CHAPTER 3

ELECTRODEPOSITION AND CHARACTERIZATION
OF CdS, Zn-DOPED, In-DOPED CdS THIN FILMS

3.1 INTRODUCTION

According to the applications of CdS, as pointed out in Chapter 2, section 2.1, various methods have been studied to optimize the deposition conditions so as to obtain good quality semiconducting CdS thin films suitable for application to device fabrication (Berg et al 1978; Jatar et al 1978; Martil et al 1986; Sebastian and Ocampo 1995). Electrodeposition is identified as one of the better methods to deposit CdS thin films on conducting substrates (Morris and Vanderveen 1992a). In electrodeposition, various techniques like anodic sulphorization, anodic deposition and cathodic deposition etc (Miller et al 1978; Peter 1978; Mc Cann and Kazacas 1981; Markov et al 1983; Balakrishnan et al 1990) have been used. Among these techniques, cathodic deposition produces CdS thin films from an aqueous solution of soluble cadmium and sulfur compounds which are highly uniform and adhesive with reduced porosity (Morris 1997), and can be effectively used in the fabrication of solar cells with reduced defect assisted recombination losses (Green 1982). During deposition, the bath solution undergoes the following chemical reaction for the co-deposition of CdS layers (Power et al 1981).

\[ \text{Cd}^{2+} + (S) + 2e^- \Rightarrow \text{CdS} \]  

(3.1)
where [S] represents the sulfur source in the deposition bath. So far, physical properties of the electrodeposited CdS films from elemental sulfur and cadmium chloride mixed solution have been analysed by Baranski et al (1983). Structural and optical properties of the electrodeposited CdS were reported by Fatas et al (1986). Deposition of hexagonal CdS and its morphological change during the cathodic electrodeposition was reported by Markov et al (1983). Identification of interstitial cadmium and sulfur vacancy associated donor native defects, cadmium vacancy associated acceptor defects and their increase and decrease with annealing temperature for the Electrodeposited CdS was extensively studied using Photoluminescence and Raman spectra by Shirai et al (1996).

Apart from these, studies on doping of foreign elements such as Al, Ga, In and Zn result in the possibilities to improve the optical band gap, electrical conductivity and activation energy respectively (Pawar et al 1984; Sebastian and Krishna 1984; Bube and Thomsen 1955).

Optical bandgap of the window layer in a solar cell is an important component that decides the rate of surface recombination losses and efficiency (Cahen et al 1997). The optical band gap of 2.42 eV of CdS influences absorption in the blue region, which results in considerable loss of photocurrent and efficiency due to enhanced surface recombination. To avoid this loss, it is important to minimize the absorption in the blue region by increasing the band gap value of CdS without changing the desirable features such as columnar growth to minimize the reverse saturation current in the solar cell, easy ohmic contacts and reasonable lattice matching with the absorber material to minimize junction defects. The band gap value of 3.7 eV in ZnS satisfies the above criterion but it has a low electron affinity as compared to the absorber materials (CdTe or CuInSe2), so that the transport of minority carriers from the absorber to ZnS at the interface is impeded. However, no such impedance is expected if CdS can be doped with ZnS to obtain ternary
Cd$_x$Zn$_{1-x}$S with $x \geq 0.65$ (Chynoweth and Bube 1980). Cd$_x$Zn$_{1-x}$S films are of interest for their application as window electrode in a variety of solar cell structures due to their higher value of band gap having a general chemical formula Cd$_x$Zn$_{1-x}$S produced from a CdS and ZnS solid solution.

The efficiency of the solar cell can be improved with increase in conductivity of CdS window electrode (Chynoweth and Bube 1980). Low resistive wide band gap window material is essential in heterojunction solar cells in order to minimize the series resistance. This conductivity can be increased by the incorporation of trivalent cation or inclusion of excess cadmium in CdS films. Also, studies on the doping of indium in CdS resulted in changes in the optical and electrical properties but lead to no remarkable changes in the crystallization behaviour of CdS.

Extensive investigations are made on CdS and the effect of Zn, In doped CdS deposited by vacuum evaporation (Romeo et al 1978, Torres and Gordillo 1992), electron bombardment (Mbow et al 1982), spray pyrolysis (Agnihotri and Gupta 1979, Ma and Bube 1977), Metal Organic Vapour Phase Epitaxy (Wright et al 1985) and chemical bath deposition (Pawar et al 1984; Joshi and Sachar 1982). However, there are only a few reports on electrodeposition (Morris and Vanderveen 1992b; Sasikala et al 1997) of Cd$_x$Zn$_{1-x}$S and CdS:In films. It is important to understand the optical and electrical properties of the films during the development of electrodeposition technique for further application to the device (solar cell) fabrication.

Present investigation is on the understanding of the basic structural, optical and electrical properties of electrodeposited CdS, Zn-doped CdS and In-doped CdS thin films from their aqueous solutions as a first step towards further application to the fabrication of G/SnO$_2$:F/CdS/CdTe and G/SnO$_2$:F/CdS/CuInSe$_2$ back wall solar cell structures.
3.2 EXPERIMENTAL

3.2.1 Deposition of CdS thin films

CdS semiconducting thin films were cathodically deposited using an aqueous solution of 0.2 M CdCl₂, 2H₂O and 0.01 M of Na₂S₂O₃ with the pH adjusted to range between 2-3 on ITO and SnO₂:F coated glass substrates having sheet resistance of 12 Ω/□ and 10 Ω/□ respectively. The cell used for electrodeposition was enclosed in glass vessel with a three electrode configuration (Baranski et al 1981) consisting of a SCE reference electrode, a platinum counter anode and working cathode. Voltammograms were obtained to optimise the co-deposition region of CdS on 3 x 3.5 cm² substrates. Voltammograms obtained with the above system were recorded with Houston model RE 0092 x-y recorder. The substrates were thoroughly cleaned using trichloroethylene, methanol and isopropanol successively before mounting for deposition. As a first step films were deposited at different temperatures of 60°, 70° and 80°C and for different applied potentials by setting the cathode potential at an interval of 0.1 V in the range from -0.4 to -0.8 V with respect to the saturated calomel electrode (SCE) in order to optimise the deposition condition for better CdS growth. The optimised conditions for CdS deposition was further used for Zn and In doping studies. An electrochemical system consisting of a PAR model 173 Potentiostat-Galvanostat and model 175 Universal Programmer was employed for electrochemical deposition of the materials. The charge that passed between the working electrode was measured by a PAR model 179 digital coulometer.
3.2.2 Deposition of CdS:Zn thin films

Cd\textsubscript{x}Zn\textsubscript{1-x}S films were cathodically electrodeposited on SnO\textsubscript{2}:F coated glass substrates from a stirred solution of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, cadmium chloride and zinc chloride at 90°C. The pH of the solution was adjusted to 2 using hydrochloric acid. The films were produced by varying the composition from CdS to Cd\textsubscript{0.52}Zn\textsubscript{0.48}S. Deposition conditions are summarized in Table 3.1. The stoichiometry of the deposited films given in Table 3.1 was determined using Inductive Coupled Plasma (ICP) technique.

Table 3.1
Experimental conditions for the deposition of Cd\textsubscript{x}Zn\textsubscript{1-x}S films

<table>
<thead>
<tr>
<th>Solution concentration (mM)</th>
<th>E\textsub{dep} (mV) vs SCE</th>
<th>Defined Film composition and chemical formula Cd\textsubscript{x}Zn\textsubscript{1-x}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd\textsuperscript{2+}</td>
<td>Zn\textsuperscript{2+}</td>
<td>S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>200</td>
<td>10</td>
</tr>
</tbody>
</table>

3.2.3 Deposition of CdS:In thin films

Optimized CdS deposition conditions were further extended to dope indium in the CdS films. The electrolyte solutions were prepared using 0.2 M
CdCl₂·2H₂O and 0.01 M of Na₂S₂O₃. The pH of the solution was adjusted to 2 using concentrated hydrochloric acid. The temperature of the bath was maintained at 90° C and a cathodic potential of -620 mV was applied during film growth. Indium doping was carried out by mixing indium chloride to the bath solution and doping concentration was varied by adjusting the concentration from 0.5 µM to 1.5 µM of indium chloride in the solution.

3.3 CHARACTERIZATIONS STUDIES

The thickness of the deposited thin films were measured using a Stylus thickness profiler. Structural, optical and morphological studies of the CdS, CdS:Zn and CdS:In films were studied using XRD, UV-Visible and Scanning Electron Microscope (SEM). The dopant concentrations were calculated using the Inductive Coupled Plasma analysis (ICP). Electrical resistivity of the films were calculated using a sandwich current-voltage characterisation method.

3.4 RESULTS AND DISCUSSIONS
3.4.1 Experimental observations
3.4.1.1 Observations on CdS deposition

The cathodic deposition of CdS films was achieved by the electroreduction of Na₂S₂O₃ in the presence of Cd²⁺. Figure 3.1 shows the Voltammograms obtained for the deposition of an individual species of Cd (0.2M of CdCl₂·2H₂O), S (0.01 M of Na₂S₂O₃) and the co-deposition of CdS (0.2 M of CdCl₂·2H₂O and 0.01M of Na₂S₂O₃) on ITO coated glass substrates. The solution was stirred during the course of deposition for the applied potential ranging from 0 to -1 V vs SCE. Single reduction wave can be observed at -0.44 V, which is due to the reduction of S₂O₃²⁻ ions (Figure 3.1a). Similarly,
Figure 3.1 Voltammograms recorded for (a) S, (b) Cd and (c) CdS at constant pH (2) and temperature (90°C).
Figure 3.1b represents the reduction wave of Cd\(^{2+}\) at -0.7 V. Figure 3.1c gives the co-deposition region of CdS from -0.43 V to -0.83 V. The reaction of \(S_2O_3^{2-}\) ions with Cd\(^{2+}\) ions, results in the deposition of CdS layers on the cathode for the proper applied voltage. Co-deposition of CdS can be expressed by the following chemical reaction,

\[
Cd^{2+} + S_2O_3^{2-} + 2e^- \Leftrightarrow CdS + SO_3^{2-}
\]

Voltage applied above -0.84 V results in the rapid increase of current density due to H\(_2\) evolution, which adversely affects the quality of the films. Since the deposition potential of sulfur is low compared to cadmium, cadmium deposition dominates at higher cathodic potentials. Colour variations were observed in the films which were deposited at different cathodic potentials. The stoichiometric yellow, cadmium-rich greenish yellow and metallic gray colour CdS films were obtained for the voltage ranges of -0.5 to -0.6 V, -0.6 V to -0.7 V and -0.7 V to -0.8 V respectively. Cadmium dendrites were also observed on films deposited at a potential of -0.8 V. Above -0.8 V, the decomposition of water with subsequent hydrogen evolution was observed. Annealing of all the films at 350° C in H\(_2\) atmosphere for 30 min resulted in bright yellowish films with smooth surfaces.

It was observed that the pH of the solution plays a major role in the stability of the electrolyte. If the pH was greater than 3, heating resulted in a turbid solution with white precipitates of cadmium hydroxide. Rapid precipitation of CdS above 40°C was observed for pH less than 2. This is because of the increasing concentration of Cd\(^{3+}\) and S\(_2\)O\(_3^{2-}\) ions in the solution. Hence it is always better to have the pH of the solution adjusted in the range of 2-3. In this pH range, Na\(_2\)S\(_2\)O\(_3\) decomposes to form thiosulphate ions which is disproportionate as follows.

\[
Na_2S_2O_3 \rightarrow Na_2S_3O_3 + SO_2 + H_2O
\]
The bath temperature was found to have remarkable effects on compound formation and deposition. As bath temperature increases the deposition time decreases for the required thickness due to an increase in the ionic concentration of the constituents which enhances the smoothness and adhesivity of the films. A constant thickness value of 1000 Å was controlled by adjusting the deposition time for the purpose of comparing their properties.

3.4.1.2 Observations on CdS:Zn deposition

Due to the presence of Zn\(^{2+}\) ion, sulfur readily precipitates in the bath vide Equation (3.3). Therefore the existing mechanism may probably be

\[
Zn^{2+} + 2S_2O_3^{2-} \rightleftharpoons ZnS_2 + S_2O_3^{2-}
\]  

(3.4)

\[
S_2O_3^{2-} \rightleftharpoons S + SO_3^{2-}
\]  

(3.5)

Increasing the S\(_2\)O\(_3\)\(^{2-}\) concentration in the solution induces the sulfur precipitates. Zn\(^{2+}\) ion concentration shifts the Cd cathodic deposition potential towards lower values and gives Cd rich films. Also increasing the pH values to more than 3 results in cadmium rich deposits. Measured thickness values reveal that an increase in Zn concentration in the film decreases the rate of deposition. To study the optical properties of the films the thickness was controlled to 1000 Å.
3.4.1.3 Observations on CdS:In deposition

Analysis on the measured thickness value implies that an increase in indium concentration increases the rate of deposition. This may be due to the improved conductivity of the deposited layers. During the deposition of CdS:In with higher doping concentration of indium, sulfur precipitates. Thickness of the films was controlled for 1000 Å.

3.4.2 Structural properties of CdS, CdS:Zn and CdS:In films

3.4.2.1 Structural properties of CdS

XRD analysis on cathodically deposited CdS reveals that the films were polycrystalline with hexagonal CdS crystallites without any preferred orientation. The dashed lines in Figure 3.2 shows the XRD patterns of the as deposited CdS films on ITO. Each pattern contains several diffraction peaks indicating the polycrystalline structure of the films. Diffraction peaks for the films deposited at applied voltages of - 0.5 V, -0.6 V and -0.7 V appears at $2\theta = 24.65^\circ$, $26.35^\circ$, $28.1^\circ$ corresponding to the (100), (002) and (101) reflections. This confirms the hexagonal phase (wurtzite) of $\alpha$-CdS (JCDS Card No: 41-1049). The change in deposition potential does not result in any change in the peak positions and there are no peaks corresponding to the crystallization of the defect related cubic phase of (sphalerite) $\beta$-CdS (Gupta and Agnihotri 1977). The continuous lines in the XRD patterns shown in Figure 3.2 have been observed for the films after annealing at 350°C for 30 min. A slight shift towards lower scattering angles and improved diffraction intensity implies an increase in lattice parameter of the crystallized grains. The shift towards lower scattering angle and the consequent increase in the lattice parameter reveals the enlargement of the CdS lattice. This is in good agreement with the report by de Melo et al (1994). The improved crystallization with the
Figure 3.2 X-ray diffractogram of as-deposited and annealed CdS films on ITO/glass substrates.
increased lattice parameter is due to the filling up of the vacancies or vacancy complexes and the appearance of sulfur interstitials (de Melo et al 1994). The calculated lattice parameter values for the as deposited and annealed films are presented in Table 3.2.

**TABLE 3.2**

Calculated lattice parameter and the band gap values for the as deposited and annealed films

<table>
<thead>
<tr>
<th>DEPOSITION CONDITION (V)</th>
<th>LATTICE PARAMETER</th>
<th>BAND GAP DIRECT ALLOWED (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>-0.5</td>
<td>4.1407</td>
<td>6.6983</td>
</tr>
<tr>
<td>As deposited</td>
<td>4.1611</td>
<td>6.7433</td>
</tr>
<tr>
<td>Annealed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.6</td>
<td>4.1245</td>
<td>6.7075</td>
</tr>
<tr>
<td>As deposited</td>
<td>4.1507</td>
<td>6.7394</td>
</tr>
<tr>
<td>Annealed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.7</td>
<td>4.1169</td>
<td>6.7188</td>
</tr>
<tr>
<td>As deposited</td>
<td>4.1316</td>
<td>6.7349</td>
</tr>
<tr>
<td>Annealed</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.3 shows the XRD pattern of the as-deposited CdS thin films on SnO$_2$:F coated glass plates for different cathodic potentials. There is no difference in the XRD patterns obtained for the films deposited on ITO and SnO$_2$:F coated substrates. This implies that the crystallization behaviour of CdS is not influenced by the ITO or SnO$_2$:F.

Figures 3.4 a,b,c & d show the surface morphology of the as-deposited CdS on conducting SnO$_2$:F/glass substrate for different cathodic potentials (a. -400 mV, b. -500 mV, c. -600 mV and d. -700 mV). It was
Figure 3.3 X-ray diffractogram of as-deposited CdS films on SnO₂:F/Glass substrates.
Figure 3.4 SEM micrograph of as-deposited CdS films on SnO$_2$:F/Glass substrates

a. $V_{\text{dep}} = -0.4$ V

b. $V_{\text{dep}} = -0.5$ V

c. $V_{\text{dep}} = -0.6$ V

d. $V_{\text{dep}} = -0.7$ V
observed that the increase in deposition potential improved the grain size (Figures 3.4 a, b, c & d) and it is also evident that the increase in deposition potential can lead to the cadmium rich deposition. According to this observation, we may conclude that the improved grain size can be related to the increase in the cadmium concentration in the film.

Figure 3.5 shows the atomic force micrograph (AFM) of CdS deposited on SnO2: F/Glass. From the AFM picture the average thickness of the films were calculated as 100 nm. Grain size varies from 200 nm to 100 nm to 250 nm width. The CdS structure was continuous with minimum number of discontinuity regions. The root square roughness of the surface is 32.34 nm which fairly agrees with already reported values (Moutinho et al 1996).

### 3.4.2.2 Structural properties CdS:Zn

Figures 3.6 a, b & c show the Scanning Electron Microscope picture of the films with compositions $Cd_{0.52}Zn_{0.48}S$, $Cd_{0.7}Zn_0S$, $Cd_{0.9}Zn_{0.1}S$. The surfaces of the films were observed to have dense granules at low Cd molar ratio ($x$) and the granule size increases along with the increase in Cd molar ratio ($x$) in the film. High Zn$^{2+}$ concentration leads to improved deposition and this is seen as white granules in Figure 3.6c.

The X-ray diffraction spectra of the as-deposited and annealed $Cd_{0.82}Zn_{0.18}S$ showed that they were hexagonal polycrystals. The X-ray diffraction spectra were similar to those reported for electrodeposited CdS (Figure 3.7) with a predominant plane along with the (101) plane. Annealing in H2 atmosphere for 30 min at 350°C improves the crystallization of (100) and (103) planes.
Figure 3.6 SEM micrograph of Cd$_x$Zn$_{1-x}$S films with film composition (a) Cd$_{0.52}$Zn$_{0.48}$S, (b) Cd$_{0.71}$Zn$_{0.29}$S and (c) Cd$_{0.9}$Zn$_{0.1}$S.
Figure 3.7 X-ray diffractogram of as-deposited and annealed Cd$_{0.52}$Zn$_{0.48}$S on SnO$_2$:F/glass substrate deposited at -0.7 V.

Figure 3.8 Variation of lattice parameter 'a' and 'c' with the mole fraction (x) of Cd$_x$Zn$_{1-x}$S films.
with the already observed (002), (101) planes. Lattice parameters calculation shows an increasing a and c values for increasing Cd molar ratio(x) as shown in Figure 3.8. Results are in good agreement with the previous reports (Mbow et al. 1982; Agnihotri and Gupta 1979).

3.4.2.3 Structural studies on CdS:In

The XRD pattern in Figure 3.9 obtained for indium doped (97 ppm) CdS results in the (101) predominant plane of crystallization along with the (100), (002) (110) and (103) planes. This XRD spectra is similar to that of CdS. The lattice parameter calculations do not result in any appreciable change in 'a' and 'c' values.

3.4.3 Optical properties of CdS, CdS:Zn and CdS:In films

3.4.3.1 Optical properties: Transmittance studies of CdS

Figure 3.10 shows the transmittance spectra for the as-deposited (AD) and annealed (AN) films. Transmittance percentages of 50% and 60% were observed above 600 nm for the applied potentials of -0.5 and -0.6 V respectively which implies that the deposition is stoichiometric. Further increase in applied potential results in very low transmittance percentage around 30% above 600 nm implying elemental deposition. Annealing at 350°C, improves the transmittance percentage for the -0.7 V deposited film and the resultant absorption edge becomes much sharper. Fundamental absorption region shifts towards lower photon energies due to the improved crystallization.

It was observed that the percentage of optical transmission also depends on the deposition potential, pH of the electrolyte and bath temperature.
Figure 3.9 X-ray diffractogram of as-deposited indium doped (97 ppm) CdS films.

Figure 3.10 Optical transmission spectrum of as-deposited(AD) and annealed(AN) CdS films.
3.4.3.2 Band-gap calculation of CdS

Bandgap values were calculated using the plot discussed in section 2.3.2. Figure 3.11 shows the photon energy dependence of $(\alpha \gamma)\dot{\gamma}$ related to the direct allowed transition for the as deposited and annealed films deposited at -0.6 V. Decrease in the band gap value was observed after annealing the films in H$_2$ atmosphere for 30 min similar to our earlier observation on CBD deposited CdS in chapter 2, section 2.3.2. This implies that the electrodeposited CdS films also undergo an electron-phonon and electron impurity interaction mechanisms (Zelaya-Angel et al 1994). Calculated bandgap values are tabulated in Table 3.2 for as-deposited and annealed films deposited for -0.5 V, -0.6 V and -0.7 V respectively. Calculated values are in good agreement with literature reported for CdS single crystals.

3.4.3.3 Studies on optical constants n, k, ε' and ε'' of CdS

Refractive index (n) and the extinction coefficient (k) values for the as-deposited and annealed films were calculated using the relations (2.11) and (2.12). The plot of the optical constants n, and k versus photon energy are shown in Figures 3.12a and b respectively and the results are in good agreement with the reported values (Khawaja and Tomlin 1975). k values are found to rise rapidly near the fundamental absorption edge. Values of `n' obtained have been plotted as a function of photon energy hν as shown in Figure 3.12a. It can be seen that the refractive index exhibits a maximum value at 2.46 eV for annealed films. In general, for a semiconductor the refractive index will have a maximum value at an energy near that at which the fundamental transition occurs. Figure 3.12a therefore suggests that the band gap of the CdS film is at 2.46 eV. At photon energies less than about 1.9 eV the refractive index remains
Figure 3.11 \((\alpha h\nu)^2\) versus \(h\nu\) plot of the as deposited and annealed CdS films deposited at -0.6 V
Figure 3.12 Variation of (a) refractive index ($n$) and (b) extinction co-efficient ($k$) with photon energy $h\nu$ of CdS Films.
virtually constant at 2.6. Figure 3.13, shows the plot of (a) the real (\(\varepsilon'\)) and (b) imaginary (\(\varepsilon''\)) parts of the dielectric constant vs incident photon energy of the as-deposited and annealed CdS films for different deposition conditions.

3.4.3.4 Optical Properties: Transmittance studies of CdS:Zn

Optical transmission spectra of pure CdS, \(\text{Cd}_0.9\text{Zn}_{0.1}\text{S}\), \(\text{Cd}_{0.72}\text{Zn}_{0.18}\text{S}\) and pure ZnS is shown in Figure 3.14. The sharp absorption edge confirms the homogeneity of the film. As the zinc molar ratio\((1-x)\) increases in the film, the percentage of transmission increases and absorption edge shifts towards the lower wavelength region.

3.4.3.5 Band-gap calculation of CdS:Zn

Band-gap of the as-deposited and annealed films were also calculated for the CdS:Zn films deposited as discussed in section 3.3.3. Deposited films are yellow in colour. The band-gap \((E_g)\) of the films were determined by obtaining the optical transmission spectra. Using the absorption co-efficient, \(E_g\) has been calculated. Figure 3.15 shows the variation of \(E_g\) depending on the Cd/Zn molar ratio in the film for both as-deposited and annealed conditions. It shows a linear relationship between the composition and the band gap.

3.4.3.6 Optical properties: Transmittance studies of CdS:In

Transmittance spectra recorded for different indium (In) doping concentration shows an immediate decrease in transmittance percentage for 48 ppm of ‘In’ concentration after which it gradually increases with respect to indium doping (Figure 3.16).
Figure 3.13 Variation of (a) real ($\varepsilon'$) and (b) imaginary ($\varepsilon''$) parts of the dielectric constants of CdS films.
Figure 3.14 Optical transmittance spectra of as-deposited Cd$_x$Zn$_{1-x}$S films for different film compositions.

Figure 3.15 The dependence of band gap for as-deposited and annealed films on the mole fraction (x) of Cd$_x$Zn$_{1-x}$S films.
Figure 3.16 Optical transmittance spectra of pure and indium doped CdS films.

Figure 3.17 Variation of electrical resistivity ($\rho$) of as-deposited and annealed CdS films on the mole fraction (x) of Cd$_x$Zn$_{1-x}$S films.
3.4.3.7 Band gap studies of CdS:In

Optical absorption coefficient of the indium doped films has been calculated using the equation (2.8). Calculated values are in the order of \( 10^{-4} \text{ cm}^{-1} \) for all the films. Table 3.3 shows the variation of absorption coefficients for pure and indium doped CdS films. The Table 3.3 clearly shows the increasing absorption coefficient values for In doped CdS films than pure CdS. This may be due to the indium impurity associated absorption.

Table 3.3

<table>
<thead>
<tr>
<th>Concentration of the InCl\textsubscript{3} in the electrolyte (μM)</th>
<th>Amount of Indium present in the film (ppm)</th>
<th>( \alpha ) at 450 nm (cm\textsuperscript{-1})</th>
<th>Band-gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CdS</td>
<td>-</td>
<td>6.06 x 10\textsuperscript{4}</td>
<td>2.6</td>
</tr>
<tr>
<td>0.5</td>
<td>48</td>
<td>14.6 x 10\textsuperscript{4}</td>
<td>2.49</td>
</tr>
<tr>
<td>1</td>
<td>97</td>
<td>12.3 x 10\textsuperscript{4}</td>
<td>2.56</td>
</tr>
<tr>
<td>1.5</td>
<td>135</td>
<td>1.08 x 10\textsuperscript{4}</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Calculated absorption coefficient values have been further used to clarify the transition mechanism of the band structure of In doped CdS films using the relation (2.9). The computed results do not reveal any change in the transition mechanism of Direct allowed transition observed for CdS. It means that the doping does not alter the native transition mechanism for CdS. Calculated bandgap value varies from 2.6 eV (pure CdS) to 2.49 eV (48 ppm In doped CdS) and increases again to 2.6 eV for the further increase in doping concentration to 135 ppm. The increase and decrease in band gap values for
increasing In doping concentration is due to the reduction of Cd vacancies and the entry of In$^{3+}$ at interstitial position in CdS lattice rather than vacancy position of Cd$^{2+}$ (Pawar et al 1984).

3.4.4 Electrical properties of CdS, CdS:Zn and CdS:In

3.4.4.1 Electrical properties of CdS

The resistivity of the as-deposited and annealed (350° C, 30 min, H$_2$ atmosphere) films were measured using I-V plot. Indium top contact was used as one electrode and ITO/Ag paste as the second electrode for the measurement. From the I-V plot resistance of the films have been calculated. Using the thickness value the resistivity of the as-deposited films were calculated as $3 \times 10^4$ Ω·cm (dark) and $8.2 \times 10^2$ Ω·cm (light, 100 mW cm$^{-2}$). After annealing in H$_2$, the values were $2 \times 10^5$ Ω·cm (dark), $4.5 \times 10^3$ Ω·cm (light, 100 mW cm$^{-2}$).

3.4.4.2 Electrical properties of CdS:Zn

Resistivity has been measured as a function of cadmium molar ratio (x) for as-deposited and annealed films at room temperature using indium as top ohmic contact and the TCO and Ag paste as back contact as shown in Figure 3.17. The resistance was measured by current voltage response which was linear for all samples. The as-deposited films resulted in increasing resistivity from $2.2 \times 10^3$ Ω·cm for pure CdS to $2.4 \times 10^4$ Ω·cm for Cd$_{0.53}$Zn$_{0.47}$S. The increase in resistivity values from $3.2 \times 10^2$ Ω·cm to $2.4 \times 10^4$ Ω·cm with an increase in zinc concentration from 0 to 0.48 is in good agreement with the previous reports (Chynoweth et al 1980).
3.4.4.3 Electrical properties of CdS:In

Table 3.4

Electrical resistivity of the pure and indium doped CdS thin films

<table>
<thead>
<tr>
<th>InCl₃ in electrolyte (µM)</th>
<th>Indium present in the film (ppm)</th>
<th>Resistivity (Ω-cm) Dark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CdS</td>
<td>-</td>
<td>2.5 x 10⁵</td>
</tr>
<tr>
<td>0.5</td>
<td>48</td>
<td>3.2 x 10³</td>
</tr>
<tr>
<td>1.0</td>
<td>97</td>
<td>5.3 x 10³</td>
</tr>
<tr>
<td>1.5</td>
<td>135</td>
<td>5.9 x 10³</td>
</tr>
</tbody>
</table>

Table 3.4 shows the InCl₃ concentration in the bath solution, resultant In concentration in the film and the measured resistivity values of the films at room temperature. It is found that the doping of In decreases the resistivity from 2.5 x 10⁵ Ω-cm for pure CdS to 3.2 x 10³ Ω-cm (48 ppm of Indium doping) and again increasing to 5.9 x 10³ Ω-cm for the further increase in doping concentration to 135 ppm. The decrease and increase in resistivity for the increasing doping concentration may be due to the removal of Cd vacancies in the lower doping concentrations and the replacement of indium in trivalent state (In⁢³⁺) at interstitial position by replacing divalent cadmium for higher doping concentrations.

3.5 CONCLUSION

CdS, Zn and In doped CdS semiconducting thin films have been successfully co-deposited by electrodeposition method using potentiostatic method. The films were deposited on ITO and SnO₂:F coated glass substrates.
Voltammograms have been drawn to optimize and obtain the co-deposition region of Cd and S. The deposition conditions for different pH values, bath temperature and applied cathodic potentials were optimized. CdS films deposited under different cathodic potentials resulted in hexagonal polycrystals with dominant (100), (002) and (101) planes of crystallization. Annealed CdS films at 350°C in H₂ atmosphere resulted in increase in lattice parameter values reveals the enlargement of the CdS lattice. This increase is due to the filling up of the vacancies or vacancy complexes and the appearance of sulfur interstitials. Optimized CdS deposition conditions were further extended to dope Zn and In. Zn doping increases the lattice parameter values 'a' and 'c' with cadmium mole fraction. Indium doping does not result in any appreciable lattice parameter change. It was observed that the optical transmittance percentage of CdS films depends on the cathodic potential, pH of the electrolyte and bath temperature. Annealing causes decrease in energy band gap value, this decrease was observed due to the electron-phonon and electron-impurity interaction mechanism. The variation of optical constants n, k, ε' and ε'' were studied for both as-deposited and annealed CdS films. Zinc doping shows a linear variation of band gap with cadmium mole fraction for both as-deposited and annealed films. Indium doped CdS films exhibiting higher optical absorption than the pure may be due to the indium impurity associated absorption. Band gap value initially increases along with indium doping and decreases due to the reduction of cadmium vacancies and the entry of In³⁺ at interstitial position of CdS lattice rather than vacancy position of Cd²⁺. Resistivity of the CdS film increases with zinc doping concentration whereas indium doped films show less resistivity compared to the pure CdS films. Further increase in indium concentration increases the resistivity due to the removal of cadmium vacancies in the lower doping concentration and the substitution of In³⁺ state at the interstitial position of Cd²⁺ at higher doping concentrations.