Chapter No. II

Preparation And Characterization Of CdS Thin Films
2.1 Introduction

Cadmium sulfide (CdS) belongs to group II and VI compound semiconductor material, which has been used in a photocell or light dependent resistor or cadmium sulfide (CdS) cell is a resistor whose resistance decreases with increasing incident light intensity. Synthetic cadmium pigments based on cadmium sulfide are valued for their good thermal stability in many polymers. It has useful properties for optoelectronics, being used in both photosensitive and photovoltaic devices. One simple use is as a photoresistor whose electrical resistance changes with incident light levels [1-5]. CdS thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. Wide band gap for CdS, $E_g = 2.4$ eV has been used as the window material together with several semiconductors such as CdTe, Cu$_2$S, InP and CuInSe$_2$ with 14 – 16% efficiency [6-11]. For the development of such optoelectronic devices, CdS thin films requires comprehensive optical characterization(11-19).

The preparation of Cadmium sulfide (CdS) thin films are made using an aqueous bath. Cadmium sulfide (CdSO$_4$) and Sodium thiosulphate (Na$_2$S$_2$O$_3$) were used as precursors with Ethylene Diamine Tetra acetic Acid (EDTA) as a complexing agent. The oxidation and reduction peaks were determined by Cyclic Voltammetry (CV) for the material deposited in thin film form. Deposited thin films of CdS were characterized by X-ray diffraction, Scanning Electron Microscopy (SEM), UV-VIS-NIR spectrophotometer, the surface wettability of the films are determine by measuring contact angle with water using (rame hart instrument) contact angle meter. The F.T. Raman spectrometer and Scanning Probe Microscope (SPM- Solver P 47, NT- MDT Russia) respectively.

2.2 Essential requirements

2.2.1 Substrate cleaning

Electrodeposition process needs an electrically conducting substrate for thin film deposition. In electrodeposition, substrate cleaning plays an important role in the deposition of thin films, which provides nucleation sites facilitating growth.
resulting into non-uniform films. Usually, metallic substrates like stainless steel, copper, and titanium are used. The conducting glass like fluorine doped tin oxide (FTO) coated glass substrates can also be used. The metallic substrates were cleaned mirror polished using zero grade polish paper, then substrates were washed with acetone and double distilled water. And the FTO coated glass substrates were cleaned with 10% HCl for 15 minute and then just before deposition.

2.2.2 Solution preparation

Electrolytic aqueous bath for Cadmium Sulfide (CdS) thin films were prepared by AR grade Cadmium sulphate CdSO₄, Sodium thiosulphate (Na₂S₂O₃) and Ethylene Diamine Tetra acetic Acid (EDTA).

Cadmium Sulfide (CdS) thin films are cathodically electrodeposited from aqueous solution containing,

(A₂) = 0.04 M CdSO₄ + 0.4 M Na₂S₂O₃ + 0.1 M EDTA.

(B₂) = 0.06 M CdSO₄ + 0.6 M Na₂S₂O₃ + 0.1 M EDTA.

(C₂) = 0.08 M CdSO₄ + 0.8 M Na₂S₂O₃ + 0.1 M EDTA.

2.2.3 Experimental set up

From Fig. 2.1, it consists of a conventional three-electrode system i.e. working electrode, counter electrode, reference electrode, bakelite holder, cylindrical glass container. Stainless steel substrate is used as working electrode having a dimensions 5 x 1 x 0.1cm³. The counter electrode is a high purity polished graphite plate of size 5 x 2 x 0.5cm³. The reference electrode is a saturated calomel electrode (SCE).

All components are washed in double distilled water. Electrolytic bath consists of solution of CdSO₄+ Na₂S₂O₃+ EDTA, in preparation 1:4:3. (EDTA) is a complexing agent.
2.3 Results and discussion

2.3.1 Reaction mechanism

The chemical reaction for the deposition of Cadmium sulphide films taking place could be considered as below,

Cadmium Sulfide dissolves in water and release Cd\(^{+}\),

\[ CdSO_4 = Cd^{+2} + SO_4^{-2} \]

The aqueous solution of Sodium thiosulphate forms,

\[ Na_2S_2O_3 + H_2O = 2Na^+ + S_2O_3^{-2} \]

\[ S_2O_3^{-2} + 2H^+ \rightarrow S + SO_2 + H_2O \]

\[ S + 2e^- \rightarrow S^{2-} \]

Cadmium ions, Cd\(^{2+}\), combine with S\(^{2-}\),

\[ Cd^{+2} + S^{-2} = CdS \]

Electrodeposition of CdS has been carried out from aqueous acidic baths. The CdS films were cathodically deposited from an aqueous solution containing Cadmium and sulphur ions. Jacobsen and Sawyer [20] reported that S\(_2\)O\(_3^{2-}\) ion is not stable in the acidic medium and decomposes into S and SO\(_2\) in the reaction, Deposition process is made to start due to application of deposition potential.
2.3.2 Cyclic Voltammetry

Fig. 2.2(a-c) shows the cyclic voltammograms recorded on stainless steel substrate from electrolytic solutions containing (a) 0.08M CdSO$_4$, (b) 0.8M Na$_2$S$_2$O$_3$ and (c) 0.08M CdSO$_4$ + 0.8M Na$_2$S$_2$O$_3$ + 0.1M EDTA, in order to find the suitable reduction potentials of CdSO$_4$, Na$_2$S$_2$O$_3$ and CdS. From figure the reduction and oxidation peaks are seen. The deposition potentials of CdSO$_4$, Na$_2$S$_2$O$_3$ and CdS were found to be -0.45 V/SCE, -0.55 V/SCE and -0.65 V/SCE respectively. The electrodeposition of CdS thin films were carried out at the deposition potential -0.8V/SCE for various deposition times. Yellow colored, uniform and stoichiometric CdS thin films were deposited onto stainless steel. In the volumetric proportion as 1:4:3 respectively. After the deposition, the films were washed with double distilled water and preserved in desiccators to avoid the oxidation[21,22]. The pH of the plating bath ranges between 9 to 10.

![Cyclic Voltammogram (CV) on stainless steel substrate in the solution containing (a) 0.08M CdSO$_4$ (b) 0.8M Na$_2$S$_2$O$_3$ and (c) 0.08M CdSO$_4$ + 0.8M Na$_2$S$_2$O$_3$ +0.1M EDTA.](image)
2.3.3 Structural analysis

Fig.2.3, 2.4 and 2.5 shows X-ray diffraction pattern of CdS thin films of (A₂)= 0.04 M CdSO₄ + 0.4 M Na₂S₂O₃ + 0.1 M EDTA, (B₂)= 0.06 M CdSO₄ + 0.6 M Na₂S₂O₃ + 0.1 M EDTA and (C₂)= 0.08 M CdSO₄ + 0.8 M Na₂S₂O₃ + 0.1 M EDTA, for different bath concentrations onto stainless steel substrate for deposition time (A₁= B₁ = C₁)=110 Sec. (A₂= B₂ = C₂)= 120 Sec. (A₃= B₃ = C₃) =130 Sec. All of the CdS samples shows similar XRD pattern. It means, growth of the films is in a particular direction. It reveals that the CdS films are polycrystalline with hexagonal crystal structure[23,24]. The structural identification of CdS film was carried out using XRD in the range of diffraction angle ‘2θ’ between 10⁰-100⁰. The observed ‘d’ values of XRD reflection were compared with standard ‘d’ values taken from the JCPDS data [25,26] and reported in Table 2.1.

We have observe the (110) plane of the X-ray diffraction profile of each sample to calculate the crystallite size of CdS thin films with the help of Sherrer’s formula [27]. As deposition time increases from 110 Sec. to 130 Sec, the crystallite size varies from 32.95 nm to 35.14 nm for (A₂) bath concentration, from 40.59 nm to 48.12 nm for (B₂) bath concentration and from 46.11nm to 65.97 nm for (C₂) bath concentration. The enhancement of crystallite size with deposition time is due to increase in thickness and growth mechanism in thin film [28], given in Table 2.2.

The Fig.2.9, Fig.2.10 and Fig.2.11 Variation of grain size, bandgap energy and crystallite size versus deposition time of CdS films for bath concentration (A₂), (B₂) and (C₂).
Fig. 2.3 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, \( (A_2) = 0.04 \text{ M CdSO}_4 + 0.4 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA} \) for various deposition times, \( (A_1^2, A_2^2 \text{ and } A_3^2) \)

Fig. 2.4 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, \( (B_2) = 0.06 \text{ M CdSO}_4 + 0.6 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA} \) for various deposition times, \( (B_1^2, B_2^2 \text{ and } B_3^2) \)

Fig. 2.5 X-ray diffraction pattern of as-deposited CdS thin film onto stainless steel substrate for bath concentration, \( (C_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA} \) for various deposition times, \( (C_1^2, C_2^2 \text{ and } C_3^2) \)
Table 2.1 Comparison of observed ‘d’ values with standard ‘d’ values of CdS thin film onto stainless steel substrate for bath concentration (A2), (B2) and (C2).

<table>
<thead>
<tr>
<th>Obs. No.</th>
<th>Standard ‘d’ values (Å)</th>
<th>Observed ‘d’ values (Å)</th>
<th>Refracting plane (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(A2)</td>
<td>(B2)</td>
</tr>
<tr>
<td>1</td>
<td>2.070</td>
<td>2.074</td>
<td>2.076</td>
</tr>
<tr>
<td>2</td>
<td>1.793</td>
<td>1.804</td>
<td>1.807</td>
</tr>
<tr>
<td>3</td>
<td>1.258</td>
<td>1.271</td>
<td>1.269</td>
</tr>
<tr>
<td>4</td>
<td>1.075</td>
<td>1.083</td>
<td>1.085</td>
</tr>
</tbody>
</table>

2.3.4 Optical absorption for band gap energy

Optical absorption in as-deposited and annealed CdS thin film is carried out in the wavelength range of 350-850 nm. Fig.2.6, Fig.2.7 and Fig.2.8 shows the plot of \( (\alpha h\nu)^2 \) versus \( h\nu \) of CdS thin film for bath concentration (A2)= 0.04 M CdSO4 + 0.4 M Na2S2O3 + 0.1 M EDTA, (B2)= 0.06 M CdSO4 + 0.6 M Na2S2O3 + 0.1 M EDTA and (C2)= 0.08 M CdSO4 + 0.8 M Na2S2O3 + 0.1 M EDTA.

In the present case the absorption coefficient \( \alpha \) was found to follow the relation [29]

\[
\alpha = \frac{A(h\nu - E_g)^n}{h\nu}
\]

(2.1)

where, \( A \) is a constant depending upon the transition probability for direct transition, \( n=1/2 \) or \( 3/2 \) depending on whether the transition is allowed or forbidden in the quantum mechanical sense, \( E_g \) is optical gap. Plots of \((\alpha h\nu)^2\) versus the photon energy \( h\nu \) for films of varying thicknesses are shown in Fig.2.6, Fig.2.7 and Fig.2.8. Linearity of the plots indicates that the material is of direct band gap nature. Extrapolation of linear portion of the graph to the energy axis at \( \alpha = 0 \) gives the band gap energy \( E_g \), which is found to be increased from 2.35 to 2.40 eV as deposition time decreases from 130 to 110 sec. [30].
Here, the lower value of $E_g$ is attributed to the creation of allowed energy states in the band gap at the time of film preparation, while the higher value of $E_g$ is accounted to the very small grain size of the film [31].

These values agree well with those reported in the literature for chemically deposited CdS[32]. The optical absorption studies show that the as deposited CdS thin films have decreasing band gap energy with increasing bath concentration, as given in table No 2.2.

These films exhibit ‘yellow shift’ in their optical spectra. Similar ‘yellow shift’ in band gap values for the films with smaller thickness and/or grain sizes has been reported for many chemically deposited chalcogenide films [33,34]. Nair et al [35] discussed thoroughly the effect of grain size on the optical bandgap of semiconductor thin films. The optical bandgap of semiconductors can be affected by the defects, charged impurities, disorder at the grain boundaries, stoichiometry as well as the three dimensional quantum size effects, which could increase the energy bandgap with the decrease of grain size [36].

![Graph](image)

Fig. 2.6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of CdS thin films for bath concentrations. $(A_2)$ for various deposition times, $(A_1^1, A_2^2$ and $A_2^3)$
Fig. 2.7. Plot of \((\alpha h \nu)^2\) vs. \(h \nu\) of CdS thin films for bath concentrations, \((B_2)\) for various deposition times, \((B^1_2, B^2_2 \text{ and } B^3_2)\)

Fig. 2.8. Plot of \((\alpha h \nu)^2\) vs. \(h \nu\) of CdS thin films for bath concentrations, \((C_2)\) for various deposition times, \((C^1_2, C^2_2 \text{ and } C^3_2)\)
### Table 2.2 Crystallite size, Grain size and Band gap energy of CdS thin films

<table>
<thead>
<tr>
<th>Bath concentration</th>
<th>Deposition Time (Sec.)</th>
<th>Crystallite size (nm)</th>
<th>Grain size (µm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A₂)</td>
<td>(A₁²)=110</td>
<td>32.57</td>
<td>2.14</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>(A₂²)=120</td>
<td>34.01</td>
<td>2.40</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>(A₃²)=130</td>
<td>35.14</td>
<td>2.73</td>
<td>2.35</td>
</tr>
<tr>
<td>(B₂)</td>
<td>(B₁²)=110</td>
<td>40.59</td>
<td>2.30</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>(B₂²)=120</td>
<td>45.16</td>
<td>2.71</td>
<td>2.36</td>
</tr>
<tr>
<td></td>
<td>(B₃²)=130</td>
<td>48.12</td>
<td>3.14</td>
<td>2.33</td>
</tr>
<tr>
<td>(C₂)</td>
<td>(C₁²)=110</td>
<td>46.11</td>
<td>2.62</td>
<td>2.32</td>
</tr>
<tr>
<td></td>
<td>(C₂²)=120</td>
<td>51.03</td>
<td>3.01</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>(C₃²)=130</td>
<td>65.97</td>
<td>1.33</td>
<td>2.29</td>
</tr>
</tbody>
</table>

![Graph](image)

**Fig.2.9** Variation of grain size, bandgap energy and Crystallite size versus deposition time of CdS films for bath concentration, (A₂), for various deposition times, (A₁², A₂² and A₃²)
2.3.5 Surface wettability

An empirical diagnostic method for evaluation of thin film property is the measurement of water contact angle on its surface. Both super-hydrophilic and super-hydrophobic surfaces are important for practical applications [37-39]. Different amorphous or polycrystalline metal and oxide surfaces could be studied by wettability.
This behavior reveals that, the surface structure has a significant thermodynamic importance in contact angle measurement. With increase in film thickness, some of entrapping air centers newly produced with increased film thickness may lead to an increase in the water contact angle. CdS thin film exhibits Super hydrophilic nature.

Table 2.3 Bandgap energy, crystallite size, Grain size and contact angle of CdS thin films for different bath concentrations \( (A_2) \), \( (B_2) \) and \( (C_2) \) For 130 Sec. deposition time.

<table>
<thead>
<tr>
<th>Bath concentration</th>
<th>Crystallite size (nm)</th>
<th>Band gap energy (eV)</th>
<th>Contact angle (deg)</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (A_2) )</td>
<td>35.14</td>
<td>2.35</td>
<td>-</td>
<td>2.73</td>
</tr>
<tr>
<td>( (B_2) )</td>
<td>48.12</td>
<td>2.33</td>
<td>-</td>
<td>3.14</td>
</tr>
<tr>
<td>( (C_2) )</td>
<td>65.97</td>
<td>2.29</td>
<td>-</td>
<td>1.33</td>
</tr>
</tbody>
</table>

2.3.6 Surface morphology

The surface morphology of the electrodeposited CdS thin films was investigated by scanning electron micrographs. Fig. 2.10, 2.11 and 2.12. From the SEM images it is seen that small grain size are uniformly distributed over smooth homogenous background. The grain size increases by increasing concentration as well as time [40,41]. Shows the SEM image of as-deposited thin films at x10,000 magnification onto stainless steel substrate for various deposition times. The SEM image shows compact spherical grains. It is observed that the increase in deposition concentration shows a substantial granular growth.

The deposited CdS nanorods under optimized parameters such as concentration of \( (C_2) = 0.08 \text{ M CdSO}_4 + 0.8 \text{ M Na}_2\text{S}_2\text{O}_3 + 0.1 \text{ M EDTA, for deposition time, (C}^3_2) = 130 \text{ Sec.} \) It is our aim to deposit good quality, uniform, well adherent and nanocrystalline CdS nanorods onto low cost stainless steel substrate.
Fig. 2.10 SEM image of as-deposited CdS thin films onto stainless steel substrate for bath concentrations. (A_2). for deposition time, (A_2^1) = 110 Sec., (A_2^3) = 120 Sec. and (A_2^3) = 130 Sec.

Fig. 2.11. SEM image of as-deposited CdS thin films onto stainless steel substrate for bath concentrations, (B_2). for deposition time, (B_2^1)= 110 Sec., (B_2^2)= 120 Sec. and (B_2^3)= 130 Sec.

Fig. 2.12. SEM image of as-deposited CdS thin films onto stainless steel substrate for bath concentrations, (C_2). for deposition time, (C_2^1)= 110 Sec., (C_2^2)= 120 Sec. and (C_2^3)= 130 Sec.
2.3.7 Fourier Transform Raman (FT-Raman) spectroscopy

Fig. 2.13 shows the Raman spectra of the CdS thin films for different bath concentrations recorded between 125 to 350 cm$^{-1}$. Raman spectra of the films were collected on a combination system including research grade FTIR model VERTEX 70 with model- Ram- II FT Raman spectrometer equipped with Nd-YAG laser at 1064nm wavelength. The absorption at 175 cm$^{-1}$ agrees with the two Raman bands reported by Koh et al [42,43]. The Raman bands probably originate from the lattice mode vibrations. The Raman spectra of CdS thin film are as shown in Fig.2.13, sharp peak was observed at about ~175 cm$^{-1}$ for bath concentrations ($A_2$)= 0.04 M CdSO$_4$ + 0.4 M Na$_2$S$_2$O$_3$ + 0.06 M EDTA, ($B_2$)= 0.06 M CdSO$_4$ + 0.6 M Na$_2$S$_2$O$_3$ + 0.08 M EDTA. ($C_2$)= 0.08 M CdSO$_4$ + 0.8 M Na$_2$S$_2$O$_3$ + 0.1 M EDTA.

![Fig. 2.13 FT-Raman spectra of CdS films onto the stainless steel substrate for different bath concentrations. (A$_2$), (B$_2$) and (C$_2$). For 130 Sec. deposition time.](image)

2.3.8 FT-IR spectroscopy

FT-IR spectra were recorded on a spectrophotometer (Perkin Elmer FTIR Spectrum-GX), at laser power 0- 450 mW, the wave number ranging from 400-3000 cm$^{-1}$. FT-IR spectroscopy gives information about the vibration and rotation of molecular groups in a material which is mainly used to determine the concentration of the impurities and their bonding with the host material[44].
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The FT-IR spectra of CdS films are shown in Fig. 2.14 for bath concentration \((A_2) = 0.04\) M CdSO\(_4\) + 0.4 M Na\(_2\)S\(_2\)O\(_3\) + 0.06 M EDTA, \((B_2) = 0.06\) M CdSO\(_4\) + 0.6 M Na\(_2\)S\(_2\)O\(_3\) + 0.08 M EDTA. \((C_2) = 0.08\) M CdSO\(_4\) + 0.8 M Na\(_2\)S\(_2\)O\(_3\) + 0.1 M EDTA. The FT-IR bands are at around 659.55, 1017.27, and 1114.80 cm\(^{-1}\), 662.15, 1012.77 and 1144.36 cm\(^{-1}\), 663.17, 1006.41 and 1129.33 cm\(^{-1}\) [45-48].

![FT-IR Spectra of CdS](image)

Fig. 2.14 FT-IR spectra of CdS Thin film for different bath concentrations. \((A_2)\), \((B_2)\) and \((C_2)\). For 130 Sec. deposition time.
References

25. JCPDS data file No- 00-041-1049.
26. JCPDS data file No. 43-1471.
