CHAPTER-IV

SUMMARY AND CONCLUSIONS
In this chapter the experimental results of the present investigation on \( \text{Cd}_{1-x}\text{Zn}_x\text{Te} \) \((0 \leq x \leq 1)\) films are summarized and the conclusions drawn from these results are presented.

In the present investigation, \( \text{Cd}_{1-x}\text{Zn}_x\text{Te} \) thin films \((0 \leq x \leq 1)\) were prepared by two-source vacuum evaporation technique. 5N pure CdTe and ZnTe compounds were used as the source materials. The films were deposited onto 7059 glass substrates maintained at 573 K, and subsequently annealed at 673 K for one hour for homogenization. The film thickness was about 1 \( \mu \text{m} \). The change in film composition \(^x\) was brought about by proper control of source temperatures.

Energy dispersive X-ray analysis (EDAX) showed that \( \text{Cd}_{1-x}\text{Zn}_x\text{Te} \) films were stoichiometric \((\text{Te}/(\text{Cd}+\text{Zn}) = 1)\) for the entire composition range \((x = 0 - 1)\).

X-ray diffraction (XRD) spectra of the films revealed that the films were polycrystalline with preferential \((111)\) orientation. All the films were of single phase with cubic structure. The evaluated lattice parameter \(^a\) was in the range \(6.484 \text{ Å} \) \((\text{for } x = 0)\) - \(6.104 \text{ Å} \) \((\text{for } x = 1)\). The value of \(^a\) was observed to decrease linearly with increasing \(^x\) and the composition dependence of lattice parameter was in accordance with Vegard's law. The grain size \(^L\) of the crystallites was in the range 95 - 174 nm. It was observed
that, the for films with composition far away from the binaries the grain size decreased, indicating degradation of crystalline quality as the composition approached the mid value ($x = 0.5$).

The optical characterization of the experimental films was carried out in the wavelength range 400 - 2000 nm, using transmittance and reflectance spectra recorded at room temperature. The films showed high transmittance with a sharp absorption edge. The absorption edge was found to be less sharp for films with composition nearer to the mid value, which is attributed to the decrease of crystallinity of these films. The absorption coefficient $\alpha$ was evaluated as a function of incident photon energy ($h\nu$) from transmission data. The linearity of $(\alpha h\nu)^2$ vs. $(h\nu)$ plots clearly established that the optical transition at the band edge was direct and allowed. The band gap energy $E_g$ estimated from these plots was found to increase from 1.48 eV (for $x = 0$) to 2.26 eV (for $x = 1$) with increasing zinc content in the films. $E_g$ values evaluated from transmission data were also in good agreement with those obtained from photoluminescence (PL) spectra of the same samples recorded at room temperature. The composition dependence of band gap was nonlinear with a bowing parameter $b$ of $-0.16$ eV.
The extinction coefficient \( k \) calculated from the transmission data in the wavelength range 400 - 2000 nm, was found to have values in the range 0.01 - 0.18. The variation of \( k \) with wavelength was similar to that of \( \alpha \) with sharp fall near the band edge.

The refractive index \( n \) near the band edge was in the range 2.5 (for \( x = 0 \)) - 2.7 (for \( x = 1 \)). These values are somewhat less than those reported for bulk Cd\(_{1-x}\)Zn\(_x\)Te. The lower values of \( n \) for Cd\(_{1-x}\)Zn\(_x\)Te films of the present study may be due to surface effects of films. A sharp increase in \( n \) values was observed near the band edge. The dielectric constant \( \epsilon_1 \), calculated using \( n \) and \( k \) values was in the range 6.3 - 7.3, increasing with increase in \( x \).

The relative effective mass \( (m^*/m) \), calculated from lattice parameter \( a \) and band gap \( E_g \) was found to be in the range 0.29 - 0.36, the value increasing with increase in \( x \).

The reflectance spectra of the films recorded at room temperature in the wavelength range 185 - 400 nm (beyond the absorption edge), exhibited three interband transitions with energies \( E_1 = 3.255 - 3.543 \) eV, \( E_1 + \Delta_1 = 3.845 - 4.165 \) eV, and \( E_2 = 5.310 - 5.417 \) eV, respectively. The values of
these energies were found to increase linearly with increasing \( x \).

The optical parameters of the films were also measured at room temperature using an automatic spectroscopic ellipsometer (SE) in the photon energy range 1.1 - 5.6 eV. \( \varepsilon_1 \), \( \varepsilon_2 \) (the real and imaginary parts of the complex dielectric function \( \varepsilon^* \)) and normal incidence reflectivity \( R \) versus photon energy (h\( \nu \)) plots also showed the three interband transitions in the films. The spectral dependence of \( \alpha \), \( n \) and \( k \) evaluated from SE data also revealed the three distinct peaks corresponding to \( E_1 \), \( E_1 + \Delta_1 \) and \( E_2 \) in confirmity with the transmission data.

Electrical properties such as thermoelectric power, carrier concentration and electrical conductivity were measured to assess the electrical behaviour of the films.

The thermoelectric power \( S \) of the films was determined in the temperature range 150 - 400 K. The positive sign of \( S \) for films of the entire composition range \( x = 0-1 \) showed that the films were of p-type conductivity. \( S \) was observed to decrease with increase of temperature for each composition. The room temperature values of \( S \) decreased from 0.5 mV/K to 0.3 mV/K with increasing \( x \) from 0 to 1. Fermi energy \( E^* \) estimated from thermoelectric
Power measurements, was found to decrease from 0.15 eV to 0.10 eV with increasing \( x \). The carrier concentration \( N_A \), also determined from thermoelectric power data was in the range \( 2 \times 10^{15} \) - \( 9 \times 10^{15} \) cm\(^{-3} \), increasing with increase in \( x \). Pure Cd\(_{1-x}\)Zn\(_x\)Te films being highly resistive, \( N_A \) of these films was determined independently from capacitance-voltage (C-V) measurements using indium / p-Cd\(_{1-x}\)Zn\(_x\)Te Schottky junctions. The measured \( N_A \) values were in the range \( 3 \times 10^{15} \) - \( 10 \times 10^{15} \) cm\(^{-3} \), \( N_A \) increasing with increase in zinc content. These values are comparable with those obtained from thermoelectric power measurements.

The room temperature conductivity \( \sigma \) of the films was found to be in the range \( 5 \times 10^{-7} \) - \( 1.7 \times 10^{-6} \) ohm\(^{-1}\)-cm\(^{-1} \), increasing with increasing zinc content. \( \log \rho \) vs. \( x \) plot, showed a nonlinear relation with a bowing \( \beta \) of \(-0.17\) eV, which is comparable to that obtained from composition dependence of band gap.

The conductivity \( \sigma \) of the films was also measured at different temperatures ranging from 100 K to 500 K. \((\ln \sigma)\) vs. \((1/T)\) plots of the films showed two slopes corresponding to two activation energies. The activation energy \( E_{g1} \) in the high temperature region (\( \sim 300 - 500^\circ \) K) was in the range \( 0.16 - 0.29 \) eV, decreasing with increasing \( x \). The activation energy \( E_{g1} \) in the temperature region
( ~ 300 K) was found to be in the range 8.6 - 20.4 meV, increasing with increase in \( x \). It was observed that the composition dependence of \( E_{o1} \) also showed bowing with a value ~ 0.15 eV for \( b \), which is close to those values obtained from the composition dependence of band gap and resistivity. The values of \( E_{o1} \) suggests that the conduction in the high temperature region (above ~ 300 K) is mainly due to the transport of charge carriers across grains by thermionic emission.

The measured values of \( \sigma \) in the low temperature region (100 - 300 K) were found to have a better fit to the theoretical plot of \( \ln (\sigma T^{1/2}) \) vs. \( (1/T) \). From this it is evident, that the electrical conduction in the low temperature region is controlled by charge carriers which are trapped by completely filled trap states in the partially depleted grains. The grain boundary barrier height \( E_b \) evaluated from \( \ln (\sigma T^{1/2}) \) vs. \( (1/T) \) plots was in the range 6 - 12 meV. The density of trap states \( Q_t \) in the films was also calculated and was found to be in the range \( 2 \times 10^{10} \) - \( 6 \times 10^{10} \) cm\(^{-2} \). For films with composition approaching the mid-value (\( x \) ~ 0.5), the values of \( E_b \) and \( Q_t \) were higher indicating a decrease in the crystallinity of these films.
In the present study, an emphasis was made on the $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films with $x = -0.3$, because of its suitable electro-optical properties for application in tandem solar cells. $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Te}$ films of $\sim 1 \mu\text{m}$ thick were deposited onto glass substrates at 573 K. The films were of polycrystalline cubic with predominant (111) orientation, having a lattice parameter of $\sim 6.34 \text{Å}$ and a grain size of $\sim 120 \text{nm}$. The films were of p-type conductivity, with a resistivity of $\sim 1.3 \times 10^6 \text{ohm-cm}$, and a carrier concentration of $\sim 5.8 \times 10^{15} \text{cm}^{-3}$. The Hall mobility of these films was so low to be measured. An attempt was made to dope these films with tellurium, antimony and oxygen with a view to reduce the film resistivity.

In the case of Te-doped $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Te}$ films, it was found that the resistivity decreased up to $\sim 5 \times 10^4 \text{ohm-cm}$, while the carrier concentration increased to $\sim 8 \times 10^{15} \text{cm}^{-3}$ for a Te/(Cd+Zn) ratio of $\sim 1.2$. However, it was observed that the crystallinity of these films substantially decreased with increasing Te.

For Sb-doped $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Te}$ films, a minimum resistivity of $\sim 1.4 \times 10^5 \text{ohm-cm}$, with a carrier concentration of $\sim 6.4 \times 10^{15} \text{cm}^{-3}$ was obtained for a dopant concentration of $\sim 3.1 \text{at.\%}$. Further increase in Sb concentration increased the film resistivity.
In the case of oxygen-doped Cd$_{0.7}$Zn$_{0.3}$Te films, a minimum resistivity of $2.4 \times 10^3$ ohm-cm with a maximum carrier concentration of $1 \times 10^{16}$ cm$^{-3}$ was achieved at an oxygen partial pressure of about $2 \times 10^{-5}$ Torr, without affecting the crystallinity in the film. For higher oxygen concentrations, the resistivity was found to increase, which may be due to the formation of complex oxide phases in the films.

From a discussion of the various results of the present study on Cd$_{1-x}$Zn$_x$Te thin films ($0 \leq x \leq 1$), the following conclusions are drawn:

1. Polycrystalline Cd$_{1-x}$Zn$_x$Te thin films in the entire composition range ($x = 0 - 1$), with reproducible properties can be obtained under controlled deposition conditions, using the two-source vacuum evaporation technique which is a less expensive technique.

2. The films exhibited good transmission with sharp absorption edge.

3. The films were of single phase cubic with predominant (111) orientation. The films with composition nearer to the respective binary, possess grains with reasonably large size.
The films were of p-type conductivity with low conductivity \((5 \times 10^{-7} - 1.7 \times 10^{-6} \, \text{ohm}^{-1} \cdot \text{cm}^{-1})\) and carrier concentration \((2 \times 10^{15} - 10 \times 10^{15} \, \text{cm}^{-3})\), these values increasing with increasing zinc content.

The electrical conduction in these films in high temperature region was due to the transport of charge carriers across the grains by thermionic emission; and in the low temperature region was due to trapped charge carriers in trap states of the partially depleted grains.

The density of trap states was relatively less in films with compositions nearer to the binaries (CdTe and ZnTe).

The films with composition \(x = 0.3\) had a band gap \(-1.65\, \text{eV}\), which was optimum for the fabrication of highly efficient tandem solar cell.

It was possible to reduce the film resistivity by doping the films with tellurium, antimony and oxygen during film deposition. Among these three dopants, oxygen-doped \(\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Te}\) films exhibited much reduced resistivity and with improved carrier concentration suitable for tandem solar cell application.