CHAPTER 3

Chemical bath deposition of II-VI semiconductor thin films for buffer layer application in solar cells
Part A

Preparation and characterisation of CdS thin films by chemical bath deposition

Cadmium sulphide thin films on glass and ITO coated glass substrates were prepared by the chemical bath deposition technique. The band gap of the as deposited films varied in the range 2.43 eV to 2.67 eV. The as deposited films were smooth and uniform with a carrier concentration of $1.97 \times 10^{17}$ carriers/cm$^3$. These films have low resistivity ($\sim 10^2 \ \Omega \cdot \text{cm}$) and high transparency (>80%) in the visible region.
3A.1 Introduction

Over the years cadmium sulphide thin films have been extensively investigated as an n-type buffer layer to form thin film heterojunction solar cells with p-CdTe and p-CulnSe2 absorber layers. Most of the high-efficiency CIS based solar cells of today have a thin (50 nm or less) CdS buffer layer and an undoped ZnO layer between the absorber and the transparent conducting oxide (see Chapter 1, Fig 1.6). The role of CdS and undoped ZnO are related to some extent [1]. Although the open circuit voltages of high-efficiency CIS devices are mostly determined by the electronic quality of the bulk absorber material [2,3], the cell performances are nevertheless heavily influenced by the formation of the ZnO/CdS/CIS heterojunction [1]. The role of the buffer layer is twofold: it affects the electrical properties of the junction and protects it from chemical reactions and mechanical damage. From the electronic point of view, the CdS layer optimizes the band alignment of the device [4,5] and builds a sufficiently wide depletion width that minimizes tunneling and establishes a higher contact potential that allows higher open circuit voltage [5]. The buffer layer plays also a very important role as a "mechanical buffer" since it protects the junction electronically and mechanically against the damage that may otherwise be induced by the oxide deposition. Moreover, in large-area devices the electronic quality of the CIS film is not necessarily the same over the entire area, and recombination may be enhanced at grain boundaries or by local shunts. Together with the undoped ZnO layer, CdS enables self-limitation of electrical losses by preventing electrical inhomogeneities from dominating the open circuit voltage of the entire device [1].

3A.2 Cadmium sulphide buffer layer

A variety of techniques are being used to deposit CdS thin films, such as; molecular beam epitaxy (MBE) [6], metal organic chemical vapour deposition (MOCVD) [7], close spaced sublimation (CSS) [8,9], screen printing [10,11] physical vapour deposition [12,13], rf sputtering [14],
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pulsed laser ablation [15], spray pyrolysis [16,17] and chemical bath deposition [8,9,18-25].

The characteristics of the CdS thin films required for the application as solar cell buffer layer are, it should be conductive (~$10^{16}$ carriers/cm$^3$), thin to allow high transmission (50-100nm) and uniform to avoid short circuit effects [26]. Thickness as well as the deposition method of the CdS layer has a large impact on device properties. During the early days of the development of CuInSe$_2$/CdS junction, a thick (about 1-3 Ωm) CdS layer [27–29] was used as the buffer layer. The CdS layers of these devices were most often prepared by evaporation at substrate temperatures between RT and about 200°C, or in some cases by sputtering [28]. The CdS film was often doped either with In [28] or Ga [30]. In some cases, a CdS bilayer was used [31,32], consisting of a thinner high-resistivity layer, prepared either by evaporation [31] or chemical bath deposition [31–33] and a thicker low-resistivity layer, doped with 2% In [32] or Ga [33]. Evaporated CdS has been used also in combination with the transparent conducting oxide layer [34–36]. Nowadays, chemical bath deposition is used almost exclusively [37,38], and therefore this section of the thesis focuses mainly on the chemical bath deposited CdS buffer layer. Solar cell with Mo/CIGS/CdS/ZnO device structure with the chemical bath deposited CdS has shown a record efficiency of 19.2% [39].

The chemical bath deposition of CdS modifies the absorber surface. The bath has been suggested to re-establish positively charged surface states and creates Cd$_{cu}$ donors at the surface region [37,40]. Thus the interface between CIS and CBD-CdS is not abrupt but the layers are intermixed to some extent [41,42]. Both Cu-and Cd-diffusion play a role, and the intermixing is further enhanced during the post-deposition air annealing [1]. According to Nakada et al. [42], substitution of Cu by Cd takes place at the surface region of CIS (depth about 10 nm). The diffusion depth of Cd atoms may be related to the thickness of the Cu-deficient surface layer (CuIn$_3$Se$_5$) of CIS [42]. On the other hand, Heske et al. [41] have observed diffusion of Se and In from CIS into CdS and the diffusion of S from CdS into CIS. The extent of
interdiffusion depends on the structure of the absorber: (220/204) oriented CIS films have been found to allow more Cd atoms to diffuse into the CIS film [43].

Recently there has been a renewed interest in the study of nanocrystalline CdS thin films. The quantum confinement in the nanocrystalline thin films leads to the blue shift in the absorption edge resulting in a wide band gap energy, which can be effectively used to spectrally tune the optical properties of semiconductors [44]. The blue shift in the band gap due to the decrease in crystallite size has achieved a special attention because of its exciting scopes in fabricating novel electronic devices and solar cells of better efficiency [45,46]. Nanocrystalline CdS thin films have been prepared by different techniques such as sol-gel [47], chemical bath deposition [44, 48–51], electrostatic deposition [52] etc.

In this section we discuss the properties of the CdS films deposited on glass and indium tin oxide (ITO) coated glass substrates by chemical bath deposition. The films deposited on the ITO/glass substrates shows a blue shift in the band gap suggesting the nanocrystalline growth of the films.

3A.3 Experimental details

Cadmium sulphide thin films were prepared by the chemical bath deposition technique. The films were smooth, reflecting, and was bright yellow in appearance. The thickness of the film was calculated using Tolansky’s multiple beam interferometry technique (see section 2.3.1). The thickness of the CdS film on ITO substrate for a deposition time of 45 minutes (single dip) was 52 nm. In order to get thicker films, multiple depositions were carried out with fresh reaction bath for each deposition. The measured thicknesses of the films are given in table 3.1.

The structural studies of the films were performed using the x-ray diffractometer. The optical absorption and transmission spectra of the as-deposited and annealed samples were recorded using UV-Vis-NIR
spectrophotometer (Hitachi-Model U3410). Four-probe method was used to study the electrical properties of the film (see section 2.3.6).

3A.3.1. Preparation of the chemical bath

CdS thin films were deposited onto glass and indium tin oxide (ITO) coated glass substrates from an aqueous chemical bath containing 0.01 M cadmium chloride (CdCl\textsubscript{2}), 0.1M thiourea (CS(NH\textsubscript{2})\textsubscript{2}), 25% ammonia solution (NH\textsubscript{4}OH) and triethanolamine (TEA). The volume mixture ratio of the cadmium chloride and thiourea was 1:1 and TEA was added by 4% of the volume of cadmium chloride. The pH of the solution was kept at 10.8 by adding ammonia solution and the bath temperature was maintained constant at 80°C.

The substrates, both glass and ITO coated glass were cleaned thoroughly with detergent solution, rinsed in distilled water and then immersed in freshly prepared Chromic acid for two hours to remove traces of organic compounds. The substrates were again cleaned with distilled water and then kept in an ultrasonic cleaner for about 20 minutes to remove the microscopic impurities. Isopropyl alcohol was used for cleaning ITO coated glass substrate. The cleaned substrates were immersed vertically in the chemical bath and the deposition was carried out without any stirring for 45 minutes. After the deposition the films were rinsed in distilled water and dried in hot air oven. The post deposition annealing of the samples were done at 300°C for one hour in vacuum (2 x 10\textsuperscript{-5} mbar).

3A.3.2 Reaction mechanism

In the growth of the CdS thin film from chemical bath, triethanolamine and ammonia act as the complexing agents to bind the Cd\textsuperscript{2+} ions. Formation of complex ion is essential to control the rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complexes hydrolyse slowly to generate the Cd\textsuperscript{2+} in the solution. Thiourea furnishes the necessary S\textsuperscript{2-} ions by hydrolysis. The deposition mechanisms
during chemical bath deposition of CdS thin films have been discussed by Chu et al.[53] and Herrero et al.[22]. The various reactions involved in the CdS growth process can be explained by the equations (3.1) – (3.7).

\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad (3.1) \\
\text{CdCl}_2 & \rightarrow \text{Cd}^{2+} + 2\text{Cl}^- \quad (3.2) \\
\text{CS(NH}_2\text{)}_2 + 2\text{OH}^- & \rightleftharpoons \text{S}^{2-} + 2\text{H}_2\text{O} + \text{H}_2\text{CN}_2 \quad (3.3) \\
\text{Cd}^{2+} + 4\text{NH}_3 & \rightleftharpoons \text{Cd(\text{NH}_3)_4}^{2+} \quad (3.4) \\
\text{Cd}^{2+} + 2(\text{TEA}) & \rightleftharpoons \text{Cd(TEA)}_2^{2+} \quad (3.5) \\
\text{Cd}^{2+} + \text{S}^{2-} & \rightarrow \text{CdS} \quad (3.6)
\end{align*}

Assuming the metallic complex of the form \(\text{CdL}_n^{2+}\), where \(\text{L}\) is the complexing agent, the general reaction for the CdS deposition can be represented as,

\[
\text{CdL}_n^{2+} + \text{CS(NH}_2\text{)}_2 + 2\text{OH}^- \rightarrow \text{CdS (substrate)} + n\text{L} + 2\text{NH}_3 + \text{CH}_2\text{N}_2 + 2\text{H}_2\text{O} \quad (3.7)
\]

The pH of the reaction mixture is controlled by the addition of \(\text{NH}_4\text{OH}\). The addition of \(\text{NH}_4\text{OH}\) increases the presence of \(\text{NH}_3\) in the solution and thereby increases the concentration of metal complex \(\text{Cd(NH}_3)_4^{2+}\) (eqn 3.4). At the same time the addition of \(\text{NH}_4\text{OH}\) increases the \(\text{OH}^-\) ion concentration in the solution and thereby favours the hydrolysis (eqn 3.3) of the chalcogen precursor. In the presence of sufficient \(\text{NH}_3\) and \(\text{TEA}\), \(\text{Cd}^{2+}\) ions exist in the solution mainly as \(\text{Cd(NH}_3)_4^{2+}\) and \(\text{Cd(TEA)}_2^{2+}\). The deposition of CdS occurs when the ionic product of \(\text{Cd}^{2+}\) and \(\text{S}^{2-}\) exceeds the solubility product. At a given temperature the rate of formation of CdS is determined by the concentration of \(\text{Cd}^{2+}\) provided by \(\text{Cd(NH}_3)_4^{2+}\) and \(\text{Cd(TEA)}_2^{2+}\) and the concentration of \(\text{S}^{2-}\) by the hydrolysis of (\(\text{NH}_2\)\text{)CS}).

3A.4 Results and discussion

3A.4.1 Structural analysis

The structure of the as-deposited and the annealed CdS films are investigated using the X-ray diffraction studies. The XRD spectra of the single dipped CdS films didn’t show any peaks. This may be due to the very low thickness (67 nm) and nanoscale clustering of the as-deposited film. The double
dipped CdS films with 167 nm thickness, showed only a single peak at $2\theta = 26.6^0$ as shown in the figure 3.1. This single diffraction peak may be due to the reflection from the (111) plane of the cubic zinc blend or (002) plane of the hexagonal wurtzite structure of CdS (Fig.3.3a). The XRD spectra of the CdS films on ITO coated glass substrates are shown in figure 3.2. Here also the film showed only a single diffraction peak at $2\theta = 26.6^0$. All other peaks are that of the ITO.

![Fig.3.1 XRD pattern of double dipped CdS thin films on glass (a) as-deposited (b) annealed at 300°C in vacuum](image)

The structure of chemical bath deposited CdS thin films is reported to be cubic [54], hexagonal [20], mixed structure or poly type [21,53,55,56]. It has been reported that the cubic structure of CdS is a metastable one and the transition from the cubic to stable hexagonal structure can be achieved by annealing the films in controlled Ar + S$_2$ atmosphere [21,24,54]. In our experiment noticeable changes in the crystalline structure, or new phases were not observed on vacuum annealing at 300°C for one hour. Similar
results have been reported for the CBD CdS films annealed at 400°C in air [57,58]. Gosh et al. [59] have reported that the CdS nanocrystallites do not exhibit any structural transitions on vacuum annealing. Gibson et al. [56] have reviewed and modelled the structure of CdS.

![XRD pattern of double dipped CdS thin films on ITO coated glass substrates](image)

**Fig.3.2** XRD pattern of double dipped CdS thin films on ITO coated glass substrates (a) as-deposited (b) annealed at 300°C in vacuum.

films and reported that when there is only a main peak near 2θ and a clear hexagonal (102) peak or a clear cubic (200) peak is absent, a random poly type structure will be predominant in the film. Most of the nanocrystalline CdS films and nanoparticles can often be associated with a randomly oriented, randomly sequenced poly type structure rather than the hexagonal wurtzite or cubic zinc blend structures. Thin CBD films of CdS are also not textured. Thicker films may show better cubic or hexagonal crystal structure and a more pronounced texture [56]. Upon annealing in air, the diffraction patterns change only very slightly and practically no crystal growth occurs,
Fig. 3.3 The crystal structure of CdS (a) cubic zinc-blend (b) hexagonal wurtzite confirming the proposal that the polytype structure is stabilized by a surface energy-volume energy competition that occurs in nanoparticles. Therefore the CdS films obtained in our experiment should be a polytype one exhibiting nanocrystallinity. The optical properties, like blue shifts in the band gap of the CdS films deposited on ITO coated substrates confirm this conclusion. The average grain sizes of the CdS films were estimated using

Fig 3.4 AFM image of the double dipped CdS film deposited on glass substrate the Scherrer’s formula (see section 2.3.4). The average grain sizes calculated for the as-deposited and annealed CdS films (double dipped) on glass
substrates were 24nm and 26nm respectively, whereas in the case of CdS films (double dipped) on ITO, these values were 11nm and 13nm. The AFM picture of the CdS films (double dipped) deposited on glass substrate is shown in figure 3.4. The film shows an average surface roughness of 10nm suggesting a uniform and smooth growth over the surface.

3A.4.2 Optical characterisation

The optical transmission spectra of the as-deposited and annealed samples show that the double dipped samples have more transparency in the visible region compared to the single dipped films (Fig 3.4). This might be due to the surface roughness of the single dipped films. The films prepared on ITO have more transparency (>85%) than that on glass substrates. This might be

![Fig. 3.4 Transmission spectra of the as-deposited CdS films](image)
due to the ordered and uniform growth of the CdS films on crystalline ITO substrates. Since CdS is a direct band gap material their band gap values are calculated from the $(\alpha h \nu)^2$ against $h \nu$ plots (see section 2.3.5). The $(\alpha h \nu)^2$ curves of the as-prepared and annealed films are shown in figures 3.5 and 3.6. The calculated values of the band gaps are summarized in table 3.1. The single dipped films show higher band gap than the double dipped films. Vacuum annealing of the films resulted in the reduction of the band gap. But in the case of double dipped CdS films on glass, the band gap didn’t show any appreciable change due to annealing. The reduction in band gap of the single dipped CdS films on glass may be due to the changes in the crystallinity of the film.

**Table 3.1** The band gap values and the crystalline sizes of the CdS thin films

<table>
<thead>
<tr>
<th>substrate</th>
<th>no of dips</th>
<th>thickness (nm)</th>
<th>band gap (eV)</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>as deposited</td>
<td>annealed</td>
</tr>
<tr>
<td>Glass</td>
<td>single</td>
<td>67</td>
<td>2.46</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>double</td>
<td>167</td>
<td>2.43</td>
<td>2.42</td>
</tr>
<tr>
<td>ITO</td>
<td>single</td>
<td>52</td>
<td>2.67</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>double</td>
<td>115</td>
<td>2.50</td>
<td>2.55</td>
</tr>
<tr>
<td>Glass</td>
<td>single</td>
<td>67</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>double</td>
<td>167</td>
<td>22</td>
<td>27</td>
</tr>
<tr>
<td>ITO</td>
<td>single</td>
<td>52</td>
<td>7.3</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>double</td>
<td>115</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

The quantum size effect causes a perturbation in the electronic structure and the conduction and valence band are broken down to discrete states resulting in the widening of the forbidden band gap compared to the bulk [48,60]. In the case of nanoparticle growth of thin films, a hyperbolic band model has been proposed to explain the change of energy gap as a function of particle size [48,61]. According to this model, the equation for the band gap of nanocrystallites ($E_n$) is given by,

$$E_n = \left( E_b^2 + \frac{2E_b \hbar^2 \pi^2}{m^* R^2} \right)^{1/2}$$

(3.8)

where, $E_b$ is the band gap for the bulk semiconductor (2.4 eV for CdS), $R$ is
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the particle radius and $m^*$ is the effective electron mass. For CdS, $m^*/m_e = 0.2$ [48], where $m_e$ is the mass of the free electron.

Fig. 3.5 $(\alpha h \nu)^2$ against $(h \nu)$ plots of the as-deposited and annealed CdS films deposited on glass substrates: (a) single dip film (67nm) (b) double dip film (167nm)

Fig. 3.6 $(\alpha h \nu)^2$ against $(h \nu)$ plots of the as-deposited and annealed CdS films deposited on ITO coated glass substrates: (a) single dip film (52nm) (b) double dip film (115nm)
The crystalline sizes of the CdS films are estimated from the blue shift using the above equation and are given in table 3.1. The crystalline size varies from 7.6 nm to 22 nm. These are in agreement with the average grain size obtained from X-ray diffraction. The single dipped films show low crystalline size indicating more quantum confinement at low thickness. The crystalline size increases due to the annealing.

3A.4.3 Electrical properties

The electrical resistivity of the as deposited and annealed CdS film on glass substrates was measured by the four-probe method. The resistivity values of the as-deposited single dip film (67 nm) and double dip film (167 nm) was $2.5 \times 10^5 \ \Omega \text{cm}$ and $1.1 \times 10^2 \ \Omega \text{cm}$ respectively. The double dipped films didn’t show any change in the order of resistivity upon vacuum annealing. The high resistivity of the single dipped CdS films might be due to the grain boundary effects due to the roughness and non-uniformity in the film at low thickness. The carrier concentration of the as deposited double dipped CdS film was $1.97 \times 10^{17}$ carriers/cm$^3$.

3A.5 Conclusion

CdS films were prepared by chemical bath deposition technique. The films deposited on ITO coated glass substrates were found to be nanocrystalline with a poly type structure. The optical band gaps of the as-deposited films were in the range 2.43eV to 2.67eV. The crystalline sizes of the films were estimated from the blue shift in the optical band gap. Vacuum annealing of the films caused a reduction in the band gap. The low resistivity (~$10^2 \ \Omega \text{cm}$), high transparency (above 80%), carrier concentration of ~$10^{17}$ carriers/cm$^3$ and the feasibility of band gap engineering by quantum confinement at low thickness suggest these films as suitable buffer layers in solar cells.
Part B

Chemical bath deposition of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films and the effect of indium doping

$\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films are prepared by chemical bath deposition. The band gap varies from 2.43 to 2.66 eV when the volume mixture ratio of Zn changes from $x = 0$ to 0.5. The resistivity of the films also increases with Zn incorporation. Resistivity of the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films decreases with In doping.
3B.1 Introduction

Cadmium sulphide continues to hold an important position in CdS/CdTe and CdS/CuInSe$_2$ solar Cells. The CIGS solar cell having the highest reported efficiency of 19.2% is based on chemical bath deposited CdS as the buffer layer. In order to decrease the optical absorption losses and to enhance the response in the short wavelength region, alternative, more transparent buffer materials have been looked for. A ternary derivative of CdS such as Zn$_x$Cd$_{1-x}$S is a promising material in this respect. CdS and ZnS form solid solutions in a wide compositional range so that the band gap tailoring of this ternary compound can be achieved by the variation in composition [62].

3B.2 (CdZn)S as a wide band gap buffer layer

Cadmium zinc sulphide thin films have been used as a wide band gap buffer layer in heterojunction solar cells [63,64] and in photoconducting devices [65]. Devaney et al. [63] deposited uniform (Cd,Zn)S buffer layers by the chemical bath deposition from ZnCl$_2$, CdCl$_2$, NH$_4$Cl, NH$_4$OH and thiourea at 85$^\circ$C. The Zn to (Zn+Cd) ratio in the best films was 15–20 %, resulting in a conversion efficiency of 12.5 % with absorbers prepared by co-evaporation. Basol et al. [64], in turn, prepared (Cd,Zn)S buffer layers with about 10 % Zn by CBD from Zn-acetate, Cd-acetate, triethanolamine, NH$_4$OH and thiourea at 55$^\circ$C, and achieved conversion efficiencies between 10 and 13 %.

Various methods have been used to deposit Zn$_x$Cd$_{1-x}$S thin films viz: screen printing [66,67], electrodeposition [62], spray pyrolysis [68,89], molecular beam epitaxy [70], sputtering [71] etc. There are a few reports on the chemical bath deposition of Zn$_x$Cd$_{1-x}$S thin films from alkaline [72–78] and acidic [79] solutions. A linear variation of band gap from 2.5eV for CdS to 3.6 eV for ZnS has reported by Padam et al. [74]. Along with the increase in the band gap, an increase in the resistivity of the Zn$_x$Cd$_{1-x}$S films has been observed due to the Zn incorporation in the film [74,78]. The resistivity was increased from $10^9$ to $10^{12}$ $\Omega$cm when the composition of Zn was varied in the range $0 \leq x \leq 1$ [74]. Dona et al.[78] have obtained films with three
mixed phases (CdS, ZnS and Zn\textsubscript{x}Cd\textsubscript{1-x}S) and the electrical conductivity of Zn\textsubscript{x}Cd\textsubscript{1-x}S films was dominated by the conductivity of the pure ZnS phase in the film. Vacuum [62] and hydrogen annealing [74] of the Zn\textsubscript{x}Cd\textsubscript{1-x}S films decreases the resistivity.

The compositional dependence of resistivity is a basic property of the (Cd,Zn)S solid solution and its is not appreciably altered by the method of preparation. This high resistivity of the Zn\textsubscript{x}Cd\textsubscript{1-x}S films limits their utilization as a buffer material in heterojunction devices. Doping of indium and hydrogen annealing are suggested to be the suitable methods for getting low resistive Zn\textsubscript{x}Cd\textsubscript{1-x}S thin films [68,69,74,77]. Subbaramaiah et al. [68] have reported the fabrication of all spray-deposited CuIn(S\textsubscript{0.5}Se\textsubscript{0.5})\textsubscript{2} solar cell with In doped Zn\textsubscript{0.05}Cd\textsubscript{0.95}S buffer layer. The conversion efficiency of the cell was only 1.1%. InCl\textsubscript{3} was used as the dopant during spray pyrolysis and its concentration was 6 at %. The as-deposited Zn\textsubscript{0.05}Cd\textsubscript{0.95}S :In films showed a resistivity of 170 $\Omega\text{cm}$ and an optical band gap of 2.41eV [68].

Lee et al. [77] have reported the thermal diffusion of In by the annealing of In/(Cd,Zn)S bilayers. Indium films of different thickness were evaporated over the chemical bath deposited (Cd,Zn)S films and the bilayers were annealed in air (150–550$^\circ$C) for 1 h. The as prepared (Cd,Zn)S films without the In doping showed a high resistivity of 2.4 x 10\textsuperscript{5} $\Omega\text{cm}$. A lowest resistivity of 0.25$\Omega\text{cm}$ was obtained for the (Cd,Zn)S film coated with 40nm In and annealed at 450$^\circ$C for 1 h in air. The decrease in resistivity at high annealing temperatures is due to the partial oxidation of (Cd,Zn)S films to CdO [77].

In this section of the thesis, studies on the chemical bath deposited Zn\textsubscript{x}Cd\textsubscript{1-x}S thin films are presented. The widening of the band gap and the increase in resistance of these films with the increase in Zn concentration are investigated. In order to decrease the high resistivity of these films, the films are doped with In during chemical bath deposition.
3B.3 Experimental Details

Zn$_x$Cd$_{1-x}$S thin films were prepared from aqueous solution containing cadmium chloride (0.01M), zinc chloride (0.1M), thiourea (0.1M), 25% ammonia solution and triethanolamine (TEA). The pH of the solution was adjusted to be 10.8 by the addition of ammonium hydroxide solution. The chemical bath is prepared from 10ml of cation precursors (total volume of CdCl$_2$ + ZnCl$_2$ solutions) and 4ml (4% of the volume of the metal precursors) triethanolamine. The solution is stirred well and required amount of ammonia solution was added to get a pH value 10.8. After proper mixing of the solution, 10 ml of thiourea was added into it and the reaction mixture was kept in a water bath at 80°C. The cleaned glass substrates (see section 3.3.1) were immersed vertically in the chemical bath and the deposition was carried out without any stirring for 45 minutes (single dip). After the deposition, the films were rinsed in distilled water and dried in hot air oven.

Zn$_x$Cd$_{1-x}$S thin films were prepared for various volume mixture ratios (x) of the ZnCl$_2$ and CdCl$_2$ solutions. The volume mixture ratio of the cation precursors, 'x' can be represented as,

\[
x = \frac{V_{Zn}}{V_{Zn} + V_{Cd}}
\]

(3.9)

where, $V_{Zn}$ and $V_{Cd}$ are the volumes of ZnCl$_2$ and CdCl$_2$ solutions respectively. The total volume ($V_{Zn} + V_{Cd}$) of the cation precursors is always kept as 10ml and the value of x was varied from x = 0.1 to 0.5 by mixing different volumes of the cadmium and zinc solutions.

The deposition process is based on the controlled precipitation of zinc and cadmium sulphide in the chemical bath. The solubility products of the metal sulphides are very small ($K_{sp}$ (ZnS) = 10$^{-25}$, $K_{sp}$ (CdS) = 10$^{-27}$) and therefore formation of complex ions is essential to control the immediate precipitation of the cation precursors. Ammonia and triethanolamine acts as the complexing agents and binds the Zn$^{2+}$ and Cd$^{2+}$ ions in the chemical bath as described in section 3.3.2.
Indium doping in the Zn$_x$Cd$_{1-x}$S was achieved by adding high purity (99.99%) indium trichloride (0.001M) solution into the chemical bath used for Zn$_x$Cd$_{1-x}$S deposition. The doping volume ratio, ‘$y$’ can be expressed as,

$$y = \frac{V_{ln}}{V_{zn} + V_{cd}}$$  \hspace{1cm} (3.10)

where, $V_{ln}$ is the volume of InCl$_2$ solution. Doping was carried out for $y = 0.1$ and 0.2.

The thickness of the film was found out using Tolansky’s multiple beam interferometry technique (see section 2.3.1). Since the thickness of the single dipped Zn$_x$Cd$_{1-x}$S films (deposition time 45 min) was less, multiple depositions were carried out with fresh reaction bath each time for getting thicker films. All the measurements were done on the films prepared by double dipping (total deposition time = 90 min.) in the chemical bath. The optical transmission spectra of the films were recorded using UV-Vis spectrophotometer. The electrical resistivity of the films were measured by the two-probe method with evaporated In electrodes.

![Graph showing variation of thickness of Zn$_x$Cd$_{1-x}$S thin films with volume mixture ratio (x)](image-url)

**Fig. 3.7** Variation of thickness of Zn$_x$Cd$_{1-x}$S thin films with volume mixture ratio (x)
3B.4 Results and Discussion

The as-deposited Zn$_x$Cd$_{1-x}$S thin films were found to be smooth adherent and reflecting. As the Zn content in the solution increases the colour of the films changes from bright yellow to pale yellow. The film thickness for a constant deposition time of 90 min was found to decrease almost linearly with increase of Zn content in the solution (Fig. 3.7).

![Fig. 3.8 The XRD patterns of the as-deposited (a) Zn$_{0.1}$Cd$_{0.9}$S and (b) Zn$_{0.3}$Cd$_{0.7}$S films](image)

3B.4.1 Structural analysis

The X-ray diffraction studies on the Zn$_x$Cd$_{1-x}$S films showed crystalline nature for the films deposited with volume mixture ratio, $x \leq 0.2$. XRD spectra showed only a single peak at 26.6$^0$ (Fig. 3.8). The single peak at 26.6$^0$ may be due to the cubic or wurtzite phase of the film. As the concentration
of Zn in the reaction bath increases ($x > 0.2$), the film growth is expected to be cluster-by-cluster deposition than ion-by-ion deposition and the film structure deviates from a solid solution, resulting in an amorphous nature of the film as shown in figure 3.8b.

### 3B.4.2 Optical properties

The optical transmission spectra of the as-deposited Zn$_x$Cd$_{1-x}$S thin films for $x = 0.1$ to 0.5 are shown in figure 3.9. The Zn$_x$Cd$_{1-x}$S films show transparency above 75% in the visible region of light. The transparency of the films decreases for $x = 0.1$ to 0.3 and then increases. The transmission edge shows a blue shift as the Zn content in the reaction mixture increases.

![Fig. 3.9 Transmission spectra of Zn$_x$Cd$_{1-x}$S thin films](image)

The band gap of the Zn$_x$Cd$_{1-x}$S thin films are calculated from the intercept of the $(\alpha h\nu)^2$ curves plotted against the photon energy, $h\nu$ (Fig.3.10). The band gap of the films increases with the increase in volume mixture ratio ‘x’. The as deposited CdS film is having a band gap of 2.43 eV. In the case of...
Zn$_x$Cd$_{1-x}$S thin films, the band gap increases from 2.46 to 2.66 when the volume mixture ratio was increased from $x = 0.1$ to 0.5 (Fig. 3.11). For higher concentrations of $x$, ie. $x \geq 0.3$, the $(\alpha h \nu)^2$ Vs $(h \nu)$ plots show two distinct linear regions (Fig.3.10) which on extrapolation give rise to two band gap values. This can be interpreted as the presence of another direct optical transition. The films prepared with $x \geq 0.3$ showed a lower band gap value around 2.45eV in addition to the wide band gap corresponding to the Zn$_x$Cd$_{1-x}$S.

The 2.45eV band gap value indicates the presence of certain amount of pure CdS phase in these samples. Similar results have reported by Abrahams et al. [80] in the co-precipitation of ZnS–CdS colloidal particles and also by Dona et al. [78]. The presence of the pure CdS in the films gives an idea of the method of formation of Zn$_x$Cd$_{1-x}$S thin films. Probably the film formation starts with the formation of the pure CdS particles, which is the fastest process. The formation of ZnS starts immediately. The final structure can be understood as CdS particle surrounded by Zn$_x$Cd$_{1-x}$S cluster. This argument is supported by the results obtained in XRD and electrical resistivity.
measurements. The films with $x \geq 0.3$ were showing amorphous nature and high resistivity.

![Fig. 3.11 The band gap energies of Zn$_x$Cd$_{1-x}$S thin films for $x = 0$ to 0.5](image)

### 3B.4.3 Electrical properties

The resistivity of the Zn$_x$Cd$_{1-x}$S films increases with the increase in the volume mixture ratio ‘x’. The zinc incorporation increases the resistivity. The as-deposited CdS films showed a resistivity of $1.1 \times 10^2$ Ωcm. In the case of Zn$_x$Cd$_{1-x}$S films, the resistivity was $\sim 10^3$ Ωcm for $x \leq 0.2$. The films become highly resistive at higher concentrations of Zn as shown in table 3.2. This high value of resistivity might be due to the presence of amorphous clustering of Zn$_x$Cd$_{1-x}$S around the CdS nuclei at higher Zn concentrations. The amorphous nature of the films by XRD for $x > 0.2$ confirms this conclusion.

### 3B.5 Effect of Indium doping

Indium doping is having significant effect on the growth, electrical and optical properties of the as deposited Zn$_x$Cd$_{1-x}$S thin films. The thickness of
the as-deposited ZnₙCd₁₋ₙS films was found to decrease with the indium doping concentration as shown in Fig 3.7. The In doped ZnₙCd₁₋ₙS films showed amorphous nature in the X-ray analysis whereas CdS films retained its crystalline nature.

An increase in band gap due to indium doping was observed for CdS and Zn₀.₁Cd₀.₉S films. The band gap of the CdS film increases from 2.43 to 2.48eV (Fig. 3.12). The broadening of band gap due to Indium doping may be due to filling up of conduction band edge by the excessive carriers donated by the impurity atoms. This leads to blue shift in optical band-to-band transitions by blocking the low energy transitions, known as Burstein Moss effect. ZnₓCd₁₋ₓS thin films prepared from chemical baths with x ≥ 0.2 showed decrease in band gap due to the In doping. But the resistivity is found to decrease. The electrical resistivity values of the as-deposited and the In doped films are summarized in table 3.2. The resistivity value of all the films decreases by 2 orders on indium doping. The appreciable variation of resistivity of ZnₓCd₁₋ₓS films due to indium doping indicates the increase in carrier concentration. The increase in electrical conductivity of these films might be due to interstitially or substitutionally doped In atoms which acts as donor impurities. The enhanced carrier concentration due to the donor

<table>
<thead>
<tr>
<th>Sample</th>
<th>y = 0</th>
<th>y = 0.1</th>
<th>y = 0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>1.10 x 10²</td>
<td>27.5</td>
<td>1.93</td>
</tr>
<tr>
<td>Zn₀.₁Cd₀.₉S</td>
<td>2.68 x 10²</td>
<td>32.6</td>
<td>6.52</td>
</tr>
<tr>
<td>Zn₀.₂Cd₀.₈S</td>
<td>4.05 x 10²</td>
<td>96.9</td>
<td>23.45</td>
</tr>
<tr>
<td>Zn₀.₃Cd₀.₇S</td>
<td>6.70 x 10³</td>
<td>4.48 x 10³</td>
<td>6.29 x 10²</td>
</tr>
<tr>
<td>Zn₀.₄Cd₀.₆S</td>
<td>6.90 x 10⁴</td>
<td>9.34 x 10⁴</td>
<td>3.79 x 10²</td>
</tr>
<tr>
<td>Zn₀.₅Cd₀.₅S</td>
<td>2.72 x 10⁵</td>
<td>1.82 x 10⁵</td>
<td>4.15 x 10²</td>
</tr>
</tbody>
</table>
Chemical bath deposition of II-VI semiconductor... 

atoms, result in band gap narrowing of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films with $x \geq 0.2$. This may be due to the band tailing by the impurity levels and also due to the many body effects. The band gaps of the indium doped films were calculated from the absorption spectra of the films by plotting $(\alpha h \nu)^2$ against $h \nu$ curves. Typical absorption spectra of the as-deposited and In doped $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films are shown in Fig.3.13. The inset of the figure shows the corresponding $(\alpha h \nu)^2$ against $h \nu$ plots. A red shift of the absorption edge occurs due to the In doping. The calculated values of the band gap of the as deposited and the In doped $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films are summarized in Table 3.3.

Table 3.3 Band gap values of the as-deposited and indium doped $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ films for various doping volume ratios of In ($y$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$y = 0$</td>
</tr>
<tr>
<td>CdS</td>
<td>2.43</td>
</tr>
<tr>
<td>$\text{Zn}<em>{0.1}\text{Cd}</em>{0.9}\text{S}$</td>
<td>2.46</td>
</tr>
<tr>
<td>$\text{Zn}<em>{0.2}\text{Cd}</em>{0.8}\text{S}$</td>
<td>2.56</td>
</tr>
<tr>
<td>$\text{Zn}<em>{0.3}\text{Cd}</em>{0.7}\text{S}$</td>
<td>2.61</td>
</tr>
<tr>
<td>$\text{Zn}<em>{0.4}\text{Cd}</em>{0.6}\text{S}$</td>
<td>2.65</td>
</tr>
<tr>
<td>$\text{Zn}<em>{0.5}\text{Cd}</em>{0.5}\text{S}$</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Fig.3.12 $(\alpha h \nu)^2$ against $h \nu$ plots of CdS films for different doping volume ratios ($y$) of Indium

77
Fig. 3.13 Absorption spectra of the as-deposited and In doped Zn$_{0.2}$Cd$_{0.8}$S films. Inset shows the the corresponding $(\alpha h \nu)^2$ against $h \nu$ plots.

3B.6 Conclusion

Zn$_x$Cd$_{1-x}$S thin films were deposited by chemical bath deposition for $x = 0$ to 0.5. The band gap of the films varied from 2.43 to 2.66 eV and the electrical resistivity of the films were found to increase with the increase in Zn content in the solution. Indium was doped into the Zn$_x$Cd$_{1-x}$S film by adding InCl$_3$ into the chemical bath during deposition and the electrical resistivity of the films was found to decrease by an order of two compared to the undoped Zn$_x$Cd$_{1-x}$S films. The low resistivity and the wide band gap of Zn$_x$Cd$_{1-x}$S:In films suggest them as a better material for the buffer layer application for heterojunction solar cells. The wide band gap along with the reduced resistivity by indium doping suggest Zn$_x$Cd$_{1-x}$S films, as a better substitute for cadmium sulphide buffer layer in heterojunction solar cells.
Part C

Preparation and characterisation of ZnS thin films by chemical bath deposition

Zinc sulphide thin films were prepared by chemical bath deposition and the properties of these films are compared with those deposited by electron beam evaporation. The variation in the optical and electrical properties of the CBD grown ZnS films with the pH of the reaction mixture was investigated. The chemically deposited ZnS films showed a wide band gap of 3.93eV and a transparency of more than 80% in the visible region. The lowest resistivity of $\sim 10^4 \ \Omega \cdot \text{cm}$ was obtained for the films prepared from a chemical bath of pH 10.6. The refractive index, extinction coefficient and the dielectric constants of CBD ZnS films are also found out.
3C.1 Introduction

Due to the environmental concerns associated with Cd-containing materials, serious efforts have been directed towards completely Cd-free buffer materials. The materials studied include Zn and In-based materials such as sulphides, selenides, hydroxy sulphides and hydroxy selenides. The conversion efficiencies of Cd-free devices are approaching those of the devices with CdS buffer layer. Recently, a conversion efficiency of 18.1 %, close to those of the best CdS window layer based devices, was achieved using a CBD-ZnS buffer layer in combination with a CIGS absorber prepared by three-stage co-evaporation in a MBE system [81]. The CBD-ZnS was found to be sensitive to oxygen-induced damage during sputter deposition of undoped ZnO, and thus the device was prepared without the undoped ZnO layer [81]. The optimum thickness of the ZnS layer was 130 nm, indicating the need for reduction of shunt paths between CIGS and ZnO:Al. As expected on basis of the higher band gap of the buffer, the cell exhibited higher quantum efficiency at short wavelengths than a cell with CdS buffer.

3C.2 ZnS thin films by chemical bath deposition

Though CBD has been effectively used to deposit different chalcogenides such as CdS, PbS, Bi₂S₃ etc., the deposition of crystalline ZnS by CBD is a difficult one. Generally the ZnS films obtained by CBD are either amorphous or poorly crystallized. Therefore annealing at high temperatures was needed to improve the crystallinity of the films [82,83]. There are a few reports on the chemical bath deposition of ZnS thin films [82–92].

Cheng et al. [84] have deposited crystalline ZnS films with wurtzite structure from alkaline solutions using tri-sodium citrate as the complexing agent. The deposition was carried out at a bath temperature of 80°C. The optical band gap of the as-deposited films was found to be 3.53eV. Though Johnson et al. [85] have used tri-sodium citrate as the complexing agent, discernable diffraction peaks was not seen. Therefore it is proposed that the
Chemical bath deposition of II-VI semiconductor... concentration of the tri-sodium citrate has a significant influence on the crystallization and orientation of the CBD-ZnS.

Ammonia and hydrazine are the popular choices as the complexing agent in the CBD of ZnS film. Vidal et al. [86] reported the influence of NH₃ concentrations on the properties of CBD-ZnS films. Dona et al. [83] have deposited ZnS films using hydrazine hydrate as a complexing agent. Oladeji and Chow [87] have reported that the presence of an ammonium salt in the chemical bath increases the thickness of the ZnS film. The importance of ternary complexes in the chemical bath deposition of ZnS has been studied and modeled by O’ Brien et al. [88]. Thiourea [83,84,86,87,92] or thioacetamide [82,89] was often used as the chalcogen precursor, and acetate [84], chloride [86,92] or sulphate [82,83,87,89] solution of Zn was used as the cation precursor for the chemical bath deposition of ZnS thin films.

In this section, the preparation and characterization of ZnS thin films by chemical bath deposition is discussed. The properties of the CBD ZnS films are compared with the ZnS films deposited by electron beam evaporation. The effect of pH on the electrical and optical properties of these films prepared from two different zinc salts (zinc chloride and zinc nitrate) is investigated. Ammonia and hydrazine were used as the complexing agents, and the deposition was carried out in the presence of an ammonium salt. The growth mechanism of ZnS films during chemical bath deposition is also discussed.

3C.3 Experimental details

The chemical bath deposition of ZnS on glass and indium tin oxide (ITO) coated glass substrates were carried out from a chemical bath containing zinc nitrate [Zn(NO₃)₂] / zinc chloride (ZnCl₂) , thiourea [CS(NH₂)₂] , 25 % ammonia solution (NH₄OH) , 80 % hydrazine hydrate (N₂H₂OH) and ammonium nitrate (NH₄NO₃) / ammonium chloride (NH₄Cl) . All the reagents used were of analytical grade. The films were prepared separately from two sources of zinc, viz: zinc nitrate and zinc chloride. The electron
beam evaporation of the ZnS films were carried out at 2 x 10^-5 mbar. Films were deposited on glass substrates at various substrate temperatures.

The transmission spectra of the as-deposited samples were recorded using an ultraviolet-visible spectrophotometer (Hitachi-Model U3410). The electrical resistivity of the as-deposited ZnS films were measured by a two-probe arrangement with the electrodes in planar geometry using a Keithley’s source measure unit (Model SMU236).

3C.3.1 Preparation and optimization of the chemical bath

The chemical bath contains 5 ml of 1 N solution of Zn(NO$_3$)$_2$ mixed with 2 ml of hydrazine hydrate and 2.5 ml of 0.5 N ammonium nitrate (buffer) solution. NH$_4$OH was added into this solution to adjust the pH at the desired value. Then 5 ml of 1 N solution of thiourea was added into this mixture and stirred well. This reaction mixture was transferred into a beaker in which the substrates were kept vertically. The deposition was carried out at a temperature of 80 °C by keeping the chemical bath in thermostated water bath. All the samples reported here are for the deposition time 2 h at a bath temperature of 80 °C. After the deposition, the samples were taken out, washed in distilled water and dried in a hot air oven. The film on one side of the substrate was removed by careful etching with dilute hydrochloric acid. The film deposition was carried out with the same bath composition for different pH values, ranging from 10 to 10.6.

ZnS films were also prepared under identical conditions from the reaction mixture containing 5 ml of 1 N solution of ZnCl$_2$, 2 ml of hydrazine hydrate, 2.5 ml of 0.5 N ammonium chloride (buffer) and 5 ml of 1 N thiourea. An ammonia solution was used to vary the pH value of the chemical bath from 10 to 10.6.

The addition of ammonium nitrate or ammonium chloride helps to control the pH value more easily [87]. In the presence of hydrazine and ammonia, the zinc complexes [Zn(NH$_3$)$_4$]$^{2+}$ and [Zn(N$_2$H$_4$)$_3$]$^{2+}$ were formed, resulting
in a slow release of $\text{Zn}^{2+}$ ions. The thickness of the film was measured gravimetrically using a microgram balance. The thickness of the ZnS films increased from 0.18 to 0.25 $\mu$m when the pH value of the solution was varied from 10 to 10.6. Figure 3.14 shows the variation of thickness of the ZnS film prepared from zinc nitrate and zinc chloride with the pH of the reaction mixture for a constant dipping time of 2 h. The bath temperature in CBD technique can be effectively used to control the rate of ZnS formation. The hydrolysis of thiourea is greatly enhanced by the increase in bath temperature. The equilibrium constants of all reactions are temperature dependent. Films with good adhesion and morphology were obtained for a bath temperature of 80 $^\circ$C.

![Fig.3.14 Thickness of CBD ZnS thin films deposited at different pH of the chemical bath for a constant dipping time of 2 h.](image)

The deposition was carried out for different volume ratios of the zinc nitrate (or zinc chloride), thiourea and the buffer ammonium salt. It was observed that when the corresponding volume mixture ratio was 2:2:1, the films obtained were smooth and uniform. The films prepared under these optimized conditions showed a Zn-to-S ratio of 1:1 in the energy-dispersive X-ray measurement.
3C.3.2 Deposition mechanism

In chemical bath deposition, a complexing agent is used to bind the metallic ions to avoid the homogeneous precipitation of the corresponding compound. The formation of a complex ion is essential to control the rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complex hydrolyses slowly to generate the positive ions in the solution. A solution containing the metal complexes was mixed with a solution that produces negative ions by hydrolysis. The deposition of the compound occurs when the ionic product exceeds the solubility product of the compound to be deposited. Either homogeneous or heterogeneous deposition can occur. The homogeneous process is the faster one, resulting in the adsorption of powdery ZnS particles on the substrate due to the bulk precipitation. So, the formation of metal complexes is essential to minimize the homogeneous process. In the heterogeneous process, due to the slow release of ions by the metal complexes, the preferential adsorption of Zn$^{2+}$ and S$^{2-}$ ions will take place, leading to uniform nucleation and growth of the thin film.

In the growth of the ZnS thin film from a chemical bath, hydrazine hydrate and ammonia act as the complexing agents to bind the Zn ions. Thiourea furnishes the necessary S$^{2-}$ ions by hydrolysis. The various reactions involved in this growth process are given in Eqs. (3.11) – (3.19):

\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \quad (3.11) \\
\text{N}_2\text{H}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{N}_2\text{H}_5^+ + \text{OH}^- \quad (3.12) \\
\text{ZnCl}_2 & \rightarrow \text{Zn}^{2+} + 2\text{Cl}^- \quad (3.13) \\
\text{Zn(NO}_3)_2 & \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- \quad (3.14)
\end{align*}

Zn$^{2+}$ ions form the metal complexes with ammonia and hydrazine hydrate by the following reaction:

\begin{align*}
\text{Zn}^{2+} + 4\text{NH}_3 & \rightleftharpoons \text{Zn(NH}_3)_4^{2+} \quad (3.15) \\
\text{Zn}^{2+} + 3\text{N}_2\text{H}_4 & \rightleftharpoons \text{Zn(N}_2\text{H}_4)_3^{2+} \quad (3.16)
\end{align*}

Hydrolysis of the thiourea can be represented by the chemical equation:

\begin{align*}
\text{CS(NH}_2)_2 + 2\text{OH}^- & \rightleftharpoons \text{S}^{2-} + 2\text{H}_2\text{O} + \text{CH}_2\text{N}_2 \quad (3.17) \\
\text{Zn}^{2+} + \text{S}^{2-} & \rightleftharpoons \text{ZnS} \quad (3.18)
\end{align*}
Assuming the metallic complex of the form ZnL$_n^{2+}$, where L is the complexing agent, the general reaction for the ZnS deposition can be represented as:

\[
\text{ZnL}_n^{2+} + \text{CS(NH}_2\text{)}_2 + 2\text{OH}^- \rightarrow \text{ZnS (substrate)} + n\text{L} + 2\text{NH}_3 + \text{CH}_2\text{N}_2 + 2\text{H}_2\text{O} \quad (3.19)
\]

The presence of hydrazine hydrate during the deposition of ZnS improves the homogeneity and the film shows a smooth and reflecting surface [83]. In the presence of sufficient NH$_3$ and hydrazine hydrate, Zn$^{2+}$ ions exist in the solution mainly as Zn(NH$_3$)$_4^{2+}$ and Zn(N$_2$H$_4$)$_3^{2+}$. The stability constant of the Zn(NH$_3$)$_4^{2+}$ complex is too high. But the presence of hydrazine in the solution helps part of this complex to exist as Zn(NH$_3$)$_3^{2+}$ which is having a low stability constant and will act as the major contributor of Zn$^{2+}$ ions [87].

The pH value of the reaction mixture is controlled by the addition of NH$_4$OH. The addition of NH$_4$OH increases the presence of NH$_3$ in the solution and there by increases the concentration of metal complexes Zn(NH$_3$)$_4^{2+}$ and Zn(N$_2$H$_4$)$_3^{2+}$ (eqn 3.15). At the same time the addition of NH$_4$OH increases the OH$^-$ ion concentration in the solution and thereby favours the hydrolysis (eqn 3.17) of the chalcogen precursor. The thickness of the as deposited ZnS thin film was found to increase when the pH value was varied from 10 to 10.6. The increase in thickness might be due to the increase in the concentration of Zn$^{2+}$ and S$^2-$ ions by the addition of NH$_4$OH, which favoured the heterogeneous growth of ZnS.

The addition of the ammonium salt increases the NH$_4^+$ concentration and thereby favours the backward reaction (eqn (3.11), resulting in more NH$_3$ and less OH$^-$ ions in the chemical bath. The excess of ammonia will enhance the complex ion formation (eqn 3.15) where as the reduction in OH$^-$ ion concentration will decrease the growth rate of ZnS formation (eqn 3.19). Therefore, the concentration of the ammonium salt has to be optimized for the heterogeneous and uniform growth of ZnS. In this work we have found that 0.5 N solution of the buffer salt gives more uniform and thicker films.
3C.4 Results and Discussion

3C.4.1 Structural analysis

The powder X-ray diffraction spectra of chemically deposited ZnS thin films showed no diffraction peaks corresponding to crystalline ZnS. The films deposited by the electron beam evaporation at different substrate temperatures showed only the peak corresponding to the (111) plane of cubic phase. This shows that the evaporated films are highly oriented with its (111) plane parallel to the substrate surface. Figure 3.15 shows the x-ray diffraction patterns of the chemically deposited and electron beam evaporated ZnS thin films together with that of ZnS powder. Considering the cubic structure of the ZnS, the lattice constant ‘a’ was determined from the X-ray diffraction data. The standard value of the lattice parameter ‘a’ of ZnS...
Chemical bath deposition of II-VI semiconductor... is 5.406 Å. The grain sizes of the electron beam evaporated ZnS films were calculated from the XRD spectra using the Scherrer’s formula. The lattice constant values and the average gain sizes of the ZnS prepared by the electron beam evaporation at various substrate temperatures are shown in table 3.4.

**Table 3.4** The lattice constant and the grain sizes of the electron beam evaporated ZnS thin film

<table>
<thead>
<tr>
<th>Substrate temperature</th>
<th>Plane (cubic)</th>
<th>Lattice constant (a) (Å)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28°C</td>
<td>111</td>
<td>5.42</td>
<td>17</td>
</tr>
<tr>
<td>150°C</td>
<td>111</td>
<td>5.47</td>
<td>27</td>
</tr>
<tr>
<td>300°C</td>
<td>111</td>
<td>5.40</td>
<td>24</td>
</tr>
</tbody>
</table>

### 3C.4.2 Optical properties

The transmission spectra of the ZnS thin films prepared from the zinc nitrate and zinc chloride solutions are shown in figure 3.16. The ZnS films prepared from the chemical bath containing nitrate solutions with pH = 10.6 showed transmission of more than 80% in the visible region. Films were prepared for different pH values of the chemical bath keeping all other bath parameters same. The thickness of the ZnS film for constant dipping time was showing maximum value when the pH value of the bath was 10.6. The high transparency in the visible region is a consequence of the wide band gap of the film (3.86 eV). The low transparency of some samples as shown in figure 3.16 might be due to adsorbed powdery colloids formed by homogeneous growth. Colloids degrade the quality of the films. Since ZnS is a direct band gap material, the band gaps of the ZnS films were calculated using the $(\alpha h \nu)^2$ against $h \nu$ plots (see section 2.3.5). The $(\alpha h \nu)^2$ against $h \nu$ plots of the ZnS films prepared from zinc nitrate and zinc chloride at different pH values are shown in figure 3.17. In the case of CBD films, band gap values varied
Fig. 3.16 Transmission curves of CBD ZnS thin films deposited at different pH of the chemical bath: (a) Prepared from ZnCl₂, (b) prepared from Zn(NO₃)₂.

Fig. 3.17 \((\alpha h\nu)^2\) against \(h\nu\) plots of CBD ZnS thin films for different pH of the chemical bath: (a) Prepared from ZnCl₂, (b) prepared from Zn(NO₃)₂.
from 3.66 to 3.93 eV, which closely agree with the reported values [83,87].

The transmission spectra and the \((\alpha h \nu)^2\) against \(h \nu\) plot of the electron beam evaporated ZnS film is shown in figure 3.18. The band gap of the electron beam evaporated film was found to be 3.42 eV. The band gap values of the ZnS thin films with pH of the chemical bath are shown in table 3.5. The refractive index and the extinction coefficient of the as-deposited thin films were determined by the method described by Manificer et al. [93], assuming weak absorption by these films in the visible region (see section 2.3.5). The variation of the refractive index and the extinction coefficient of the as-deposited CBD ZnS films are shown in figure 3.19. In the visible range of wavelength, the refractive index is 2.5.

![Transmission curve of electron beam evaporated ZnS thin film. The inset shows the \((\alpha h \nu)^2\) against \(h \nu\) plot.](image)

**Fig. 3.18** Transmission curve of electron beam evaporated ZnS thin film. The inset shows the \((\alpha h \nu)^2\) against \(h \nu\) plot.
Table 3.5 Band gap values (in eV) of the CBD ZnS films

<table>
<thead>
<tr>
<th>Prepared using</th>
<th>pH = 10</th>
<th>pH = 10.3</th>
<th>pH = 10.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCl₂</td>
<td>3.68</td>
<td>3.78</td>
<td>3.66</td>
</tr>
<tr>
<td>Zn(NO₃)₂</td>
<td>3.84</td>
<td>3.75</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Fig. 3.19 Variation of refractive index and extinction coefficient of CBD ZnS films deposited from a bath containing ZnCl₂ for a pH value of 10.6.

3C.4.3 Electrical properties

The resistivity of the ZnS films was found to vary considerably with the pH of the chemical bath, as shown in figure 3.20 a. The resistivity of the films reduced from \(~10^6\) to \(~10^4 \, \Omega\text{-cm} \) when the pH varied from 10 to 10.6. The addition of ammonia produces more zinc complexes in the bath and also favours the hydrolysis of thiourea, resulting in a more uniform growth of ZnS films of low resistivity. The variation of resistivity of the electron beam evaporated ZnS films with the substrate temperature is shown in figure 3.20b.
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**Fig. 3.20** The Resistivity of the ZnS thin films (a) deposited under various pH of the chemical bath (b) prepared by electron beam evaporation at different substrate temperatures.

deposited by thermal evaporation on the ZnS films prepared by CBD over the ITO substrates. An impedance analyzer (model HP 4192A) was sued to measure the capacitance of the films at various frequencies. From the capacitance value, the dielectric constants of the films in the frequency range 1 – 9 MHz were found out. The dielectric constant was found to be around 6. Figure 3.21 shows the dependence of dielectric constant on frequency for the ZnS films prepared by chemical bath deposition. This value of dielectric constant closely agrees with that of evaporated [94] stoichiometric ZnS films.
ZnS thin films were prepared by chemical bath deposition from two zinc salts, viz. zinc nitrate and zinc chloride. The optical and electrical properties of CBD ZnS films are in agreement with that of electron beam evaporated ZnS films. The optical and electrical properties of the as-deposited ZnS thin films were found to vary with the pH value of the reaction mixture. The films prepared from a chemical bath containing a zinc nitrate solution with pH = 10.6 showed a transmission of more than 80 % in the visible region. The ZnS films produced from the zinc nitrate precursor have found to be more transparent and smooth compared to the films grown from the zinc chloride precursor. The presence of the buffer ammonium salt in the solution along with hydrazine increases the ZnS deposition rate. The refractive index of the film was around 2.5 in the visible region. The ZnS films deposited at a pH = 10.6 showed a resistivity of ~10^4 Ωcm. The band gap of the films varied from 3.66 to 3.93 eV. The wide band gap of these films makes it possible to use them as buffer layer for solar cells.

3C.5 Conclusion

ZnS thin films were prepared by chemical bath deposition from two zinc salts, viz. zinc nitrate and zinc chloride. The optical and electrical properties of CBD ZnS films are in agreement with that of electron beam evaporated ZnS films. The optical and electrical properties of the as-deposited ZnS thin films were found to vary with the pH value of the reaction mixture. The films prepared from a chemical bath containing a zinc nitrate solution with pH = 10.6 showed a transmission of more than 80 % in the visible region. The ZnS films produced from the zinc nitrate precursor have found to be more transparent and smooth compared to the films grown from the zinc chloride precursor. The presence of the buffer ammonium salt in the solution along with hydrazine increases the ZnS deposition rate. The refractive index of the film was around 2.5 in the visible region. The ZnS films deposited at a pH = 10.6 showed a resistivity of ~10^4 Ωcm. The band gap of the films varied from 3.66 to 3.93 eV. The wide band gap of these films makes it possible to use them as buffer layer for solar cells.
ZnS thin films prepared by the chemical bath deposition were thermally oxidized into ZnO films by annealing in air at 800°C for one hour. The thermal conversion of the ZnS to ZnO is analysed using XRD. The oxidized films show an optical band gap of 3.23 eV and an electrical resistivity of $10^4 \Omega \cdot \text{cm.}$
3D.1 Introduction

The high efficiency heterojunction solar cell devices nowadays utilize an oxide bilayer (see Chapter 1, Fig 1.6) that consists usually of a thin (50-100 nm) high-resistivity layer, and a thicker (100-1500 nm) low-resistivity layer. The high resistivity layer is most often undoped ZnO. The conducting part of the oxide bilayer is most often ZnO doped with either Al, B or Ga. Tin doped indium oxide (In$_2$O$_3$:Sn, ITO) is also widely used. The purpose of this high resistive ZnO layer is to increase the open circuit voltage ($V_{OC}$) by decreasing the dark saturation current [95]. The transparent conducting oxide layer serve as low resistance contact to the cell and also as an antireflection coating for the active region.

In this section a simple and low cost technique for the preparation of ZnO films from the chemical bath deposited ZnS films is discussed. The chemical bath deposited ZnS thin films were thermally oxidized to ZnO films by annealing in air and oxygen ambient.

3D.2 ZnO thin films

ZnO thin films with their wide band gap (3.37 eV) at room temperature are of great interest due to the applications such as ultraviolet emitting devices, transparent conductors and ultra fast nonlinear optical devices in optoelectronics [96]. In the last few years zinc oxide has gained increasing attention as a transparent conducting oxide (TCO) material because of its higher abundance compared to the other TCO materials. Another advantage of the zinc oxide is its better stability in hydrogen plasma than that of Indium Tin oxide, which makes it useful in the fabrication of hydrogenated amorphous silicon solar cells [97]. The ZnO thin films have been grown by different techniques such as magnetron sputtering [98], chemical vapour deposition [99], sol-gel method [100], pulsed laser deposition [101], spray pyrolysis [102] etc.
In the case of solar cells, the ZnO resistive layer is usually prepared by sputtering in Ar/O_2 (about a partial pressure of 0.1–2 %) ambient [95,33,34]. Besides sputtering intrinsic ZnO, the resistive layer may also be made from a doped target (ZnO:2 wt.% Al_2O_3), provided that the sputtering ambient contains enough oxygen. The films are usually sputtered in pure Ar ambient and in some cases relatively small amount of O_2 is also introduced for better crystallinity.

Preparation of ZnO thin films by the thermal conversion of the crystalline ZnS thin films deposited by MOCVD [103] and PLD [104] has been reported earlier. The formation of ZnO thin films with high photoconductivity [82,89] and waveguiding applications [92] was reported by the thermal oxidation of chemical bath deposited ZnS films. The possibility of doping Ga during thermal oxidation of ZnS to increase the electrical conductivity was also reported by Jayatissa [105]. The ZnO films formed by the thermal oxidation of ZnS were always showing wurtzite structure.

3D.3 Experimental details

ZnS thin films were deposited on quartz substrates by chemical bath deposition (as described in Section 3C.3) using the zinc nitrate solution at a pH = 10.3. The thermal oxidation of the ZnS thin films was investigated by annealing the ZnS films at different temperatures in air and under oxygen ambient. The annealing temperature was varied from 400 to 800°C.

The structure of the films was investigated using X-ray diffraction. The optical properties of the as-deposited ZnS and the annealed samples were compared using the transmission spectra. The transmission spectra of the samples were recorded using UV-Vis-NIR spectrophotometer (Hitachi 3410). The electrical resistivity of the samples was calculated from the current voltage measurements using the Keithley source measure unit (SMU 236). Two probe measurements were made in the planar electrode configuration with highly conducting silver paint as the electrodes.
3D.4 Results and discussion

The XRD spectra of the films annealed at different temperatures show that the thermal conversion to ZnO was not complete below 800°C. It has been reported earlier that in the case of thermal oxidation of crystalline ZnS films prepared by the MOCVD, annealing in oxygen ambient below 700°C showed mixed phases with reflections corresponding to the cubic ZnS and hexagonal ZnO [103]. In the present study, the annealing of ZnS films at 800°C was the optimum temperature for the complete conversion of the ZnS to ZnO (Fig.3.22). This was confirmed by the absence of sulphur atoms in the EDX analysis of converted ZnO films. The electron beam evaporated crystalline ZnS films and the powder samples were also annealed in the same conditions to find out the exact processes behind the thermal oxidation.

![XRD spectra](image)

**Fig.3.22** The XRD spectra of the ZnO films prepared by the thermal oxidation of CBD ZnS at 800°C. (a) as-deposited CBD ZnS thin film (b) annealed in air for 1 hour (c) annealed in O₂ for 1 hour (d) annealed in air for 3 hours.
3D.4.1 Structural changes during thermal oxidation

The as deposited ZnS films by CBD were found to be amorphous by X-ray. The film annealed in air at 800°C for one hour shows peaks corresponding to (100), (002) and (101) planes of the hexagonal ZnO phase. The crystallinity of the films improved, when the annealing was carried out in oxygen flow. The films annealed in air at 800°C for longer duration (3hrs) show polycrystalline nature of the films with a relatively strong textured orientation along the (002) plane. Figure 3.22 shows the XRD spectra of the films annealed at various conditions. The lattice constants of the thermally converted ZnO films (Table 3.6) were found to be consistent with the standard values; \( a = 3.2539 \text{Å} \) and \( c = 5.2098 \text{Å} \) [95].

![XRD spectra of EBE ZnS](image)

**Fig.3.23** XRD spectra of EBE ZnS (a) as deposited (b) after annealing in O\(_2\) for 1 hour at 800°C

ZnS powder and crystalline ZnS films prepared by electron beam evaporation were also annealed in oxygen ambient at 800°C for one hour.
The electron beam evaporated ZnS films showed only a strong reflection corresponding to the (111) plane of the cubic zinc blend structure. After the oxidation, the converted films showed the peaks corresponding to the (100), (002), (101) and (102) reflection of the hexagonal wurtzite structure of the ZnO (Fig. 3.23). These films showed a preferred orientation along the (002) plane just like in the case of the thermally converted CBD ZnS (Fig. 3.22 and 3.23). The XRD patterns of the ZnS powder before and after oxidation are shown in figure 3.24. The XRD spectrum of the thermally oxidised ZnS powder is similar to that of the ZnO powder as shown in figure 3.24.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Annealing at 800°C</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD ZnS</td>
<td>Air, 1 hr</td>
<td>3.26</td>
<td>5.23</td>
<td>14</td>
</tr>
<tr>
<td>CBD ZnS</td>
<td>O₂, 1 hr</td>
<td>3.25</td>
<td>5.20</td>
<td>15</td>
</tr>
<tr>
<td>CBD ZnS</td>
<td>Air, 3 hrs</td>
<td>3.28</td>
<td>5.25</td>
<td>31</td>
</tr>
<tr>
<td>EBE ZnS</td>
<td>O₂, 1 hr</td>
<td>3.28</td>
<td>5.25</td>
<td>25</td>
</tr>
<tr>
<td>ZnS powder</td>
<td>O₂, 1 hr</td>
<td>3.27</td>
<td>5.25</td>
<td>26</td>
</tr>
</tbody>
</table>

The XRD pattern of the converted ZnO in the Fig 3.22d indicates hexagonal wurtzite structure with a preferential (002) orientation. When the duration of annealing increased, the diffraction peaks became sharper and more intense due to the increased particle size as well as the enhanced crystallinity. The mean grain sizes of the films (Table 3.6) were calculated by the Scherrer’s formula. The average grain sizes of the thermally oxidized EBE-ZnS and ZnS powder were around 25 nm. In the case of CBD-ZnS, the films after oxidation showed an average grain size of 14 nm for air-annealed sample and 16 nm for those annealed in oxygen flow. The grain size increased to 31 nm when the duration of the annealing increased to 3 hrs indicating better crystallinity.
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Fig. 3.24 XRD spectra of (a) ZnS powder (b) ZnS powder annealed in O\textsubscript{2} at 800\textdegree{}C for 1h (c) ZnO powder

3D.4.2 Physical process of thermal oxidation

The possible oxidation process of the ZnS might be due the diffusion of the oxygen atoms into the ZnS matrix via interstitial sites and bond to Zn, forcing the sulphur atoms to occupy the interstitial sites and get oxidized to escape as SO\textsubscript{2}. This will transform the unitcell and it recrystallises to the stable wurtzite structure. The possibility of the direct occupation of the sulphur sites of the cubic ZnS by the oxygen atoms can be ruled out since that can form only a zinc blend ZnO, which was not observed in the present study by XRD analysis. In our experiment both the amorphous and the crystalline ZnS were oxidized in the same manner resulting in the wurtzite ZnO structure. Since the unit cell volume of the hexagonal ZnO is less than that of cubic ZnS, the relaxation of the structure will be favored to attain the more stable wurtzite structure.
3D.4.3 Optical and Electrical Properties

The optical transmission spectra of the as-deposited and oxidized films are shown in figure 3.25. The band gap values of the films were calculated from the extrapolated intercept of the straight-line portion of \((\alpha h\nu)^2\) against \(h\nu\) plot on to the energy axis (see section 2.3.5) as shown in the inset of Fig. 3.25. The chemical bath deposited ZnS films have a band gap of 3.75eV and EBE-ZnS has a band gap of 3.42eV. The ZnS film shows a band gap of 3.23eV after the thermal oxidation.

![Graph showing transmission spectra](image)

**Fig.3.25** Transmission spectra of the CBD ZnS as deposited and after oxidation. The inset shows the respective \((\alpha h\nu)^2\) against \(h\nu\) curves

The CBD ZnS films in the present study showed an average transmission less than 50% in the visible region, which is less compared to the EBE ZnS (see section 3.15.2). The ZnO films obtained by the thermal oxidation of these ZnS films showed an average transmission above 55% in the visible region indicating that the thermally converted ZnO is more transparent compared to the as-deposited films. Better transparent ZnO film may be
obtained if more transparent ZnS films are used for oxidation. The SEM micrograph of the ZnO film prepared by the thermal oxidation technique was rather rough and has micro pores (Fig. 3.26). The roughness may be the reason for the reduced transmission of ZnO films prepared by the thermal oxidation of CBD ZnS films.

The chemical bath deposited ZnS films show a high resistivity of $6.6 \times 10^6 \, \Omega \text{cm}$. The resistivity of these films reduced considerably to $1.05 \times 10^4 \, \Omega \text{cm}$ after the thermal oxidation to ZnO. The high resistivity of the thermally converted ZnO films implies that films are nearly stoichiometric. The ZnO films prepared without any intrinsic or extrinsic dopants will show a very high resistivity [107]. The ZnO films prepared by the thermal oxidation of CBD ZnS films might be having very low lattice defects such as oxygen vacancies or zinc interstitials, which accounts for the high resistivity of these films.

![SEM micrographs of ZnO thin film prepared by the thermal oxidation of CBD ZnS.](image)

**3D.5 Conclusion**

ZnO thin films with hexagonal wurtzite structure was prepared by the thermal oxidation of the chemical bath deposited ZnS thin films. The air annealing of the samples at 800°C for one hour resulted in the complete
conversion of the ZnS to ZnO, which was confirmed by the XRD and EDX measurements. The physical process of oxidation of the CBD ZnS was compared with that of EBE ZnS and ZnS powder using the XRD studies. The high electrical resistivity ($1.05 \times 10^4 \, \Omega \text{cm}$) of the converted ZnO indicates an intrinsic growth of the ZnO film. The ZnO films showed an average transmission above 55% in the visible region and an optical band gap of 3.23eV.
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