4.1 Introduction

Cadmium sulfide (CdS) is a semiconducting material used in a variety of applications. The wide band gap, low absorption loss, compact crystallographic cell structure and electronic affinity makes CdS a promising opto-electronic device for making solar cells with CuInS$_2$ (CIS), CuInSe$_2$ (CISe), InP [1]. Thin films of CdS have received considerable attention towards other device applications such as electrochemical cells [2], gas sensors [3], and metal-Schottky barrier cells [1]. It is mainly used as an optical window material. Nanoparticles of CdS doped with other semiconductor materials working as photo sensor detection [4].

Thin films of CdS can be grown by chemical and physical methods such as chemical bath deposition (CBD)[5–14], spray pyrolysis [15–16], electrodeposition [17, 18], solution growth [19], Sol-Gel [20], successive ionic layer of adsorption and reaction (SILAR) [21, 22], vacuum deposition [23–26], sputtering [27], sintering [28], sublimation [29], molecular beam epitaxy [30, 31] etc,. Among these methods, CBD is found to be inexpensive as well as the simplest method to deposit large area thin films.

In the present work, we have prepared the CdS thin films on to the glass substrate by chemical bath deposition (CBD) method at 80 °C temperature. Preparative parameters such as concentration of cationic and anionic precursor solutions, pH of the solution, temperature, complexing agent and deposition time are optimized to get homogeneous, large area deposition with good quality adherent and uniform thin films. The as-deposited CdS thin films were characterized for their structural, surface morphological, optical, electrical properties, and photosensitivity of the films.
4.2 Chemical Bath Deposition Technique

4.2.1 Experimental set-up

Fig. 4.1 Schematic diagram of experimental set-up for the chemical bath deposition technique [Lab setup].

Fig 4.1 shows the schematic diagram and photograph of experimental set-up for the deposition of thin films by chemical bath deposition technique. It consists of water bath, chemical reaction bath, and constant speed motor cum regulator, substrate and substrate holder. For maintaining the temperature of the main reaction bath, it was kept into the water bath. For getting uniform deposition throughout the substrate, a magnetic stirrer was kept into the main reaction bath and continuously stirred the solution throughout the deposition time. The glass slides were used as a substrate. For maintaining the pH, the pH electrode was inserted into the reaction beaker for pH measurement.

Ph. D. Thesis submitted by Mr. Jagannath Babu Chaudhari
4.2.2 Reaction bath

A 250 ml glass beaker (Borosil make) with the mixture of chemical reactants serves as the chemical bath. It is immersed in the constant temperature water bath as shown in Fig. 4.1, whose temperature can be controlled. The chemical reactants containing solution is stirred by magnetic stirrer.

4.3 Preparation of CdS Thin Films

4.3.1 Substrate cleaning

In chemical bath deposition technique, substrate has adverse effect on the characterization of material deposited. The contamination can give rise to the unexpected results leading to the output in unidentified way. So this can be avoided by thoroughly cleaning the substrate. The glass slides of the dimension 7.3 cm x 2.5 cm x 0.2 cm have been used as the substrates. The following procedure has been used for cleaning of the substrates.

- The slides were washed with water.
- Boiled in concentrated chromic acid (0.5M) for 1h and kept in it for 24 h.
- Again washed with double distilled water.
- Finally, the substrates were dried, degreased in AR grade acetone and were kept in dust free airtight container.

4.3.2 Preparation of solutions

Chemicals used for preparing CdS films were as follows:

- A. R. grade cadmium chloride [CdCl₂].H₂O was used as a cationic precursor solution,
- For maintaining the pH of the precursor solution ~ 11.5, 25% concentrated NH₃ solution was used.
• Thiourea (CS)[NH₂]₂ was used as anionic precursor solution supplied by Loba Chemie, Mumbai.

All solutions were prepared in deionized water.

4.3.3 Volumetric reactions for CdS formation

Volumetric calculations of reactants were made for CdS deposition; 20 ml of 0.1M cadmium chloride and 0.1M thiourea were taken. The pH of the resultant mixture was kept ~ 11.5 by the addition of aqueous ammonia with the constant rate (2 ml/min) and constant stirring. The temperature of the reaction bath was maintained at 80±5°C.

4.4 Characterization of CdS Thin Films

4.4.1 Film thickness

The film thickness measurement of CdS thin films were carried out by interferometer technique as explained in section 3.1 of chapter 3. Thickness of film was found to be ~320 nm for deposition time of 120 min.

4.4.2 X-ray diffraction

The X-ray diffraction method is useful for structural investigation as well as for the calculation of interplanar distance ‘d’. The XRD studies were carried out using Bruker AXS Germany, D8 Advanced X-ray diffractometer (Cu-Kα radiation; λ = 1.5405 Å). The X-ray diffractometer was operated at 40kV, 100mA. XRD data analysis was done by using JCPDS and compared with the results reported by various researchers.

4.4.3 Energy dispersive X-ray analysis (EDAX)

The elemental composition of the thin film has been obtained by using EDAX spectrum. The as deposited thin film was characterized by EDAX using JEOL-JSM 5600.
4.4.4 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) has been proved to be a unique, convenient and versatile method to analyze surface morphology of a film and to determine the grain size. The surface morphology of the film was studied by scanning electron microscopy (SEM) (Model: JEOL–JSM–5600)

4.4.5 Optical analysis

A double beam spectrophotometer (Perkin Elmer UV–VIS spectrophotometer Lambda 25 with automatic computer data acquisition) was employed to record optical spectrum over the wavelength range of 350–850 nm, at normal light incident.

4.4.6 Electrical analysis

4.4.6.1 Electrical resistivity

The two probe method was used to study the variation of resistivity with temperature. The experimental setup is schematically shown in Fig. 3.6 of section 3.6. The thin film of size $1 \times 1$ cm$^2$ deposited on the glass substrate is used for the resistivity measurement. Silver paste was applied for making the good ohmic contacts to the film. A mica sheet was used between the film and the brass plate to provide the insulation.

4.4.6.2 I–V characteristics

The room temperature resistivity was measured from I-V characteristics (Lab equipment unit {model no. 2004} interfaced with computer), the voltage applied over the range ±3V. Silver paste was employed to ensure good ohmic contacts with the films. Photosensitivity property of CdS films were studied by I-V curves in dark and under illumination with in visible range.
4.5 Result and Discussions

4.5.1 Reaction process and growth mechanism

The solution chemistry involved in the deposition of CdS thin films takes place by the process of hydrolysis in alkaline medium. The formation of a solid phase from a solution involves two steps; as nucleation and particle grown. The size of the particles of solid phase is dependent upon the relative rates at which the two competing process takes place. It also depends on temperature, rates of mixing reagent, concentration of reagent and solubility of the precipitate during precipitation.

For precipitate, there is some minimum number of ions and molecules required to produce a stable second phase in contact with solution called a nucleus. The rate of formation of nuclei in a solution depends on the degree of supersaturation. The growth of the particles begins when nuclei or other seed particles are present.

The formation of solid CdS phase in the aqueous medium takes place as follows:

\[
\begin{align*}
\text{NH}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{Cd}^{2+} + 4\text{NH}_3 & \rightarrow \text{Cd}\left(\text{NH}_3\right)_{4}^{2+} \\
\left(\text{NH}_2\right)_2\text{CS} + \text{OH}^- & \rightarrow \text{CH}_2\text{N}_2 + \text{H}_2\text{O} + \text{HS}^- \\
\text{HS}^- + \text{OH}^- & \rightarrow \text{S}^{2-} + \text{H}_2\text{O}
\end{align*}
\]

(4.1) (4.2) (4.3) (4.4)

Perfect crystalline nuclei appeared on the substrate in the early stage of CdS deposition under the effects of thermodynamics, dynamics and chemistry factors which coalescence to form the final CdS film. Fig. 4.1 shows the formation of CdS films. The crystalline nuclei deposited on the substrate, which was grown and coalescence with NH$_3$ released from Cd(NH$_3$)$_4^{2+}$ and S$^{2-}$, combined to form the final CdS film. The reaction was described as follows [32].

\[
\text{Cd(NH}_3\text{)}_{4}^{2+} + \text{S}^{2-} \rightarrow \text{CdS} \downarrow + 4\text{NH}_3\uparrow
\]

(4.5)
The deposition process is based on the slow release of Cd\(^{2+}\) and S\(^{2-}\) ions. The amount of sulfide ions in the bath is controlled through setting up of appropriate chemical equilibrium, i.e., by adjusting properly the bath parameters and considering the solubility product.

### 4.5.2 X-ray diffraction (XRD)

The X-ray diffraction pattern for CdS thin film shows in Fig. 4.2. The XRD pattern reveals polycrystalline nature of as-deposited material. The diffraction peaks at 2\(\theta\) = 26.67\(^0\), 28.33\(^0\) and 48.09\(^0\) are attributed to (002), (101) and (103) planes, respectively of hexagonal CdS, as can be seen in comparison with the JCPDS Card No. 80-0006. It has been argued that the ion-by-ion process (heterogeneous reaction) results in compact film. The crystallographic phases of samples are in good agreement with the typical hexagonal wurtzite structure.

The lattice constants ‘\(a\)’ and ‘\(c\)’ are obtained from the X-ray analysis using the following relationship for hexagonal crystal [22],

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]

(4.6)
where \( h, k, l \) are the miller indices and ‘\( d_{hkl} \)’ is the distance between the crystallographic planes.

The crystallite sizes (\( D \)) were calculated using the Scherrer’s formula from the full-width at half maximum (FWHM) (\( \beta \)) by using the relation,

\[
D = \frac{0.9 \lambda}{\beta \cos \theta} A^o
\]

(4.7)

The values give a range estimate of typical crystallite size, due to non uniformity of the size and mixed phase in the film [33]. The various structural parameters for CdS thin films are calculated using standard formulae and are systematically represented in table 4.1. The lattice parameters calculated matches very well with the standard values reported by other workers [34–36].

![XRD pattern of as-deposited CdS thin film](image)

Fig. 4.2 XRD pattern of as-deposited CdS thin film

<table>
<thead>
<tr>
<th>Composition</th>
<th>( 2\theta ) (deg.)</th>
<th>( d ) (( \AA ))</th>
<th>(hkl)</th>
<th>( a ) (( \AA ))</th>
<th>( c ) (( \AA ))</th>
<th>Crystallite size ( D ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>26.670</td>
<td>3.342</td>
<td>002</td>
<td>-</td>
<td>6.684</td>
<td>27.90</td>
</tr>
<tr>
<td></td>
<td>28.332</td>
<td>3.150</td>
<td>101</td>
<td>4.122</td>
<td>6.692</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48.098</td>
<td>1.892</td>
<td>103</td>
<td>4.122</td>
<td>6.692</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Various structural parameters calculated for CdS thin films.
4.5.3 Energy dispersive X-ray analysis (EDAX)

Quantitative analysis of the film was carried out using the EDAX technique to study stoichiometry of the film. The elemental analysis was carried out only for Cd and S. Fig. 4.3 shows EDAX spectrum of chemically deposited CdS thin films. It was significant to note that films deposited at optimized preparative parameters are nearly stoichiometric with average atomic percentage of Cd:S = 48.86: 51.14. There were some other peaks presents in the spectra, which might be due to oxygen (0.5keV), silicon (1.75keV) and some other peaks due to calcium, sodium, magnesium etc. The extra peaks arise due to the presence of these elements in amorphous glass substrate [37].

![Typical EDAX spectrum of CdS thin film.](image)

4.5.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) has been proved to be a unique, convenient and versatile method to analyze surface morphology of a film and to determine the grain size. The as-deposited film has been found to exhibit a uniform, homogeneous and granular morphology covering entire substrate surface. All the grains are almost spherical in shape (nanocrystalline) with the average grain size ~90–100 nm. The film
grown as a hexagonal wurtzite structure with the (002) plane parallel to the substrate surface and the c-axis perpendicular to the substrate [38].

Fig. 4.4 SEM image of CdS thin film at different magnifications.

4.5.5 Optical analysis

In order to study the nature of the electronic transitions for the as-grown CdS thin films, optical absorption was studied. Fig. 4.5 shows the optical absorption spectra for the as-grown CdS thin films. This spectrum reveals that CdS thin films have low absorbance in the visible region, which is a characteristic of CdS thin films.
The nature of the transition was determined using the Tauc’s relation,

\[ \alpha h\nu = A(h\nu - E_g)^n \]  \hspace{1cm} (4.8)

where ‘\( h\nu \)’ is the photon energy, and ‘\( A \)’, ‘\( n \)’ are constants. The exponent ‘\( n \)’ depends upon the type of transition and has values of 1/2, 2 and 3/2 for direct, indirect and direct forbidden transitions, respectively.

**Fig. 4.5** Plot of variation of absorbance versus wavelength for CdS thin film.

**Fig. 4.6** Plot of energy band gap \((\alpha h\nu)^2\) versus \(h\nu\) of CdS thin film.
To understand the onset of high photon energy corresponding to the direct band gap we plotted \((a \nu)^2\) versus \(\nu\) and is shown in Fig. 4.6. Extrapolating the straight-line portion of the plot of \((a \nu)^2\) vs \(\nu\) for zero absorption coefficient value gives the band gap, which is found to be 2.4 eV which is in good agreement with value reported earlier [39].

### 4.5.6 Electrical analysis

#### 4.5.6.1 Electrical resistivity

To study the electrical resistivity of CdS thin films, the dark resistivity measurement was carried out in the temperature range 323 to 423 K using D.C. two probe method. The measurement shows that the as-deposited CdS films have the resistivity of \(0.15 \times 10^3 \Omega\text{-cm}\) at 423 K.

The variation of \(\log \rho\) with \(1000/T\) is depicted in Fig. 4.7. It is observed that resistivity decrease with increase in temperature suggesting the semiconductor behavior of CdS. The activation energy for the as-deposited CdS films is calculated from slope of Fig. 4.7 and is found out to be 0.24 eV.

![Fig. 4.7 Plot of Log \(\rho\) Vs 1000/T for CdS thin film.](image)
4.5.6.2 I–V characteristics

To study the transport properties, we have calculated dark electrical resistivity of ‘as-deposited’ CdS thin film at room temperature. The dark electrical resistivity was carried out from the I–V characteristics curve and is shown in Fig. 4.8. From the plot the room temperature electrical resistivity was found out to be $0.83 \times 10^3 \ \Omega\text{-cm}$. The observed value of the resistivity is quite lower than the values reported earlier [40]. Usually, binary compounds like CdS, CdSe etc. are known to have hexagonal, cubic or mixed structures. But film form shows high conductivity due to close packing, where as the cubic modification or a mixture of the two shows poor conductivity [41]. On many occasion researchers have reported the high conductivity shown by CdS films as due to growth of the hexagonal phase [42].

4.5.7 Photo response

The as-deposited CdS thin films were used for the photo sensor studies. When the surface of the sample is illuminated with photons of energy greater than the optical band gap of materials, valence electrons get excited and jump across the forbidden energy gap and acts as a free charge carriers in the conduction band. This process produces ‘electron-hole’ pairs which results in enhancement of conductivity of material. The phenomenon is known as ‘photoconductivity’ or process is called as ‘photosensing’.

The photosensitivity property of CdS was studied by I–V curve in dark and under illumination with different light intensities. The distance between 60 watt bulb and sensor was varied to change the intensity of light. The change in intensity of light with respect to change in distance of lamp was standardizes by ‘Lux-meter’. Fig. 4.8 shows I–V plot of sample in dark and under illumination for intensities 600, 900, 1200 and 1500 Lux. In the surrounding of the incandescent bulb it generates heat and the excitement of electrons from valence band may also take place due to thermal energy. Therefore,
absorption of photons by the sensing material may result either in a quantum or thermal response.

In our results, current increases with change in voltage for different light intensities and the characteristic shows ohmic behavior. The dark resistivity of the sample shows $0.83 \times 10^3 \ \Omega\text{-cm}$ and it decreases to $0.615 \times 10^2 \ \Omega\text{-cm}$ for light of intensity 1500 Lux.

![Fig. 4.8 I-V characteristic of CdS film in dark and under illumination.](image)

For the photosensor characterization of the film, photosensitivity is an important parameter which calibrates directly the quality of the photosensor. The photosensitivity [43–45] is calculated by using the equation as,

$$S = \frac{I_{ph} - I_d}{I_d}$$

(4.9)

where, $I_d$ and $I_{ph}$ are the dark and photo currents respectively. It is concluded that the enhancement of the photoconductive sensitivity is due to the electron-hole pairs excited by the incident light [46–48].
Fig. 4.9 shows the plot of photosensitivity versus illuminated intensity. The photosensitivity shows linear response, this behavior is consistent with the increase in the number of free carriers in the semiconductor under illumination, as expected from optical properties [45, 47].

**Fig. 4.9 Photosensitivity versus light intensity for CdS thin films**

Many of the researchers have reported the photosensitivity depends on the molar concentration of cationic and anionic precursor and it is also affected by concentration of NH₃, Triethanolamine (TEA), annealing temperature and deposition techniques [48-51].
References


