical conductivity and Hall mobility in the lower temperature range for generating data for the analysis of the grain boundary effects by using the existing theories of Seto [13, 14] and Baccarani et al [15] become difficult. We have analysed the data by using the modified version [16-19] of the Dow-Redfield model [20, 21] and evaluated the barrier height  $(E_b)$ , density of trap states  $(Q_t)$  at the grain boundary, grain size and the carrier concentration of the above films by measuring the reflectances (specular and diffuse) in the films.

Considering the excess absorption in polycrystalline semiconductors at the band edge caused by the Franz-Keldysh effect arising out of the built-in electric field in the material, Bujatti and Marcelja [18] modified the Dow-Redfield model by considering spherical crystallites with radius R. The surface states for large crystal-

![](_page_5_Figure_1.jpeg)

Figure 10. Variation of electrical resistivity ( $\rho$  in  $\Omega$  cm) of CdS<sub>x</sub>Te<sub>1-x</sub> films with composition x.

lites were considered to be all occupied by the charge carriers such that the grains were partially depleted and the electric field F close to the surface decayed exponentially. The expression for normalized total absorption  $A/A_0$  (i.e.  $\alpha/\alpha_0$ ) becomes [18]

$$A/A_{0} = \alpha(\nu)/\alpha_{0} = D \int_{y_{*}}^{y_{*}} \frac{I}{I_{0}} \left(\frac{y_{s}}{y}\right)^{1/2} \times \left[KR/3 - (\frac{1}{2})\ln(y/y_{s})\right]^{2} \frac{dy}{y}$$
(8)

where  $A_0$  is the total absorption at the band gap,

$$I = K_1 \omega^{-1} \int_y^\infty A_i^2(z) \,\mathrm{d}z$$

and

$$y = \gamma^{1/3} F^{-2/3} (E_{\rm g} - h\nu)$$

where  $A_i$  is the Airy function,  $K_1$  is a constant of the material and  $D^{-1} = 2(KR/3)^2 - 4(KR/3) + 4$ with  $y_m = (E_g - h\nu)^{1/3}\gamma^{-1}(K)^{-2/3}$  and  $y_s = (E_g - h\nu)\gamma^{-1}(F_s)^{-2/3}$ . Here,  $\gamma = 2m^*/\hbar^2$ , K is the inverse of Debye length  $(\lambda_d)$  and

$$F = F_{\rm s} \exp\left[-(R - r)/\lambda_{\rm d}\right] \tag{9}$$

 $F_s$  is independent of crystallite size and is equal to the surface charge divided by the static dielectric constant.

The integral in equation (8) becomes zero for  $E_{g} - h\nu = E_{b}$  and  $y_{m} = y_{s}$ ; thus  $A/A_{0} \rightarrow 0$ . A plot of  $A/A_{0}$  (or  $\alpha/\alpha_{0}$ ) against  $(E_{g} - h\nu)$  would indicate a sharp fall at  $E_{g} - h\nu = E_{b}$ . Thus equation (9) will allow one to evalute the field and hence the potential barrier  $E_{b}$ . Figure 11 shows the plots of  $\alpha/\alpha_{0}$  against  $(E_{g} - h\nu)$  for three representative films which indicate distinct falls in the  $\alpha/\alpha_{0}$  value at  $(E_{g} - h\nu) = E_{b}$ .

As indicated by equation (9), the field in the partially depleted grain would decay exponentially in the grain so long as  $\exp(-R/\lambda_d) \ll 1$ , i.e.  $R > \lambda_d$ . In the limit of full depletion,  $\lambda_d$  will tend to R and  $F = F_s(r/R)$ . This means that the field will vary linearly in the grain. So, for partially depleted grains,  $R > \lambda_d$  and  $R \simeq \lambda_d$ 

![](_page_5_Figure_14.jpeg)

Figure 11. Plots of  $\alpha/\alpha_0$  against  $E_9 = h\nu$  for three representative films with x = 0.18 (- $\bullet$ -), 0.32 (- $\Delta$ -) and 0.79 (-O-).

would mean that the grains are fully depleted. This indicates that the potential form given in equation (9) is a generalized form which can describe both partially and fully depleted conditions of the grains and as such the condition for small crystallites in describing the fully depleted grains by Bujatti and Marcelja [18] becomes redundant. It is now apparent that the effect of grain boundaries with the inherent space charge region due to depletion at the interface results in band bending, and this will be reflected by the presence of a potential barrier  $(V_b)$ . The potential V can be obtained by integrating equation (9) with respect to r and can be given by

$$V = F_{\rm s} \lambda_{\rm d} \exp\left(-\frac{R-r}{\lambda_{\rm d}}\right) + C. \tag{10}$$

Now, at r = 0, the potential should be constant and will be equal to the crystal field potential  $V_{BO}$  such that

$$V_{\rm BO} = F_{\rm s}\lambda_{\rm d}\exp(-R/\lambda_{\rm d}) + C. \tag{11}$$

Thus

$$V = F_{\rm s}\lambda_{\rm d}\exp\left(-\frac{R-r}{\lambda_{\rm d}}\right) + V_{\rm BO} - F_{\rm s}\lambda_{\rm d}\exp(-R/\lambda_{\rm d}).$$
(12)

The potential at the surface  $V_s$  can be obtained from equation (12) by putting r = R:

$$V_{\rm s} = F_{\rm s}\lambda_{\rm d} + V_{\rm BO} - F_{\rm s}\lambda_{\rm d}\exp(-R/\lambda_{\rm d}). \tag{13}$$

Thus the grain boundary potential  $V_b$  at the interface becomes

$$V_{\rm b} = V_{\rm s} - V_{\rm BO} = F_{\rm s} \lambda_{\rm d} [1 - e^{-(R/\lambda_{\rm d})}]$$
 (14)

such that for partially depleted grains when  $\exp(-R/\lambda_d) \ll 1$ ,  $V_b = F_s \lambda_d$ . The expression for  $F_s$  can be obtained by considering that the total charge on the surface of the crystallite is equal to  $4\pi R^2 q Q_t$  so that the surface

![](_page_6_Figure_1.jpeg)

**Figure 12.** Variations of  $Q_t$  and  $N_d$  with  $x = 0, N_d$ ;  $\Delta$ ,  $Q_t$ .

charge density becomes equal to  $qQ_t$  and the field at the surface  $F_s$  becomes  $qQ_t/\epsilon$ . Therefore

$$V_{\rm b} = (qQ_{\rm t}/\epsilon)\lambda_{\rm d}.$$
 (15)

Then the barrier height  $E_b$  becomes equal to

$$E_{\mathbf{b}} = \frac{q^2 Q_{\mathbf{t}}}{\epsilon} \lambda_{\mathbf{d}}.$$
 (16)

The Debye length  $\lambda_d$  is expressed as follows

$$\lambda_{\rm d}^2 = \left[ (\epsilon kT) / (N_{\rm d} dq^2) \right]. \tag{17}$$

Thus, by measuring the absorption coefficient and using the equations (8), (16) and (17), we can evaluate the barrier height  $E_b$  and density of trap states  $Q_t$  at the grain boundaries, provided that the carrier concentration  $N_d$  is known.

The values of  $N_d$  have been evaluated from Hall measurements and/or C-V data for the films studied here. The values of  $Q_t$  were then evaluated by using equation (16). The variations of  $Q_t$  and  $N_d$  with x and  $E_{\rm b}$  with  $N_{\rm d}$  are shown in figures 12 and 13 respectively. The densities of trap states and carrier concentrations were seen to increase with the increase in CdS content of films. The increase in carrier concentration will result in filling of the additional trap states created at the grain boundaries due to the increased grain size arising out of the addition of CdS in the films. The increase in trap states is small compared with the increase in carrier concentration of the films due to addition of CdS, and as such the grains remain partially depleted with traps fully filled. Once all the traps are filled, additional increases in carrier concentration would culminate in a decrease in both the width of the dipole layer and the magnitude of  $E_b$ , while the total charge in the region should remain constant. This has been reflected in the variation of barrier height  $E_b$  at the grain boundary with carrier concentration (figure 13) indicating partially depleted grains. This has also been reflected by  $R > \lambda_d$ for all the films studied here.

![](_page_6_Figure_11.jpeg)

Figure 13. Variations of  $E_{\rm b}$  with  $N_{\rm d}$ .

#### 4. Conclusion

 $CdS_{x}Te_{1-x}$  films prepared by co-evaporating CdS and CdTe were highly resistive and the resistivity was seen to decrease monotonically (from  $\approx 10^4 - 10^1 \ \Omega \ \text{cm}$ ) with increasing CdS content. The films were p type for x < 0.25 beyond which they were always n type. The films are polycrystalline in nature and columnar growth is distinctly visible for all the films. An increase in grain size with CdS content was observed. The films did not show any change of phase with composition and indicated a predominant wurtzite structure for all the films studied here. Grain boundary scattering was found to be a dominant factor controlling the conduction mechanisms in the films. The density of trap states at the grain boundaries and the carrier concentration were found to increase with increasing CdS content of the films. The increase in carrier concentration was sufficiently large compared with the increase in trap states for the grains to remain partially depleted with filled traps. The barrier height was seen to decrease with increasing CdS content. The band gap was seen to vary nonlinearly with composition and showed a minimum value of ~ 1.36 eV at  $x \sim 0.3$ . The Raman spectra indicated the local mode of S in CdTe  $\sim 236$  cm<sup>-1</sup> and the gap mode of Te in CdS  $\sim 157$  cm<sup>-1</sup>.

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