Chapter - IV

GROWTH AND OPTICAL CHARACTERIZATION OF CdS THIN FILMS
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4.1 Introduction

Thin films of CdS have been grown onto suitably clean glass substrates by chemical bath deposition (CBD) technique. CBD is an "electroless" technique that is attractive as a simple, low cost deposition method and also promising for large area film deposition. CBD is also a useful method for obtaining CdS thin films as a buffer layer in a window of thin film solar cell, because, it is inherently a low temperature process which does not damage the surface of the deposited thin film as an absorber during deposition and can be applied to rough one. Although the CdS polycrystalline films grown by CBD method have a poor crystalline quality, as compared with CdS films grown by other techniques, they have shown to be the most suitable for CdTe-based solar cells as the maximum efficiency of 16.5% has been achieved with a window layer grown by the CBD technique [1]. Again one of the advantages of CBD is that the films can be deposited nearly on all substrates [2]. However, as it is well known, the mechanical properties and the adherence of the films are influenced also by the substrate material. The method is widely used for the growth of CdS film for various applications and has been reported by various workers from time to time [3-26].

However, depending on starting material, complexing agent used, bath composition and bath parameters (deposition time, temperature, pH etc.) film quality, structure, morphology, electronic and optical properties etc. may be
different. In this chapter, growth of CdS thin films by CBD technique and their characterization have been discussed.

4.2 Growth of CdS thin film by chemical bath

Due to toxicity and suspected carcinogenic activity of many cadmium containing compounds [29], all experiments were performed under carefully controlled conditions. All reagents were selected as analytical grade or of better quality. Films were deposited onto suitably cleaned microscopic glass slides (Blue Star Deluxe, Mumbai) and described below.

4.2.1 Chemical Bath Deposition

Chemical bath deposition technique is based upon the controlled precipitation reaction of an insoluble salt. It is the analogue in liquid phase of the well-known chemical vapour deposition technique in the vapour phase. In CBD, the deposition of thin films takes place from aqueous solutions at low temperatures by a chemical reaction between dissolved precursors, with the help of a complexing agent. Several complexing agents have been utilized in the deposition of CdS, such as NH₃, tri-ethanol-amine (TEA), ethylenediamine, nitrilo-triacetic acid (NTA), cyano-complex, citrato-complex, tartaric acid etc.

In our case, tetra-amine complex method has been used by adding NH₃ solution as complexing agent for growth of CdS thin film because of advantage of proper adhesion to the substrate at higher bath temperatures also. The solution was prepared by mixing 0.001 M CdI₂, 0.0075 M TU, 0.005 M NH₄Cl in de-ionized water in 100 ml volumetric flask. (As determined by our earlier worker [30]). The variation of growth temperature was also studied in our case. Films
were grown up to a maximum temperature of 80°C from room temperature. The bath temperature of 60°C was fixed for better growth of the films. The effect of pH variation was also studied by varying the pH value from 9 to 12 by adding NH₃ solution. The optimum value of pH of the solution was found to be 11.5 and a deposition time of two hours had been found to be suitable for better adhesion and good quality film.

The experimental arrangement together with the prepared films are shown in Fig. 4.1 & Fig. 4.2 respectively.

The chemical reaction taking place for the growth of the films in tetra-amine complex method can be considered as follows:

\[
\begin{align*}
\text{CdI}_2 &\rightleftharpoons \text{Cd}^{2+} + 2\text{I}^- \\
\text{Cd}^{2+} + 4\text{NH}_3 &\rightleftharpoons [\text{Cd(NH}_3)_4]^{2+} \\
[\text{Cd(NH}_3)_4]^{2+} + \text{SC(NH}_2)_2 + 2\text{OH}^- &\rightarrow \text{CdS} + 4\text{NH}_3 + \text{CO(NH}_2)_2 + \text{H}_2\text{O} \quad \text{(4.1)}
\end{align*}
\]

The properly pre-cleaned substrates were dipped into the prepared solution for two hours and were then removed from the solution. The deposited films along with the substrates were then rinsed properly by double distilled water and allowed to air dry and then kept in a desiccators for further experimental work.

For growth of thicker film, double deposition of the film after the first deposition was found to be effective. This is because of catalytic activity of the first deposit in which nucleation process has begun on the substrate. Thus it generally becomes easier for the film to grow over the first deposit, which has been nucleated on the clean glass surface. Similar result has been reported by other workers in CBD CdS films [31].
Fig. 4.1: An experimental set up for chemical bath deposition of Cadmium sulphide thin films (a) at the beginning of the reaction (b) at the end of the reaction.
Fig. 4.2: (a) CdS thin films on glass substrate.
(b) Arrangement for sample preservation after preparation.
4.2.2 Etching of the films

In order to make the films free from colloidal particles of CdS adhering to the substrate and organometallic impurity of the chemical used for the film deposition, the substrates were kept in 2% acetic acid solution for 5 minutes and then rinsed with distilled water. It is seen that there is not appreciable variation in film thickness after etching.

4.2.3 Adhesion test

The prepared films were also tested for their adhesion to the substrates by "Scotch Tape" method. No peeling off the films from the substrates occurred, which indicated proper adhesion of the CdS films to the glass substrates.

4.2.4 Thickness measurements

Thickness of the prepared films was measured by Gravimetry method using high precession electronic microbalance (AB 54-S, METTLER TOLEDO) available at XRF laboratory of Deptt. Of Instrumentation & USIC, G.U.

According to Gravimetry method the film thickness can be calculated as

\[
\text{Thickness (t)} = \frac{M}{\rho A}
\]

Where \( M \) = mass of the deposited film, \( \rho \) = density of CdS and \( A \) = area of film. The mass of the film was obtained by measuring its weight before and after deposition. The value of \( \rho \) (density) for CdS thin film = 4.87 g/cc, was determined from the measurement of lattice parameter as described in section 4.3.1 (b).
4.3 Various characterization methods

For characterization of the CdS thin films the following techniques were employed.
(a) Characterization by X-ray optics.
(b) Characterization by optical absorption spectroscopy.
(c) Characterization by optical emission spectroscopy (Photoluminescence).
(d) Morphological characterization.

4.3 (a) Characterization by X-ray optics

The crystal structure identification and grain size determination of the films were carried out by using X-ray Diffraction (XRD) recorded by PANALYTICAL X'PERT PRO automated powder X-ray diffractometer, available at the Deptt. Of Instrumentation & USIC of Gauhati University. The source of radiation used in the diffractometer was monochromatic Cukα (λ = 1.542 Å) radiation. A Nickel filter was used to block the Kβ radiations. The operating voltage of the X-ray tube was 40 KV - 30 mA. The data obtained from the diffractogram were analysed by suitably suppressing (smoothening) the noise level by using origin graphic software (version 6.0). Prior to each observation, the diffractometer was calibrated by using standard silicon sample. For XRD studies films of suitable size (25 mm × 25 mm) were prepared during solution growth process.

Structural studies by XRD have shown the formation of CdS film of cubic zinc blende structure (spheletite) with three diffraction peaks corresponding to (111), (220) and (311) plane of cubic phase. The peaks are found to be broad, superimposed on an amorphous background due to glass substrate. The small
broad peak arises due to smaller grain size of the film. Some contribution due to strain and instrumental broadening may also affect the peak broadening.

Fig. 4.3 (a, b, c) show three different diffractograms of as grown CdS thin film observed at different pH value prepared from one single deposition process. It is seen that crystalline nature of the films improves as pH of the solution increases by adding dilute NH$_3$ solution.

Fig. 4.3 (a) shows the XRD pattern of a CdS thin film within the 2θ range of 15° to 80°. For this film, grown at pH value 10, a small peak appears at 2θ = 26.3069 corresponding to (111) plane of cubic (β CdS) phase. Other peaks corresponding to (220) and (311) hkl plane of cubic phase are not prominent for this film. At this value of pH (10) of the solution, two small peaks of 2θ values of 24.80 and 27.79 corresponding to (100) and (101) hkl plane of hexagonal phase appear in the diffractogram showing the tendency of mixed phase growth. Such
mixed phase in chemically deposited CdS thin films have also been reported by other workers [3, 4, 13, 30] also. Besides predominantly cubic phase of CdS sample, some extra peaks probably due to CdO phase and of starting material (CdI₂) are also identified in the XRD pattern. Since II-VI material - CdS exposed to air are prone to oxidation, some peaks may be due to CdO phase, as samples were recorded in ambient condition. Similar results have also been reported in CdS film and nanocrystalline film [36].

It is also seen from all the diffractograms that before etching of the films, at 2θ < 20°, a prominent additional peak appears which may be due to some organic or organometallic compounds present in the overgrowth of the film surface arising from the chemicals used. Similar observation in chemically deposited CdS thin film was reported by various other workers [32, 33].

As the pH value of the solution is gradually increased to 11 [Fig. 4.3 (b)], crystalline nature of the film increases and is evident from increase of peak height. At this value of pH, peaks corresponding to (220) and (311) hkl plane of cubic phase also become prominent. Further increase in pH value to 11.5 [Fig. 4.3 (c)] shows that all the peaks corresponding to (111), (220) and (311) hkl plane of cubic phase become prominent showing polycrystalline growth of the film having different orientations parallel to the substrate.

Fig. 4.4 shows the XRD pattern of the CdS film of Fig. 4.3 (c), after etching the film in dilute acetic acid. It is seen from the diffractogram that the additional peaks now disappear; indicating that the overgrowth impurities are removed by etching the film. Thus XRD observation shows that etching of the film is essential step for chemical bath deposition of CdS film. The peak positions of the film are found to be in good agreement with JCPDS (file 10 - 454) data showing the
formation of cubic phase in the CdS film. It was found that when the pH value was 12 or more, the crystallinity of the film deteriorated (not shown in the Fig.). Similarly at lower value of pH (below 10), no prominent peaks were observed and films were of mainly amorphous nature probably due to poor adhesion and smaller thickness. Thus it is seen that pH plays an important role in the process of film formation. The pH controls the rate of reaction and thus affect the growth of the film.

1. **Grain size**

For calculation of mean grain size of the deposited films, Scherrer formula [34, 35] was used and is given by equation (4.2).

$$D_{hk\ell} = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (4.2)

The full width at half maxima ($\beta$) was calculated using Origin graphic software (6.0 version), which was subsequently corrected for the instrument
related broadening as mentioned earlier in Chapter-II. Figs. 4.5 to 4.7 show the zoomed peaks of XRD spectra corresponding to (111) plane of cubic phase of CdS films represented in figures 4.3 (a, b, c) respectively. The calculated apparent grain size after correction in our deposited CdS films lies between (11 to 13 nm).

Fig. 4.5 : Determination of FWHM by zooming the peak position of fig. 4.3 (a)

Fig. 4.6 : Determination of FWHM by zooming the peak position of fig. 4.3 (b)

Fig. 4.7 : Determination of FWHM by zooming the peak position of fig. 4.3 (c)
It is seen that the grain size increases as the pH value of the solution increases from 10 to 11.5, probably due to the increased thickness of the films within this range of pH value. Similar result has been reported by other workers also [37]. The small grain size of our samples indicates that the deposition process was dominated by ion-by-ion deposition [38, 39, 40]. The values of the calculated grain size along with other values of bath parameters for different films are shown in Table 4.1.

Table 4.1
Calculated grain size of various films using Scherrer formula.

<table>
<thead>
<tr>
<th>Film No.</th>
<th>pH value</th>
<th>Thickness (nm)</th>
<th>Bath temperature (°C)</th>
<th>2θ (Degree)</th>
<th>FWHM (radian)</th>
<th>Cosθ</th>
<th>Grain size D_hkl (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS_1</td>
<td>10</td>
<td>625</td>
<td>60</td>
<td>26.30</td>
<td>.0122</td>
<td>0.9737</td>
<td>11.67</td>
</tr>
<tr>
<td>CdS_2</td>
<td>11</td>
<td>683</td>
<td>60</td>
<td>26.74</td>
<td>.0115</td>
<td>0.9728</td>
<td>12.36</td>
</tr>
<tr>
<td>CdS_3</td>
<td>11.5</td>
<td>832</td>
<td>60</td>
<td>26.63</td>
<td>.0107</td>
<td>0.9731</td>
<td>13.28</td>
</tr>
</tbody>
</table>

2. **Lattice parameters and density**

As the CdS films prepared by us were found to be mainly of cubic phase, the lattice parameter 'a' has been calculated using the equation.

\[ a_{\text{cal}} = d \sqrt{h^2 + k^2 + l^2} \]  \hspace{1cm} (4.3)

Using the above equation, the lattice parameter obtained for various films are shown in table-4.2. Fig. 4.8 shows the Nelson Riley plot obtained for three different samples by plotting ‘a’ values against the extrapolation function.
\[ f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \]  \hspace{1cm} (4.4)

**Table 4.2**

Lattice parameter of CdS film from standard 'd' value and Nelson Riley Plot.

<table>
<thead>
<tr>
<th>Film No</th>
<th>PH</th>
<th>Hkl</th>
<th>Observed 'd' value (Å)</th>
<th>( \bar{a} ) (Å)</th>
<th>Average calculated 'a' (Å)</th>
<th>( \theta ) (degree)</th>
<th>( f(\theta) )</th>
<th>'a' from Nelson Riley plot (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS 2</td>
<td>11</td>
<td>111</td>
<td>3.3386</td>
<td>5.7826</td>
<td>5.7854</td>
<td>26.748</td>
<td>4.0737</td>
<td>5.7858</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>2.0446</td>
<td>5.7829</td>
<td></td>
<td>44.340</td>
<td>2.2445</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>311</td>
<td>1.7460</td>
<td>5.7908</td>
<td></td>
<td>44.340</td>
<td>2.2445</td>
<td></td>
</tr>
<tr>
<td>CdS 3</td>
<td>11.5</td>
<td>111</td>
<td>3.3516</td>
<td>5.8041</td>
<td>5.8074</td>
<td>26.634</td>
<td>4.0935</td>
<td>5.8052</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>2.0534</td>
<td>5.8063</td>
<td></td>
<td>44.18</td>
<td>2.2551</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>311</td>
<td>1.7523</td>
<td>5.8117</td>
<td></td>
<td>52.24</td>
<td>1.7999</td>
<td></td>
</tr>
<tr>
<td>CdS4</td>
<td>11.5</td>
<td>111</td>
<td>3.3634</td>
<td>5.8256</td>
<td>5.8227</td>
<td>26.528</td>
<td>4.1112</td>
<td>5.8200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>2.0579</td>
<td>5.8206</td>
<td></td>
<td>44.062</td>
<td>2.2629</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>311</td>
<td>1.7554</td>
<td>5.8220</td>
<td></td>
<td>52.162</td>
<td>1.8039</td>
<td></td>
</tr>
</tbody>
</table>

From the table, it is observed that the corrected values of the lattice parameters obtained from Nelson Riley plot by extrapolation of the line to \( \theta = 90^\circ \), are almost same as calculated average value. The parallel nature of the curves indicates that the systematic errors in our observation are almost absent. Further the values of the lattice parameters of CdS films obtained from our CBD technique is almost close to bulk value 5.83 Å [41]. The agreement of lattice parameter 'a' value for our cubic CdS films with standard value also shows the formation of stoichiometric CdS films by our CBD technique under optimized growth conditions. The error in calculation of lattice parameters of cubic CdS films by XRD technique in our case ranges between 0.17% to 0.75%.

From our observation, it is seen that the values of lattice parameter in our films are slightly smaller than the bulk value 5.83 Å. The slight decrease in the
value of lattice parameter from bulk value is expected to occur because of lattice contraction due to smaller crystallite size of nanometric range.

The density of the film is calculated by using the formula

\[ \rho = \frac{nM}{Na^3} \]  

Fig. 4.8: Nelson-Riley plots for three different representative CdS films grown at pH value a = 11, b = 11.5 and c = 11.5 respectively.
Where \( M \) is the molecular weight of CdS (144.464) [42], 'a' is the lattice parameter, \( N \) is the Avogadro's number \((6.02 \times 10^{23})\) and \( n \) is the number of molecules per unit cell which is 4 in our case as the deposited films are found to be cubic zincblende (FCC) structure. Putting these values we get the density of our CdS films to be 4.869 gm/cm\(^3\), which is in good agreement with that of the bulk value [43, 44].

4.3(b) **Characterization by optical absorption spectroscopy (Optical absorption and band gap estimation)**

The optical properties of semi-conducting material mainly depend upon band gap. The optical absorbance is a powerful method to determine the energy gap as well as optical properties of the sample. Precise determination of the optical energy gaps gives a clearer understanding of the optical transitions in thin films. CdS is the only material with a suitable band gap value of 2.42 eV, that fulfils the requirement of having both high optical transmittance and high optical absorbance within the visible spectrum of radiation.

Fig. 4.9 (a, b, c, d) show the absorption spectra of four representative CdS films prepared at different value of pH of the solution at 60\(^\circ\) bath temperature. The optical absorbance of the films were observed using double beam-automated spectrophotometer (HITACHI - U 3210) at room temperature available at Chemistry Department of Gauhati University. All the films exhibit absorption edges, which are blue shifted with respect to the bulk value 512 nm within the wavelength range (482.5 - 504.07) nm. The shift in absorption edge is a clear indication of quantum confinement effect observed in these nanocrystalline films [45].
Fig. 4.9 (a, b, c, d) : Absorption spectra of four different CdS thin films grown at pH value a = 10, b = 11, c = 11.5 and d = 11.5 after etching.

Fig. 4.9 (a) shows the absorption spectra of an as deposited CdS film grown at pH value 10. The optical absorption for this film is found to be less due to smaller thickness of the film. On the other hand the band edge at 482.5 nm shows the maximum blue shift due to smaller grain size of nanometric range, which is supported by XRD observation also.

Fig. 4.9 (b) shows the absorption spectra of an as deposited CdS film grown at pH value 11, with the band edge at 488.18 nm. Fig. 4.9 (c) shows the absorption spectra of an as deposited CdS film prepared under optimum growth condition with pH 11.5. The film shows good optical absorbance and sharp increase below its band edge wavelength 504.07 nm. As the film is un-etched and without
annealing, the absorbance is more as the colloidal particles present on the film surface also absorb light. Fig. 4.9 (d) shows the absorption spectra of the same film as shown in Fig. 4.9 (c), after etching with dilute acetic acid. It is observed that absorbance is now low as the colloidal particles are removed from the film.

From the above figures it is seen that the nature of the curves are similar, with absorption edge near about 500 nm and corresponds to band edge wavelength 510 nm for CdS film. Again it is clearly seen from the figures that the deposited CdS thin films acquire better crystalline nature with sharp rise in optical absorption in lower wavelength side when pH increases to 11.5. The strong absorbance of nanocrystalline CdS film can be utilized in the design of optical and optoelectronic devices.

The optical band gaps of the deposited CdS films have been calculated for direct transition from the optical absorbance data using the equation (4.6).

\[ \alpha h\nu = C_d (h\nu - E_g)^{1/2} \]  

(4.6)

Where \( C_d \) is a constant and \( E_g \) is the band-gap energy. The value of \( \alpha \) is obtained from relation

\[ \alpha = 2.3026 \left( \frac{A}{t} \right) \]  

(4.7)

Where \( A \) is the absorbance and \( t \) is the thickness of the film, which has been calculated as mentioned earlier. By plotting \((\alpha h\nu)^2\) versus photon energy \( h\nu \) from equation (4.6), for different CdS films, the direct band-gap has been obtained by extrapolation of linear portion of the curves to \( \alpha^2 = 0 \). The \( \alpha^2 \) value has been calculated within the wavelength range 350 nm to 600 nm, at an interval of 15 nm. The best fit curves of \( \alpha^2 \) versus \( h\nu \) for some representative films corresponding
to Fig. 4.9 (a, b, c, d) are shown in Figs. 4.10 (a, b, c, d) respectively. It is seen from the figures that as the pH value of the solution increases from 10 to 11.5, the band-gap value decreases from 2.57 eV to 2.46 eV, indicating that thinner films having higher band-gap value. Similar variation of band gap with film thickness has also been reported by other workers in CdS films [46, 47]. Fig. 4.10 (d) represents $\alpha^2$ versus $h\nu$ plot for the same film represented in Fig. 4.9 (c) after etching. It is seen that in case of the etched film, the value of band-gap decreases from 2.46 eV to 2.44 eV and agrees well with that of standard value for CdS, which is 2.42 eV [48, 49]. Similar value of band gap in cubic (zinc blende) type of CdS films grown by chemical bath deposition technique have been reported by Nakanishi et al [50].
The close agreement of band gap value to the bulk value of CdS suggest that the films prepared under optimum growth conditions are stoichiometric [51]. The stoichiometric nature of the films are supported by the close agreement of their cubic lattice parameter 'a' with the accepted lattice parameter value determined from XRD observations.

Again in one of the films, the band gap has been found to be 2.37 eV. This lower value of band gap of the film can be explained considering mainly the effect of impurities, strain, change in stoichiometry and excitonic transitions in the film. However, there might have been some contribution from the presence of the hexagonal phase along with the cubic phase. The lower value of band gap for CdS films have been reported by other workers also [52, 53].

Table 4.3 shows the calculated values of band gap for various films. From the table it is clearly seen that the band gap increase to higher value from its bulk value 2.42 eV. The increase in band gap is due to decreasing size of the crystallite and formation of nanocrystalline film. Such increase of band gap value in CBD nanocrystalline film has also been reported by other workers.

Table 4.3

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>PH of the bath</th>
<th>Temperature of bath (°C)</th>
<th>Post growth treatment</th>
<th>Band gap energy (eV)</th>
<th>Blue shift energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>10</td>
<td>60</td>
<td>Without etching</td>
<td>2.57</td>
<td>0.15</td>
</tr>
<tr>
<td>S2</td>
<td>11</td>
<td>60</td>
<td>Without etching</td>
<td>2.54</td>
<td>0.12</td>
</tr>
<tr>
<td>S3</td>
<td>11.5</td>
<td>60</td>
<td>Without etching</td>
<td>2.46</td>
<td>0.04</td>
</tr>
<tr>
<td>S4</td>
<td>11.5</td>
<td>60</td>
<td>After etching</td>
<td>2.44</td>
<td>0.02</td>
</tr>
</tbody>
</table>
4.3(c) **Characterization by optical emission spectroscopy (Photoluminescence)**

Photoluminescence (PL) spectra of CdS thin films were recorded using PL spectrometer (Aminco. Bowman Series 2, Model No. FA-357) available at IIT, Guwahati in the wavelength range 450 nm to 750 nm. All the films were excited by radiation of wavelength 250 nm, 275 nm and 300 nm respectively. Fig. 4.11 shows the typical emission spectra of a freshly prepared nanocrystalline thin film taken at temperature 300 K, in the wavelength range (440-500) nm. The excitation wavelengths are 250 nm, 275 nm and 300 nm respectively. It is seen that the pL peak intensity increases with increase of excitation wavelengths. Four peaks with corresponding peak positions at 450 nm, 467 nm, 481 nm & 492 nm respectively are observed. The peak positioned at 492 nm is close to the fundamental absorption edge for CdS (512 nm) and hence can be attributed to the band edge related recombination. The other three emission bands can be attributed to defect luminescence. It is observed that the fundamental absorption edge is blue shifted, which confirms the formation of nanocrystalline thin film in our CdS samples.

![Fig. 4.11](image-url): Emission spectrum of a CdS thin film prepared under optimum growth condition when excited by three different wavelength.
To examine stability of our samples, we recorded the PL data for different duration of storage up to 6 months. A typical result of PL emission in a representative sample following 180 days of storage has been shown in Fig. 4.12. No significant difference was noticed in the absorption edge as well as the other photoluminescence peak positions recorded for the fresh and the aged sample, indicating that the nanocrystallite in our sample is stable, not collapsing into bigger size, for which luminescence band is expected to be red shifted. The observed size stability of our sample is indeed a remarkable achievement of the present work. Similar results have been reported by other workers also [55].

![Emission spectrum of a CdS thin film](image)

**Fig. 4.12**: Emission spectrum of a CdS thin film prepared under optimum growth condition after 10 days and 180 days of aging.

### 4.3.4 Morphological characterization

The morphological characterization of the deposited films was performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

The SEM images of CdS thin films [Fig. 4.13 (a, b) and Fig. 4.14 (a, b)] prepared by tetraamine complex method under optimum growth condition show
Fig. 4.13: (a) Scanning electron micrograph of a representative CdS thin film with magnification 11.80 KX and grown under optimum growth condition.

Fig. 4.13: (b) Scanning electron micrograph of the film shown in Fig. 4.13 (a) with particle size.
Fig. 4.14: Scanning electron micrograph of two representative CdS thin films with magnification (a) 14.48 KX and (b) 7.02 KX.
that the surface of CdS is homogeneous with some large particles deposited on it. The particles are seen to be spherical and symmetrical. The top layer is seen to be containing isolated grains of CdS formed above a compact polycrystalline CdS layer. It is therefore concluded that the CdS films follow a multilayer growth pattern.

The SEM observation of the films indicates larger value of particle size (61.40 nm - 160.8 nm) as compared to XRD observation. This may be explained as XRD observation gives the value of average particle size including the amorphous phase. From the scanning electron micrographs it is also clearly observed that CdS films deposited by us are free from microscopic cracks and pinholes making them suitable for device applications.

The AFM images of the CdS thin films were taken using a molecular imaging microscope (Pico Scan 2500) available at IIT, Guwahati. All the images were taken in contact mode in order to evaluate surface roughness and grain size.

![AFM images of two representative CdS thin films grown under optimum growth condition.](image)

**Fig. 4.15 (a, b):** AFM images of two representative CdS thin films grown under optimum growth condition.
Typical morphologies of the CdS films grown under optimum growth conditions are characterized by compact and polycrystalline growth of CdS, which is supported by SEM observation also. It is evident from the micrographs shown in Fig. 4.15 (a, b) that the surface of the as grown CdS films is composed of single phased and dense grains having blurred grain boundaries. The individual grains in fact agglomerate to form clusters.

4.4 Conclusion

1. Good quality polycrystalline thin films having grain size in nanometric region have been prepared by chemical bath deposition (CBD) technique using tetraamine complex method. The optimum value of pH of the solution was found to be 11.5 and bath temperature 60°C for better growth of the films. Under optimum growth conditions films with better adhesion to the substrates were obtained for deposition time 2 hours. Etching of the films with dilute acetic acid removed the suspended colloidal particles and other impurities.

2. XRD characterization have confirmed the polycrystalline growth of CdS thin films having cubic zinc blende structure at optimum pH. Peaks corresponding to (111), (220) and (311) plane of cubic zinc blende phase are obtained at this optimum growth condition. The grain size of the films lies between (11 to 13) nm indicating nanocrystalline form. The lattice parameters of CdS films in found to be 5.83 Å almost close to bulk value. The density of deposited films is found to be 4.869 gm/cm³.

3. Optical absorption studies show that for CdS thin films, there is sharp absorption below 504 nm wavelength. The absorption also shifts to blue
region with decreasing grain size for thinner film. The band gap of the films is found to be direct and have value 2.79 eV for thinner film with smaller grain size and decreases to 2.46 eV for thicker films grown at optimum condition. Further the band gap also decreases to a value 2.44 eV after etching and is close to bulk value 2.42 eV.

4. Characterization of CdS thin films by photoluminescence (PL) show four peaks at wavelengths 450 nm, 467 nm, 481 nm and 492 nm respectively. The peak at 492 nm is close to band to band emission of electron-hole recombination. The other three emission bands can be attributed due to defects. The PL peak intensity increases with increase of excitation wavelength.

5. Optical absorption and PL studies show that absorption and emission wavelength does not shift even after ageing of the sample and indicates size stability. The close agreement of band gap value (2.46 eV), lattice parameter (5.83 Å), density (4.87 gm/cc) obtained from various characterization with those bulk value suggest that our CdS films are of stoichiometric nature.

6. The morphological characterization by SEM and AFM confirms the polycrystalline nature of growth. The top layer of CdS film is composed of some isolated grains formed above compact polycrystalline layer. The grain sizes obtained from SEM have larger value (61-160 nm) compared to XRD as it gives average value including the amorphous phase. Both SEM and AFM photographs show that films are free from crack and pinholes.
Reference


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50. pp. 171-178 in Ref. 3.