CHAPTER - V

OPTICAL AND ELECTRICAL PROPERTIES

OPTICAL PROPERTIES

5.1 Introduction

Optical absorption in solids results from any of the following principal processes. (i) excitation of crystal vibration, (ii) formation of exitons, (iii) excitation of free holes and electrons within allowed bands, (iv) excitation of electrons across the gap from the valence band to the conduction band and (v) absorption due to the presence of imperfection. Of all the above absorption processes, only the last two give rise directly to photoconductivity. The photocurrent in junction is primarily due to excitation of electrons across the forbidden gap.

The absorption of radiation that leads to electronic transitions between the valence and conduction bands is split into direct and indirect processes. Direct transitions require that in the excitation process no change in the K value of the electron occurs. Indirect transitions represent the condition that there is a change in crystal momentum (K) of the electron. Thus vertical (direct) transitions are important when the valence and conduction band extrema are located at the sample point in Brillouin zone. For indirect transitions the band extrema differ in their position in K space. The indirect absorption process requires the annihilation or creation of phonons to balance the crystal momentum. The performance of a photoelectrochemical solar cell depends on the preparation of the thin film photoelectrode. The characterization of such films is therefore important and optical properties of those films are of great interest.
5.2 Review of earlier work

Fantini et al prepared CdSe thin films on SnO₂ coated glass slides. They observed that the interference extrema in the transmittance spectrum and the reflectance spectrum of the CdSe coated film are coincident /1/. Mondal et al studied the optical properties of CdSe thin films prepared by hot wall technique. Informations on the refractive index and absorption coefficient were derived. Direct transitions corresponding to band gaps of 1.7 and 1.9 eV were obtained /2/. Sebastian et al deposited CdSe thin films by a physical vapour deposited method and studied the optical transmittance and the near-normal specular reflectance in the range 0.40 - 2.40 μm and spectral distribution of reflected and transmitted intensities in the same range /3/.

Hanus et al prepared cadmium telluride thin films and studied the optical phenomena. They observed that the as formed CdTe exhibits a band gap of 1.45 eV /4/.

Mangalhara et al have reported the optical properties of CdSe₁ₓTeₓ thin films /5/. Gutierrez has determined the absorption coefficient, α(λ), and energy gap, Eg, of CdSe₁ₓTeₓ thin films from the measured transmittance and reflectance at normal incidence of light in the wavelength range 450-2500 nm. He has used a combined method from Goodman and Lubberts to determine the absorption coefficient and its dependance on the wavelength /6/.

5.3 Aim of the present work

Development of semiconductors with controlled energy gap is necessary for the increased applications of alloys in the solar cell fabrication and other optoelectronic devices. The optical properties of CdSeₓTe₁₋ₓ films are of much interest due to their alloying nature. Hence the absorption and transmission properties were studied to calculate their band gap variation.
II-VI semiconductors form an important class of optoelectronic devices. The binary II-VI semiconductors have been studied well with respect to their fundamental properties and device application. The II-VI compounds attract great interest since band gaps in these series can be tailored to encompass the wavelengths of relevance to both light (solar) to electrical energy conversion and detectors for optical communications. CdSe$_x$Te$_{1-x}$ is an interesting material because its band gap is in the optimal range (1.4 - 1.7 eV) for a photovoltaic cell. More recently, CdSe$_x$Te$_{1-x}$ alloy layers were used as semiconductor electrodes in photoelectrochemical cell (PEC). Optical characterization and post treatments are very important for both photovoltaic and PEC Cells.

5.4 Optical absorption studies

For solar cell fabrication and other opto-electronic devices, we require semiconductors with controllable energy gap. The semiconducting film structure used for optical measurements is GdSeTe/SnO$_2$ glass. The glass slide coated with conducting tin oxide (SnO$_2$) has a sheet resistance of 20 Ω/cm$^2$ and thickness 0.1 μm. It has been assumed that the film thickness of SnO$_2$ (0.1 μm) is negligible when compared with the semiconductor thickness (> 0.5 μm). With this assumption, the transmittance and reflectance spectra are only due to the semiconducting thin film. Optical transmission and absorption spectra of all cadmium chalcogenide thin films were obtained and the absorption coefficients ($\alpha$) were estimated.

5.4.1. Cadmium selenide films

The variation of optical absorbance with wavelength for a cadmium selenide film is shown in figure 5.1. The figure shows an absorption edge at 540 nm which corresponds to the band gap of the semiconductor. The absorbance data is used to obtain band gap for the CdSe using the relation.
Fig. 5.1. The variation of optical absorption with wavelength for a typical CdSe film. 

(insert) \((\alpha h\gamma)^2\) versus \((h\gamma)\) plot.
where $\alpha$ is the absorbance of the film. The replotted data is shown in figure 5.1 (insert) from which the band gap of the electrodeposited CdSe film is estimated as 1.71 eV at 300K. This value is in excellent agreement with an accepted value of 1.70 eV.

5.4.2 Cadmium telluride films

The optical absorbance curve for cadmium telluride film is shown in figure 5.2. The absorption coefficient satisfies the equation,

$$(\alpha h\nu)' = A(h\nu - E_g) \quad \text{(5.1)}$$

for a direct band gap material. The band gap $E_g$ is obtained by extrapolation of the plot of $(\alpha h\nu)'$ versus $h\nu$ (figure 5.2 insert) and found to be 1.44 eV. This value is in agreement with a reported value of 1.46 eV for CdTe film/11/.

5.4.3 Cadmium selenotelluride films

The optical absorption studies have also been carried out for various compositions of CdSe$_x$Te$_{1-x}$ films. The optical absorbance curves for three compositions are shown in figure 5.3 (a, b and c). It has been found that the absorption edge is correspondingly shifted for each composition. The band gap ($E_g$) of the CdSe$_x$Te$_{1-x}$ films were determined from extrapolation of the straight line portions of the $(\alpha h\nu)'$ versus $h\nu$ curves for three compositions in figures 5.4.

The band gap for CdSe and CdTe are 1.71 and 1.45 eV respectively and for the solid solution of CdSe$_x$Te$_{1-x}$, the band gap shifted from 1.45 eV towards the shorter wavelength side as Se concentration increased.

The band gaps for films of various compositions determined from optical absorption studies are shown in fig.5.5. Figure 5.5 shows that there in a minimum
Fig. 5.2. The variation of optical absorption with wavelength for a typical CdTe film.

(insert) $(\alpha h\gamma)^2$ versus $(h\gamma)$ plot.
Fig. 5.3. Optical absorption curves of CdSe$_x$Te$_{1-x}$ films for three compositions
(a: $x = 0.3$, b: $x = 0.5$, c: $x = 0.7$)
Fig. 5.4. $(\alpha h \gamma)^2$ versus $h \gamma$ plot for CdSe$_x$Te$_{1-x}$ films.
Fig. 5.5. The variation of band gap as a function of film composition 'x' in CdSe$_x$Te$_{1-x}$ films.
for the band gap at ground $x = 0.7$ and indicates the possibility of a tunable band gap for CdSe$_x$Te$_{1-x}$ film. Films prepared by two-source evaporation /12/ and three source elemental evaporation /13/ showed a similar behaviour. Tai et al /14/ have reported the band gap variation with composition and crystal structure for synthesized CdSe$_x$Te$_{1-x}$ alloys. Table 5.1 shows the variation of band gap with composition ‘x’ for typical CdSe$_x$Te$_{1-x}$ films.

5.5 Evaluation of optical constants

The increasing interest in solar absorption has created a new demand for techniques to determine the optical constants of thin films of absorbing semiconductor materials /15-24/. The performance of polycrystalline thin film semiconductor photoelectro-chemical cells depend heavily on the preparation of active thin film electrode. The characterization of such semiconductor thin films is therefore necessary and the optical characterization of thin films are of paramount interest.

5.5.1 Introduction

Several methods are used to determine the optical constants (n and k) of thin polycrystalline films. Each method has its own limitations. All these require measurements of transmittance T and reflectance R. It has been shown by many workers /24-28/ that the optical properties are influenced by the various parameters such as thickness of the film, molecular fraction and experimental uncertainties.

A classification of the methods that use reflection at oblique incidence is given by Minikov et al and Eriksson et al /29, 30/. In this work, photometric measurements of R and T at normal incidence are used for the determination of optical constants. A modified Continuous Descent Derivative (CDD) method /31/, is used for the determination of n and k of electrodeposited CdSe, CdTe, CdSe$_x$Te$_{1-x}$ films from the normal incidence measurements.
TABLE 5.1

Variation of bandgap ($E_g$) with composition, $x$, for typical CdSe$_x$Te$_{1-x}$ films

<table>
<thead>
<tr>
<th>S.No</th>
<th>Composition 'x' in the film</th>
<th>Energy gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.71</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>1.65</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>1.58</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>1.47</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>1.43</td>
</tr>
<tr>
<td>7</td>
<td>0.6</td>
<td>1.40</td>
</tr>
<tr>
<td>8</td>
<td>0.7</td>
<td>1.38</td>
</tr>
<tr>
<td>9</td>
<td>0.8</td>
<td>1.39</td>
</tr>
<tr>
<td>10</td>
<td>0.9</td>
<td>1.41</td>
</tr>
<tr>
<td>11</td>
<td>1.0</td>
<td>1.45</td>
</tr>
</tbody>
</table>
5.5.2 Theory

The interaction between a light wave and a semiconductor is important in various parts of the spectrum. The optical properties of a semiconductor are governed by the interaction between the semiconductor and the electric field of e.m wave. It is convenient to describe the propagation of a plane wave in a solid by a frequency dependent complex refractive index \( N^x = n - ik \) where the real part of the refractive index \( n \) is related to the velocity of propagation of the wave and the extinction coefficient \( k \) represents the decay of the amplitude of oscillations of the electric field.

\[
E(x,t) = E_0 \exp \left[ \frac{N^x x}{c} \right] \exp \left[ i \omega \left( t - \frac{x}{c} \right) \right] \quad (5.3)
\]

\[
= E_0 \exp \left[ i \omega \left( t - \frac{nx}{c} \right) \exp \left( -\frac{k \omega x}{c} \right) \right] \quad (5.4)
\]

The optical parameters \( n \) and \( k \) are related to the frequency dependent electrical conductivity and electrical susceptibility.

It is known that the optical constants cannot be measured directly and they are often determined through their relation with the experimentally measurable transmittance, \( T \), reflectance, \( R \) of the film and reflectance \( R' \) of the substrate. This relation can be obtained from phenomenological theory of the optical properties of thin film. For light of wavelength \( \lambda \) normally incident on a film of thickness \( 'd' \) we have /22/.
\[
T = \frac{16 n_1 n_2 (n' + k')}{\epsilon \epsilon^* + K \sigma e^{iv} + 2s \cos \alpha + 2t \sin \alpha} = F_r \quad \ldots \quad (5.5)
\]
\[
R = \frac{K \epsilon \epsilon^* + \rho \epsilon^* e^{iv} + 2q \cos \alpha + 2r \sin \alpha}{\epsilon \epsilon^* + K \sigma e^{iv} + 2s \cos \alpha + 2t \sin \alpha} \quad \ldots \quad (5.6)
\]
\[
R' = \frac{\sigma \epsilon e^{iv} + \rho \epsilon^* e^{iv} + 2q \cos \alpha - 2r \sin \alpha}{\epsilon \epsilon^* + K \sigma e^{iv} + 2s \cos \alpha + 2t \sin \alpha} \quad \ldots \quad (5.7)
\]
\[
= F'_{R'}(n, k, d/\lambda)
\]

where \( K = (n-n_1) + k' \),

\( \rho = (n+n_1)' + k' \)

\( \sigma = (n-n_1)' + k' \)

\( \tau = (n+n_2)' + k' \)

\( t = 2K(n_2 + n_1)(k' + n' - n_1) \)

\( q = (n'+k')(n_2' + n_2) - (n'+k') - n_1 n_2 ' - 4n_1n_2 k' \)

\( s = (n'+k')(n_1' + n_1) - (n'+k') - n_2 n_2 ' + 4n_1n_2 k' \)

\( r = 2k(n_2 - n_1)(k' + n' - n_1n_2) \)

and \( \alpha = 4\pi d/\lambda \) and \( n_1 \) and \( n_2 \) are the refractive indices of the air and the substrate respectively.
When using equations, the experiment meets with two problems: direct and inverse. The direct problem is to determine $T$, $R$ and $R'$ from given $n$, $k$ and $d$ and is solved easily and unambiguously. The inverse problem, the determination of $n$, $k$ and $d$ from known $T$, $R$ and $R'$ has no analytical solution and these unknowns can be obtained through approximate formulae or graphical or computational methods /32-35/. Usually the thickness is found from independent measurements so that $n$ and $k$ can be evaluated from any pairs of equations given above.

Numerous attempts to solve the inverse problem have shown that its solutions are multivalued especially at small $d/\lambda$. When four or even six solutions are obtained /36/. Cases are also reported when for $d/\lambda < 0.01$, no physically meaningful solution of the inverse problem can be obtained /37-38. This is attributed to an increased role of the measurement error which leads to instability of the solution. To the authors knowledge, no method has been proposed for solving the inverse problem in these cases. It often appears that an inverse physical problem is mathematically incorrect and instability of the problem to small errors of the measured values is one of the indications of incorrectness. Two non-linear simultaneous inverse equations cannot be solved for a definite solution at the same time and the validity of the correctness of this inverse problem is well analysed by Bondar et al /31/. It is known that a set of non-linear algebraic or transcendental can be solved to a certain extent by the descent method. The continuous descent method was found to be successful in the present case. The basis of this method for a set of equations and the validity of this method for solving incorrect problems has been well analysed by Bondar et al /31/.

The continuous descent derivative method employs descending through the non-linear curves through very small intervals using converging iterations by numerical iterative techniques. In the present work, $n$ and $k$ values of electroplated cadmium chalcogenide films are obtained by using Runge-Kutta method.
The reflectance R and transmittance T of the electrodeposited CdSe, CdTe and CdSe$_x$Te$_{1-x}$ for $x = 0, 0.2, 0.8$ and 1 are measured at normal incidence using UV-VIS-NIR double beam spectrophotometer (Hitachi 20-200). An identical SnO$_2$ substrate is placed in the path of the reference beam. Measurements were done in the range of 340 nm - 2000nm with respect to the reference plate.

The thickness of the electrodeposited CdSe$_x$Te$_{1-x}$ thin films for $x = 0, 0.2, 0.8$ and 1 are determined independently by multiple beam interferometer and weight loss methods in their appropriate ranges. The various values of T and R were fed into the computer program alongwith the values of wavelength, thickness and refractive indices of air and substrate. The initial approximate values were chosen from literature and the value of refractive index and extinction coefficient are obtained. The various values obtained by C.D.D method for electrodeposited CdSe, CdTe and CdSeTe films are presented in this chapter.

5.5.3 Solution of the inverse problem by the continuous descent derivative method

The basis of the method for set of equations of the form,

$$f_n(x_1, ..., x_n) = 0 \quad \text{.......................... (5.8)}$$

$$f_n(x_1, ..., x_n) = 0 \quad \text{or in general}$$

$F(x) = 0$ is that the solutions sought through determination of the minimum points of the function $u(x) = |F(x)|^2$ by means of the set of equations.

$$dx_i \frac{\sum_{j=1}^{n} f_j \frac{df_i}{dx}}{\sum_{k=1}^{n} \left[ \sum_{j=1}^{n} \frac{df_j}{dx} \right]} \quad \text{.......................... (5.9)}$$

$$dt \frac{\sum_{k=1}^{n} \left[ \sum_{j=1}^{n} \frac{df_j}{dx} \right]}{dx_i}$$
For almost all initial points the differential descent trajectory \( \frac{dx}{dt} \) approaches the minimum point of the function \( u(x) \). It has been proved that this point is the solution of the set of non-linear equations (5.8). The solutions of the set of equations (5.9) is calculated using Runge-Kutta method. It is clear that for the determination of \( n \) and \( k \) we can use any pair of equations \( T \) and \( R \), \( T \) and \( R' \) and \( R \) and \( R' \). Here CDD set for calculating \( n \) and \( k \) from \( T \) and \( R \) has the form

\[
\frac{dn}{dt} = -\left(f_R^2 + f_T^2\right) \frac{\partial f_R}{\partial n} + \frac{\partial f_T}{\partial n} \\
\frac{dk}{dt} = -\left(f_R^2 + f_T^2\right) \frac{\partial f_R}{\partial k} + \frac{\partial f_T}{\partial k}
\]

\[
\begin{bmatrix}
\frac{\partial f_R}{\partial n} + \frac{\partial f_T}{\partial n} \\
\frac{\partial f_R}{\partial k} + \frac{\partial f_T}{\partial k}
\end{bmatrix}
\]

(5.10)

(5.11)

where \( \frac{dn}{dt} \) and \( \frac{dk}{dt} \) are the trajectories of the continuous descent to, the minimum points of the function \( u = |F(n, k, d/l)| \), ‘t’ is the interaction number \( f_R = R - F_R(n, k, d/l) \) and \( F_T = T - F_T(n, k, d/l) \). Any other pair of equations (\( T, R' \) and \( R, R' \)) as initial pair give the same results. \( n \) and \( k \) are determined from eqn (5.8) according to the flow chart for the computer program. For most of the wavelengths small number of iterations is required for this process to converge so that the machine time is not large. We find that an unambiguous solution can be obtained in almost all cases except those in which experimental values of \( T \) and \( R \) do not satisfy the relations,
\[ R \geq \frac{(1-T-R)^{\prime}}{4T}; \quad T \geq \frac{(1-T-R)^{\prime}}{4R} \] 

which follow from the law of conservation of energy and

\[ R \geq \frac{n'-1}{n'} (1-T) \]  

The relations are the criteria for the experimental results to be trustworthy. From earlier analysis of experimental results, it is seen that for a realistic measurement accuracy in optical experiments, when \( d = 0.05 \), the exact inverse problem is unstable to small measurement errors. For such cases \( n \) and \( k \) will be incorrect.

For calculating \( n \) and \( k \) for the electrodeposited thin films, the reflectance \( R \) and transmittance \( T \) are measured at normal incidence using UV-Vis-NIR spectrophotometer. The sample is placed in the path of the reference beam and measurements were carried out in the range of 400 to 1000 nm with respect to the reference plate (SnO\(_2\)). Films of almost same thickness which are optically transparent are used for taking \( R \) and \( T \) measurements. The values obtained were fed to the computer as data in the program along with the values of wavelength, thickness and refractive indices of air and substrate.

5.5.4 Result and discussions

The optical performance of thin films is determined by the thickness and optical constants of the layers. Thus a knowledge of the optical constants and thickness of the deposited layers is necessary for effective coating design. It is well known that the optical properties of materials in thin film form greatly depend on the film microstructure and are usually different from the known bulk properties. Microstructure is in turn determined by the method of deposition and various conditions prevailing during deposition.
Polycrystalline thin films of CdSe, CdTe and CdSe$_x$Te$_{1-x}$ within a wide range have been electrodeposited onto SnO$_2$ plates of nearly same thickness ($\approx 0.1$ $\mu$m). The optical properties of the films in the wavelength region of 400-2000 nm have been studied. The film thickness of CdSe, CdTe and CdSe$_x$Te$_{1-x}$ electrodeposited films are approximately 0.5 $\mu$m. The maximum transmittance of the samples varied between 40% and 80% A complicated set of equations for electrodeposited films have been given by Tomlin /39/. However, these relations of $T$ and $R$ can be simplified under experimental conditions. An identical SnO$_2$ film on glass was used as reference plate to determine the total transmission of the prepared layers. The SnO$_2$ substrates are not found to exhibit any interference with respect to glass in the wavelength range 400-1000 nm.

The variation of refractive index ($n$) and extinction co-efficient ($k$) of a typical CdSe film of thickness 500 nm is represented in fig. 5.6. The maximum value of refractive index for the CdSe film is found to be 2.70 for a wavelength of 730 nm. A peak value of 2.68 for single crystal CdSe has been reported at a wavelength of 680 nm by Elizalde et al /27/. This might be associated with the onset of absorption at the fundamental absorption edge. A similar variation in the refractive index of CdSe films with wavelength has also been reported in the range of 700 - 900 nm. The extinction co-efficient on the other hand, slowly decreases from 0.35 to 0.015 as the wavelength increases from 450 to 800 nm. This is in conformity with earlier results on CdSe thin films /40/.

Fig 5.7 represents the variation of refractive index and extinction co-efficient for a CdTe film. It is observed from the figure that $n$ decreases from 3.10 at 550 nm to 2.77 at 2000 nm. A small peak at 860 nm corresponds to the absorption edge of CdTe. The extinction co-efficient in found to decrease from 0.38 to 0.02 as the wavelength increased from 450 to 900 nm. Similar dispersion behaviour for vacuum evaporated CdTe film has been reported /5/.
Fig. 5.6. Variation of refractive index (n) and extinction co-efficient (k) with wavelength for a typical CdSe film.
Fig. 5.7. Variation of refractive index (n) and extinction co-efficient (k) with wavelength for a typical CdTe film.
The variation of refractive index with wavelength for CdSe$_x$Te$_{1-x}$ films ($x = 0.3, 0.5, 0.7$) are given in figure 5.8. It is observed from the figure that the refractive index of CdSeTe films with various compositions decrease slowly and attain saturation at 2000 nm. The peaks observed for CdSeTe films correspond to the absorption edge of the films with different compositions. The dispersion of refractive index with wavelength is similar to the result reported for electron beam gun evaporated CdSe$_{1-x}$Te$_x$ films for various compositions by Mangalhara et al /5/.

Fig 5.9 shows the variation of extinction coefficient with wavelength for three compositions of CdSe$_x$Te$_{1-x}$ films. It is observed from the figure that the extinction coefficient decreases from 0.4 to 0.01 as the wavelength increases from 400 to 900 nm. Similar behaviour has been reported for CdSe and CdTe films /32,41/.

5.6 Packing density of chalcogenide films

The refractive index of a material obtained on a thin film usually deviates from that of the bulk form of the same material. This deviation is due to the presence of voids present in the thin film. The ratio of the solid volume to the total volume of a film has been termed as packing density 'p'. Guenther /42/ has derived a relation to estimate the packing density of the films from the refractive index data which is given as,

$$n_f = n_b P + (1-P) n_v$$

(5.14)

where $n_f$ is the refractive index of the film, $n_b$ is the refractive index of the bulk material, and $n_v$ is the refractive index of the void /43-45/.

In the present work, optical measurements were carried out in air, it is assumed that the voids in the films are generally filled with moisture, and therefore $n_v$ is equal to 1.33. The packing density of the cadmium selenide, cadmium telluride and cadmium seleno telluride films are estimated and presented in table 5.2.

It is found from the table that the packing density of the chalcogenide films are better than 0.97. The higher value of the packing density indicates that electrodeposition process is a suitable technique to prepare compound and alloy semiconducting thin films.
Fig. 5.8. Refractive index (n) versus wavelength curves of CdSe<sub>x</sub>Te<sub>1-x</sub> films for three compositions.
(a: x = 0.3, b: x = 0.5, c: x = 0.7)
Fig. 5.9. Variation of extinction co-efficient (k) with wavelength for three compositions of CdSe$_x$Te$_{1-x}$ films.
(a: $x = 0.3$, b: $x = 0.5$, c: $x = 0.7$)
**TABLE 5.2**

**Packing density of cadmium chalcogenide thin films**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Film</th>
<th>Longer Wavelength $n_b$</th>
<th>$n_r$</th>
<th>Packing density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CdSe</td>
<td>2.56</td>
<td>2.52</td>
<td>0.97</td>
</tr>
<tr>
<td>2</td>
<td>CdTe</td>
<td>2.80</td>
<td>2.77</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>CdSe$<em>{0.3}$Te$</em>{0.7}$</td>
<td>2.85</td>
<td>2.70</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>CdSe$<em>{0.5}$Te$</em>{0.5}$</td>
<td>2.82</td>
<td>2.65</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>CdSe$<em>{0.7}$Te$</em>{0.3}$</td>
<td>2.80</td>
<td>2.60</td>
<td>0.98</td>
</tr>
</tbody>
</table>
5.7. Introduction

In recent years, the studies on the transport properties of CdSe and CdTe have attracted much attention due to their high potentials in photovoltaic and photoelectrochemical solar cell applications. Thin films of these materials are widely used in devices such as photodiodes, photoconductors, photodetectors, radiation detectors, solar cells etc. The electrical and optical properties of CdSe and CdTe have been studied extensively by many workers. However, thin films based on CdSe and CdTe alloys (CdSe$_x$Te$_{1-x}$) have not been studied in detail with respect to their electrical properties. CdSe$_x$Te$_{1-x}$ thin films are promising candidates for photoelectrochemical solar cell applications. The electrical properties of this system is found to depend on the various deposition parameters and annealing conditions of the films. Hence, a detailed study of the electrical conduction through these alloy films is important.

The available literature regarding the studies of electrical properties of CdSeTe thin films are only scarce. However, most of the available literature is on the electrical properties of the bulk samples of this system. The present study deals mainly with the electrical conduction through these films and their related parameters.

5.8. Electrical conductivity studies

The electrical properties of cadmium chalcogenide films (CdSe, CdTe and CdSe$_x$Te$_{1-x}$) prepared by electrodeposition technique were studied in a vacuum better than $10^{-4}$ torr. The current-voltage characteristics were studied in the temperature range 300-450K. The temperature was measured using calibrated chromel-alumel thermocouple.
The electrical characterization of electrodeposited semiconducting thin films by resistance measurements is complicated by the fact that the film must be removed from the conducting substrate without damage prior to any measurement. Previously, only few reports are available for peeled samples of electrodeposited CdSe and CdTe films /46,47/.

Cadmium chalcogenide films were removed from the conductive substrate by attaching a plate to the surface of the film using an epoxy. After the epoxy was dried for ten hours, the epoxy and the cadmium chalcogenide film came away with the plate when force was applied between the plate and the substrate. Crack and pin-hole free films of area 0.5 to 1.0 cm\(^2\) were removed from tin oxide coated glass plate. Thickness of typical films used for the electrical studies ranged from 2 to 3 \(\mu\)m. Contacts to the semiconductor films were made with colloidal graphite, painted on the film to obtain low resistance ohmic contacts /48/.

5.8.1 Cadmium selenide films

The effect of temperature on electrical conductivity (\(\sigma\)) of cadmium selenide films are studied. Figure 5.10 shows the variation of \(\ln \sigma\) with inverse absolute temperature for a typical CdSe film of thickness 2\(\mu\)m annealed in argon atmosphere. The conductivity of the CdSe film is found to increase from \(2.4 \times 10^{-3}\) to 0.37 mho.cm\(^{-1}\) as the temperature increases. Thermal activation energy (\(E_a\)) of electrical conduction is estimated using the conductivity relation, 
\[
\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)
\]
and a least square fit method. The activation energy of the CdSe is estimated as 0.30 eV. This value is in good agreement with the values reported for CdSe films prepared by vacuum evaporation and solution growth techniques. Electrodeposited CdSe films have been reported in the literature with low resistivities in the range 1 to 100 ohm.cm depends upon the doping and annealing treatment. CdSe films prepared by vacuum evaporation /49,50/ exhibited resistivities in the same order of magnitude whereas solution grown films yielded higher values > 10\(^6\) ohm.cm /51/.
Fig. 5.10. Variation of \( \ln \sigma \) with inverse absolute temperature for a typical CdSe film.
In the present work, the reduction in the film resistivity is caused by annealing the CdSe films at high temperatures (350° C) in argon atmosphere. Annealing caused an improvement in grain size which reduce the carrier scattering at the grain boundaries.

5.8.2 Cadmium telluride films

The effect of temperature on the electrical conductivity of cadmium telluride films are studied. The variation of ln \( \sigma \) with \( 1/T \) for a typical CdTe film of thickness 1.5 \( \mu \)m annealed in argon atmosphere is shown in figure 5.11. It is observed from the figure that the conductivity increases from \( 10^{-8} \) mhos cm\(^{-1} \) to \( 10^{-6} \) mhos cm\(^{-1} \) as the temperature increases from 300 to 450 K.

The activation energy was estimated to be 0.60 eV which is in good agreement with the values reported for CdTe films prepared by other techniques. Cadmium telluride films reported in this work are prepared at more negative potentials and hence belong to n-type with excess cadmium. Windheim et al /52/ carried out resistivity studies of doped electrodeposited CdTe films and reported a value of \( 10^7 \) ohm.cm for undoped films.

5.8.3 Cadmium selenotelluride films

The variation of conductivity at room temperature for CdSe\(_x\)Te\(_{1-x}\) films for various values of composition (x) were estimated and represented in figure 5.12. It is found that the conductivity of the film vary linearly with composition in the range \( 10^{-8} \) to \( 10^{-2} \) mhos cm\(^{-1} \). The exact value of the conductivity depended on the solid solution film composition. It is found that an increase in the percentage of CdSe led to an increase in the sample conductivity. It is observed that all the CdSe\(_x\)Te\(_{1-x}\) exhibited n-type which is contrary to vacuum evaporated CdSe\(_x\)Te\(_{1-x}\) films which showed dependence on their film composition.
Fig. 5.11. $\ln \sigma$ with $1/T$ curve for a typical CdTe film.
Fig. 5.12. Room temperature conductivity versus composition $x$ of CdSe$_x$Te$_{1-x}$ films.
It has been found from hot probe studies that the charge carriers are electrons. They arise due to excess Cd or deficiency of Se or Te in the films. Electrodeposited CdSe films are expected to have large number of selenium vacancies and hence they exhibited lowest film resistance. As the percentage of CdSe in CdSe\textsubscript{x}Te\textsubscript{1-x} films increased, the film resistance also increased due to reduction in Se vacancies in the film. Also, the electron traps due to free Te may increase with increase in CdTe percentage in CdSe\textsubscript{x}Te\textsubscript{1-x} films. In the case of CdTe films, the number of vacancies may be too less to give rise to any appreciable conductivity and hence the film resistance remained very high.

The influence of film thickness on film resistance is shown in figure 5.13. The plot is drawn between ln (R) versus T\textsuperscript{-1} according to Seto's polycrystalline model \textsuperscript{53}. Seto formulated a model to interpret the electrical conduction in polycrystalline thin films exhibiting grain boundary limited conduction. According to Seto's theory, the electrical conduction of semiconductors at high temperature (>300K) is given by,

\[ \sigma = \frac{e' l n}{(2-m KT)^{\frac{1}{2}}} \exp \left[ \frac{E_{\sigma}}{KT} \right] \]  \hspace{1cm} (5.15)

where \( l \) is the grain size, \( n \) is the average carrier concentration, \( m \) is the effective mass of the carriers at the Fermi surface and \( E_{\sigma} \) is the activation energy for grain boundary limited conduction. Dawar et al \textsuperscript{54} have applied this model successfully for CdTe thin films.

The figure 5.13 reveals a steady decrease in film resistance with increase in film thickness. According to Seto's model, the film conductivity \( \sigma \) is directly proportional to the grain size \( l \) of the film. The above method assumes a grain boundary limited conduction in which electrical conduction is brought about by thermionic emission of charge carriers across the grain boundaries. Hence, an increase in grain size is expected to reduce the grain boundary width which in turn enhances the film conductivity. The decrease in film resistance with
Fig. 5.13. Ln R versus 1/T curves for CdSe$_{0.7}$Te$_{0.3}$ films for various film thickness.
increase in film thickness for CdSe$_x$Te$_{1-x}$ film may be attributed to the improvement in the grain size of the films with increase in film thickness.

The grain size estimation has become very significant as the electrical properties of II - VI semiconducting compounds depend very much on the crystalline size. It has been reported earlier that grain size depends on film thickness \( /55-57/ \). The improved crystallinity observed in these films with increase in film thickness may result in the reduction of grain boundary width. Since the predominant scattering mechanism at high temperatures (300 to 450K) is mainly grain boundary scattering, the grain boundary width may considerably affect the electron transport in these films. The effect of improved crystallinity on film resistivity is shown as a reduction in the resistivity of the films with increase in film thickness.

The conductivity of thin films depend on the size of the films. Due to the drastic reduction in one dimension of the material the grain boundary scattering and other size dependent effects become predominant in addition to the normal bulk and defect scattering. Due to large surface to volume ratio of thinner films, the film resistance increases as the film thickness decreases. However, the size effects becomes appreciable only when the film thickness becomes very small (ie) when the film thickness is of the order of De-Broglie wavelength and the electron mean free path of charge carriers in the film \( /58/ \).

The effect of temperature on the electrical conductivity \( (\sigma) \) of CdSe$_x$Te$_{1-x}$ films are studied at various compositions \( (x) \). The variation of \( \ln \sigma \) with \( 1/T \) for CdSe$_x$Te$_{1-x}$ films of various compositions annealed in argon atmosphere are shown in figure 5.14. It is observed from the figure that the conductivity increases linearly with temperature in the range 300 to 450k. It is found that CdTe films exhibited very low conductivity in the range \( 10^{-8} \) to \( 10^{-7} \) mhos cm$^{-1}$. As the value of \( x \) (selenium content) increases, the conductivity is found to increase and for pure CdSe \( (x=1) \), films the conductivity is of the order of \( 10^{-3} \) to \( 10^{-2} \) mhos cm$^{-1}$. Similar behaviour has been reported for vacuum evaporated polycrystalline CdSe$_x$Te$_{1-x}$ thin films \( /49,59/ \).
Fig. 5.14. Variation of $\ln \sigma$ versus $1/T$ curves for CdSe$_x$Te$_{1-x}$ films of various composition annealed in argon atmosphere.
Activation energies of electrical conduction were estimated from the Arrhenius plots shown in figure. The activation energies observed in CdSe$_x$Te$_{1-x}$ films vary between 0.30 eV and 0.60 eV which may be attributed to deep impurity levels in the films. The activation energy of the films increased with increase in CdTe percentage in the film. This may be due to the fact that Te may form deep trap states with increase in CdTe percentage in the films. According to Seto's model for polycrystalline semiconductor films, electrical conduction at high temperatures (>300K) is due to thermionic emission of charge carriers across grain boundaries. Therefore, the major scattering mechanism in CdSe$_x$Te$_{1-x}$ films is the grain boundary scattering. Previous workers /55,60-66/ observed both shallow and deep, donor (acceptor) and trap states in n-CdSe and n-and p-CdTe thin films. In n-CdSe films, free Se forms trap states and in n-CdTe films, free Te form trap states. Excess Cd forms donor states in n-CdSe and n-CdTe. Table 5.3 gives typical results of conductivity studies carried out on cadmium chalcogenide thin films.

From EDAX (Energy Dispersive Analysis using X-rays), it has been found that CdSe$_x$Te$_{1-x}$ films always be deficient in Se and contain excess Cd or Te depending on the deposition parameters. Since the two binary films (CdSe and CdTe) and their solid solution CdSe$_x$Te$_{1-x}$ exhibited only n-type conductivity, it may be assumed that excess Cd forms donors and excess Te forms trap in the films.

5.9 Conclusions

The optical and electrical properties of cadmium chalcogenide films are studied. It is observed that for CdSe$_x$Te$_{1-x}$ solid solution films, the band gap shifted from 1.45 eV towards the shorter wavelength side as Se concentration increased. The optical constants (n & k) of the films are estimated using a modified continuous descent derivative method and their variation with wavelength are studied. The packing density of the films are estimated to be 0.98.
TABLE 5.3

Results of conductivity studies carried out on CdSe$_x$Te$_{1-x}$ films

<table>
<thead>
<tr>
<th>S.No</th>
<th>Composition 'x' for CdSe$<em>x$Te$</em>{1-x}$ films</th>
<th>Conductivity at room temperature mho.cm$^{-1}$</th>
<th>Conduction activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>2 X 10$^{-9}$</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>2 X 10$^{-7}$</td>
<td>0.55</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>2 X 10$^{-6}$</td>
<td>0.48</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>5 X 10$^{-5}$</td>
<td>0.42</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>3 X 10$^{-4}$</td>
<td>0.34</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>2 X 10$^{-3}$</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Electrical properties of cadmium chalcogenide films are studied in vacuum in the temperature range 300 to 450 K. It is observed that the resistivity of CdSe$_x$Te$_{1-x}$ films is found to decrease with increase in film composition ‘$x$’ and this may be attributed to a greater number of ionisable Se vacancies available with increase in ‘$x$’. Thermal activation energies of the films are estimated and the results are discussed.

CdSe thin films exhibited electrical conductivity in the range of $10^{-3}$ to $10^{-2}$ mho cm$^{-1}$ and this lower value is attributed to excess Cd vacancies in grain boundary regions and annealing treatment given to the films. The conduction activation energy is estimated to be 0.30 eV which is in good agreement with the values reported for CdSe films prepared by other methods. Electrical studies carried out on n - CdTe films revealed high resistivities of the order of $10^6$ to $10^7$ ohms cm. Hence these films showed high activation energies (0.60 eV) for the conduction process.

The influence of thickness and composition of CdSe$_x$Te$_{1-x}$ films on the electrical conductivity and activation energy were studied. The observed reduction in resistivity and conduction activation energy with increase in film thickness may be attributed to the increase in grain size with thickness. Conductivity of CdSe$_x$Te$_{1-x}$ films is found to increase with film composition ‘$x$’ which is attributed to a greater number of ionizable Se vacancies available with increase in ‘$x$’. The reduction in film resistance with increase in film thickness and the reduction in activation energy with increase of film composition ‘$x$’ in polycrystalline CdSe$_x$Te$_{1-x}$ film suggest that Seto’s polycrystalline model could produce a good approximation to explain the electrical conduction in these films. In the temperature range studied, the electrical conduction is effected by charge carriers excited to the conduction / valence band from the impurity levels and may be explained by Seto’s polycrystalline model of thermionic emission across the grain boundaries.
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