CHAPTER-4

GROWTH AND CHARACTERIZATION OF STOICHIOMETRIC CdS THIN FILMS

This chapter presents the details of sample preparation and characterization of stoichiometric thin films cadmium sulphide (CdS). In this chapter, we present the detailed investigations on the characterization of CdS thin films during the course of research work. X-ray differection (XRD), UV-Visible spectroscopy, scanning electron microscopy (SEM) with EDAX, Atomic force microscopy (AFM), X-ray photoelectron spectroscopy and I-V measurements have been used to investigate the optical, structural, surface morphology, elemental composition and electrical studies of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.
CHAPTER 4
GROWTH AND CHARACTERIZATION OF STOICHIOMETRIC CdS THIN FILMS

4.1 Introduction:

Thin films of sulphide semiconductors are of great interest for their efficient use in the fabrication of many solid state devices. Cadmium sulphide is a very important II-VI semiconducting, optoelectronic [1,2] and piezo-electric [3,4] material. Cadmium sulphide is a direct band gap semiconductor (band gap 2.42 eV [5]) and yellow in color. The deposition technique and its associated growth parameters have a characteristic effect on the nucleation, growth-dominated microstructure and physical properties of the thin film.

Thin films of CdS are of considerable interest for their potential use in the fabrication of solar cells [6-11] and gas sensors [12-14]. A wide variety of techniques have been employed for the deposition of CdS thin films such as sputtering [15,16], molecular beam epitaxy (MBE) [17], chemical bath deposition [18-20], spray pyrolysis [21], thermal evaporation [22-26], flash evaporation [27], pulsed laser deposition [28] and dip coating technique [29]. Comparing with some other sophisticated techniques, vacuum thermal evaporation is very simple and inexpensive method which can be used for large area thin film deposition. The problem associated with this technique is maintaining the stoichiometry in the deposition of materials composed of elements having different vapor pressures such as Cd and S in CdS [30].

The structural, electrical and optical properties of vacuum deposited thin films of sulphide semiconductors are very sensitive to the deposition conditions [31]. Evaporated thin films of CdS are usually polycrystalline and have excess of cadmium owing to the dissociation of CdS during evaporation. Stoichiometry can be restored by several techniques as by, co-deposition of sulphur together with CdS [32] annealing the film in
CdS powder [33] and depositing the film in a controlled hydrogen sulphide atmosphere [34]. The deposition of sulphide semiconductors in a controlled H$_2$S ambient atmosphere yields better crystallinity, orientations and pin-hole free films, which would be of great importance in device fabrication.

The present chapter deals with the deposition of CdS thin films by evaporation of powdered CdS material without and with H$_2$S atmosphere under vacuum. The compensation the sulphur deficiency in vacuum evaporated CdS thin films deposited without H$_2$S atmosphere has been done by exposing the film to a hydrogen sulphide (H$_2$S) ambient atmosphere during deposition. The higher reactivity of hydrogen sulphide will ensure a better conversion of the dissociated cations (Cd ions) into compound sulphide semiconductors (CdS) and also will not produce any excess of sulphure at the substrate. From the point of view vacuum evaporation, the thermal decomposition of thiourea [CS(NH$_2$)$_2$] is a convenient source of hydrogen sulphide (H$_2$S) which can be controlled by regulating the temperature at the electrically heated borocil test tube in the evaporation chamber.

### 4.2 Sample Preparation:

In the present research work, the thin films of cadmium sulphide (CdS) have been deposited by thermal vacuum deposited technique onto highly cleaned glass substrates. For comparison, films of CdS are deposited without and with H$_2$S atmosphere. For sample preparation cadmium sulphide powder of AR grade of sigma Aldrich Company was used to evaporate in deep mouthed molybdenum boat. The deposition takes place in a vacuum of the order of $10^{-5}$ torr. Prior to deposition, the glass substrates were cleaned in aqua-regia, acetone, washed in distilled water and iso-propyl alcohol (IPA). H$_2$S atmosphere was obtained by controlled thermal decomposition of thiourea inside the vacuum chamber. For ambient atmosphere of H$_2$S a borosil test tube was used for the
thermal decomposition of \( \text{CS(NH}_2\text{)}_2 \) at 150ºC, it was separated from the CdS molybdenum boat by a stainless steel heat shield. Before deposition keeping the substrates at an elevated temperature of about 200ºC helps to eject any sulphur atoms deposited due to thermal decomposition of CdS during evaporation. The cadmium ions promptly recombined with the \( \text{H}_2\text{S} \) it give better stoichiometry of the deposited films. The general detailed summarized flow diagram of above used modified thermal vacuum deposition technique for deposition of stoichiometric sulphide semiconductors films has been discussed and illustrated in figure 2.5 of chapter 2 of the thesis.

**4.3 Sample Characterization:**

Thin films characterization is a main part of thin films process. The optical properties of as-deposited films especially optical energy band gap, nature of band gap and optical constants have been evaluated at room temperature by spectro-photometric examination. Structural analysis has been done by X-ray diffraction (XRD) patterns. The surface morphology was examined by scanning electron microscope (SEM) with EDAX and atomic force microscope (AFM). The elemental analysis for evaluation the stoichiometry of as-deposited films has been done by x-ray photoelectron spectroscopy (XPS). Electrical properties have been studied by measurement of I-V characteristics of the films using electrometer.

**4.4 Optical Properties:**

To define the optical properties, absorption and transmission spectra of vacuum deposited thin films of CdS both without and with \( \text{H}_2\text{S} \) atmosphere were taken at room temperature with the help of Hitachi spectrophotometer Model U- 3400 as shown in figure 4.1 and figure 4.2 respectively. The films deposited with \( \text{H}_2\text{S} \) atmosphere are more uniform, more adherent, pin hole free and have better crystallinity as has been inferred by the sharpness of absorption spectra. It can be seen that films produced in \( \text{H}_2\text{S} \), with the
good transparency of about 85% in the visible region, have somewhat steeper absorption edge than as-grow films, implying the good homogeneity in the distribution of the composition for the former. Also one can observe from transmission spectra (figure 4.2) the number of peak increasing in the films deposited with H₂S atmosphere.

4.4.1 Energy band gap:

To energy band gap of these films (for both without and with H₂S atmosphere) has been determined with the help of absorption spectra in the spectral range 350-850 nm as shown in figure 4.1. The Tauc relation is used to determine the energy band gap from the absorption spectra [35-37].

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

\( \alpha \) is the absorption coefficient, \( h\nu \) is photon Energy, \( A \) is a constant, \( E_g \) is the energy band gap of the film material and exponent \( n = \frac{1}{2} \) for allowed direct transition. Taking the logarithm of this Tauc’s equation, we have,

\[
\ln(\alpha h\nu) = \ln A + n \ln(h\nu - E_g)
\]

To measure of energy band gap from the absorption spectra a graph \((\alpha h\nu)^2\) verses \(h\nu\) is plotted. The extrapolation of the straight line to \((\alpha h\nu)^2=0\) axis gives the value of the energy band gap. Figure 4.3 and figure 4.4 shows the plot graph of \((\alpha h\nu)^2\) Vs \(h\nu\) for the vacuum deposited CdS thin film without and with H₂S atmosphere respectively. From these graphs the value of energy band gap of CdS without and with H₂S atmosphere comes out as 2.38 eV and 2.4 eV respectively. The band gap of the films prepared with H₂S atmosphere show good results then that without H₂S atmosphere. The value of \(E_g\) of CdS thin films deposited with H₂S atmosphere can then be used to calculate the value of \(n\) from the slope of plot of \(\ln(\alpha h\nu)\) vs \(\ln(h\nu-E_g)\) as shown in figure 4.5. The slope of linear
region of this plot comes out n value ~ ½, which indicated allowed direct transition in as-deposited CdS film material.

4.4.2 Optical Constants:

The optical constants of vacuum evaporated thin films of CdS have been determined by transmission spectra of these films by using Manifacier’s envelope method [38]. Both films deposited without and with H$_2$S atmosphere shows in general, good transparency exhibiting an interference patterns. The transmission spectra of CdS films deposited both without and with H$_2$S atmosphere in the wavelength range of 300-850 nm as shown in figure were used to determine the refractive index (n) and extinction coefficient (k) of as-deposited CdS thin films. The wavelength dependence of refractive index (n) and extinction coefficient (k) of the CdS films deposited both without and with H$_2$S atmosphere are calculated from the aforesaid expression as given in equation 4.3 and 4.4 respectively. The full descriptions of these equations are given in chapter 3 of the thesis.

\[
    n = \left[ N + (N^2 - n_0^2n_1^2)^{1/2} \right]^{1/2} \\
    k = (-\lambda/4\pi t)\ln P
\]

\[
    t = \frac{M \lambda_1 \lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)}
\]

The thickness of these films was measured by a spectrophotometric method using transmission spectra which is given by the equation.
Figure 4.1: Absorption Spectra of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.

Figure 4.2: Transmission Spectra of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.
**Figure 4.3:** Plot of \((\alpha h \nu)^2\) Vs \(h \nu\) for vacuum evaporated CdS film deposited without \(\text{H}_2\text{S}\) atmosphere.

\[\text{CdS without } \text{H}_2\text{S atmosphere} \quad \text{Eg}=2.38\text{ eV}\]

**Figure 4.4:** Plot of \((\alpha h \nu)^2\) Vs \(h \nu\) for vacuum evaporated CdS film deposited with \(\text{H}_2\text{S}\) atmosphere.

\[\text{CdS with } \text{H}_2\text{S atmosphere} \quad \text{Eg}=2.4\text{ eV}\]
Figure 4.5: Graph between \( \ln(h\nu-E_g) \) and \( \ln(\alpha h\nu) \) of vacuum evaporated CdS thin films deposited with H\(_2\)S atmosphere.

The thickness of CdS films deposited without and with H\(_2\)S atmosphere comes out 374 nm and 608 nm respectively. Plots of \( n \) and \( k \) versus \( \lambda \) for vacuum evaporated CdS films deposited without and with H\(_2\)S atmosphere are shown figure 4.6 and figure 4.7 respectively. It is seen that the CdS films deposited H\(_2\)S ambient atmosphere are dark orange color, uniform, pin hole free and have better adhesion to the substrate. Their transparency is also better than that of the films deposited without H\(_2\)S atmosphere. The thickness of CdS films grown in H\(_2\)S atmosphere is better than the CdS films deposited without H\(_2\)S atmosphere at the same deposition time. The given table 4.1 and 4.2 shows the variation of refractive index (\( n \)) and Extinction coefficient (\( k \)) with wavelength for CdS thin films deposited without H\(_2\)S atmosphere and with H\(_2\)S atmosphere respectively. It is seen that both the refractive index (\( n \)) as well the extinction coefficient (\( k \)) of the CdS film deposited with H\(_2\)S atmosphere are decreased as a result of better stoichiometry of the films deposited in H\(_2\)S atmosphere [39].
Table 4.1: Variation of refractive index (n) and extinction coefficient (k) with wavelength (λ) for CdS thin films deposited without H₂S atmosphere.

<table>
<thead>
<tr>
<th>λ(nm)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt;(%)</th>
<th>T&lt;sub&gt;min&lt;/sub&gt;(%)</th>
<th>N</th>
<th>n</th>
<th>k</th>
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<tr>
<td>550</td>
<td>54.560</td>
<td>42.300</td>
<td>3.219</td>
<td>2.463</td>
<td>0.0244</td>
</tr>
<tr>
<td>575</td>
<td>68.750</td>
<td>51.230</td>
<td>3.117</td>
<td>2.419</td>
<td>0.0495</td>
</tr>
<tr>
<td>600</td>
<td>71.210</td>
<td>53.850</td>
<td>2.983</td>
<td>2.358</td>
<td>0.0552</td>
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<td>625</td>
<td>72.320</td>
<td>55.650</td>
<td>2.868</td>
<td>2.305</td>
<td>0.0590</td>
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<td>650</td>
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<td>57.550</td>
<td>2.837</td>
<td>2.290</td>
<td>0.0656</td>
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<td>675</td>
<td>75.860</td>
<td>58.560</td>
<td>2.793</td>
<td>2.269</td>
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<td>700</td>
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<td>59.450</td>
<td>2.768</td>
<td>2.257</td>
<td>0.0736</td>
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<tr>
<td>725</td>
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<td>59.990</td>
<td>2.761</td>
<td>2.254</td>
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<td>750</td>
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<td>60.697</td>
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<td>2.256</td>
<td>0.0826</td>
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<td>79.750</td>
<td>61.364</td>
<td>2.752</td>
<td>2.249</td>
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<tr>
<td>800</td>
<td>81.050</td>
<td>62.080</td>
<td>2.756</td>
<td>2.251</td>
<td>0.0920</td>
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<td>825</td>
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<td>62.790</td>
<td>2.734</td>
<td>2.240</td>
<td>0.0962</td>
</tr>
<tr>
<td>850</td>
<td>82.041</td>
<td>63.360</td>
<td>2.703</td>
<td>2.225</td>
<td>0.0996</td>
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</tbody>
</table>

Table 4.2: Variation of refractive index (n) and extinction coefficient (k) with wavelength (λ) for CdS thin films deposited with H₂S atmosphere.

<table>
<thead>
<tr>
<th>λ(nm)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt;(%)</th>
<th>T&lt;sub&gt;min&lt;/sub&gt;(%)</th>
<th>N</th>
<th>n</th>
<th>k</th>
</tr>
</thead>
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<tr>
<td>550</td>
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<td>51.22</td>
<td>2.800</td>
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<td>0.0242</td>
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<tr>
<td>575</td>
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<td>53.56</td>
<td>2.718</td>
<td>2.232</td>
<td>0.0277</td>
</tr>
<tr>
<td>600</td>
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<td>56.84</td>
<td>2.698</td>
<td>2.223</td>
<td>0.0337</td>
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<tr>
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<td>58.71</td>
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<td>0.0414</td>
</tr>
<tr>
<td>675</td>
<td>77.240</td>
<td>61.12</td>
<td>2.649</td>
<td>2.198</td>
<td>0.0440</td>
</tr>
<tr>
<td>700</td>
<td>78.330</td>
<td>62.05</td>
<td>2.630</td>
<td>2.189</td>
<td>0.0468</td>
</tr>
<tr>
<td>725</td>
<td>78.960</td>
<td>62.49</td>
<td>2.626</td>
<td>2.187</td>
<td>0.0491</td>
</tr>
<tr>
<td>750</td>
<td>80.060</td>
<td>63.41</td>
<td>2.609</td>
<td>2.178</td>
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</tr>
<tr>
<td>775</td>
<td>81.770</td>
<td>64.699</td>
<td>2.593</td>
<td>2.170</td>
<td>0.0556</td>
</tr>
<tr>
<td>800</td>
<td>82.500</td>
<td>65.63</td>
<td>2.560</td>
<td>2.153</td>
<td>0.0582</td>
</tr>
<tr>
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<td>83.560</td>
<td>66.35</td>
<td>2.556</td>
<td>2.151</td>
<td>0.0612</td>
</tr>
<tr>
<td>850</td>
<td>85.310</td>
<td>67.36</td>
<td>2.562</td>
<td>2.154</td>
<td>0.0651</td>
</tr>
</tbody>
</table>
Figure 4.6: Variation of refractive index (n) with wavelength (λ) of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.

Figure 4.7: Variation of Extinction coefficient (k) with wavelength (λ) of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.
4.5 Structural Properties:

The crystallinity and phase of the vacuum evaporated CdS thin films deposited without and with H$_2$S atmosphere on glass substrates were characterized by X-ray diffraction (XRD) measurement using an x-ray diffractometer with CuKα radiation.

4.5.1 XRD:

The fact that X-ray have a wavelength of the order of angstroms, which is suitable for inter-atomic distances in solids, makes this technique an excellent instrument to investigate the crystalline structure of the materials. The XRD patterns of as-deposited samples were taken by Bruker D8 Advance X-ray diffractometer using the characteristic CuKα (1.5418 Å), lines of metal anticathode. X-ray diffraction patterns of the CdS thin films deposited on glass substrate without and with H$_2$S atmosphere with 2θ ranging from 20° to 80° are shown in figure 4.8. The XRD pattern (figure 4.8) revealed that the CdS/glass deposited with H$_2$S atmosphere had a strong and high intensity peak with 2θ value about 26.52° corresponds to the cubic (111) crystalline plane with cubic (222) peak at 2θ value about 54.67°and hexagonal (103) peak at 2θ value about 48.11°. While CdS/glass deposited without H$_2$S atmosphere had a strong and high intensity peak at 2θ value about 26.52° corresponds to the cubic (111) crystalline plane with low intensity hexagonal (103) peak at 2θ value about 54.2°, By comparison with the data from JCPDF cards No. 80-0019 and 80-0006. So, the XRD patterns depicts that the vacuum evaporated CdS/glass films deposited without and with H$_2$S atmosphere have cubic and hexagonal phase and are polycrystalline in nature. The crystallite size (d) has been estimated by using Scherrer formula [40].

$$b = \frac{k\lambda}{\beta \cos \theta}$$
Where $\lambda$ is the wavelength used ($\lambda=1.54 \text{ Å}$), $\beta$ is the full width half maximum (FWHM) in radians, $\theta$ is the Bragg angle and $k$ is a constant equal to 0.9. The crystallite size using (111) peak was calculated for CdS films deposited with H$_2$S atmosphere and comes out as 28.93 nm.

![XRD patterns of vacuum evaporated CdS thin films deposited without and with H$_2$S atmosphere.](image)

**Figure 4.8:** XRD patterns of vacuum evaporated CdS thin films deposited without and with H$_2$S atmosphere.

### 4.6 Surface Morphology:

The Surface Morphology of vacuum evaporated CdS thin films deposited without and with H$_2$S atmosphere was examined by scanning electron microscopy (SEM) with EDAX and atomic force microscopy (AFM).

#### 4.6.1 Scanning Electron Microscopy (SEM) with EDAX:

Scanning electron microscopy (SEM) with Energy dispersive X- ray analysis (EDAX) is a suitable technique to study the microstructure and composition of the as-deposited thin films. The SEM micrographs (at magnifications 25000X and 50000X) of
vacuum evaporated CdS thin films deposited without and with \( \text{H}_2\text{S} \) atmosphere are shown in figure 4.9 and figure 4.10 respectively.

**Figure 4.9:** SEM micrograph of vacuum evaporated CdS thin film deposited without \( \text{H}_2\text{S} \) atmosphere at different magnifications (i) at 25,000X and (ii) at 50,000X.

**Figure 4.10:** SEM micrograph of vacuum evaporated CdS thin film deposited with \( \text{H}_2\text{S} \) atmosphere at different magnifications (i) at 25,000X and (ii) at 50,000X.

The SEM micrographs show typical tightly adherent CdS films on highly cleaned glass substrates. It is cleared that the surface of CdS films deposited without \( \text{H}_2\text{S} \) atmosphere is rough and grains are not distributed uniformly. On the other hand the surface of CdS film deposited with \( \text{H}_2\text{S} \) atmosphere has fine grains which are more
uniformly distributed. So, the films deposited in H$_2$S atmosphere are homogeneous, without any crack, rather dense and exhibit almost complete coverage of the substrate. This shows that the better surface morphology is achieved in the films grown in controlled H$_2$S atmosphere.

EDAX analysis was performed for the elemental compositional analysis of the films. Figure 4.11 and figure 4.12 shows the EDAX spectrum of vacuum evaporated CdS films deposited without and with H$_2$S atmosphere. Electron beam induced inner-shell ionization and subsequent emission of characteristic fluorescence are analyzed in order to obtain the composition. The strong peaks for Cd and S shown in both EDAX spectrums (figure 4.11 and figure 4.12) confirm the presence of the Cd and S as the components of the as-deposited thin films of CdS. The Si peak appears in EDAX is due to the glass substrates used in the deposition of film material. As shown in figure 4.11 and figure 4.12, the subsequent characteristic fluorescence of Cd L-fluorescence (L$_\alpha$ & L$_\beta$ around 3-4 keV energy range), Cd M-fluorescence (M$_\alpha$ at around less than 0.5 keV energy range) and S K$_\alpha$-fluorescence (around 2-3 keV energy range) confirms the presence of Cd and S components in CdS thin films deposited without and with H$_2$S atmosphere. The element weight% and atomic% of Cd and S in EDAX spectroscopy of vacuum evaporated CdS thin films deposited without and with H$_2$S atmosphere are presented in Table 4.3 and Table 4.4 respectively. The atomic percentage of Cd and S shows excess of Cd in the vacuum evaporated CdS thin films. The average atomic percentage of Cd:S was found to be 51.85:48.15 in CdS thin film deposited without H$_2$S atmosphere whereas it is found 50.43:49.57 in CdS thin film deposited with H$_2$S atmosphere. These results shows that S is slightly increasing in vacuum evaporated CdS thin film deposited in H$_2$S atmosphere which indicates that the CdS films deposited with H$_2$S atmosphere have better stoichiometry in comparison to CdS films deposited without H$_2$S atmosphere.
Figure 4.11: EDAX analysis of vacuum evaporated CdS thin film deposited without H₂S atmosphere.

Table 4.3: EDAX analysis of vacuum evaporated CdS thin film deposited without H₂S atmosphere.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SK</td>
<td>20.95</td>
<td>48.15</td>
</tr>
<tr>
<td>CdL</td>
<td>79.05</td>
<td>51.85</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction</td>
<td>ZAF</td>
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</tbody>
</table>
Figure 4.12: EDAX analysis of vacuum evaporated CdS thin film deposited with H$_2$S atmosphere.

Table 4.4: EDAX analysis of vacuum evaporated CdS thin film deposited with H$_2$S atmosphere.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Matrix</td>
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</table>
4.6.2 Atomic Force Microscopy (AFM):

The 2D and 3D atomic force microscopy (AFM) images and histograms distribution of vacuum evaporated CdS thin films deposited on glass substrate without and with H₂S atmosphere are show in figure 4.13 (i), (ii), (iii) and figure 4.14 (i), (ii), (iii) respectively. All the AFM images were taken for an area of 1000x1000 nm orders show that the particles are closely bonded. The AFM images of the vacuum evaporated CdS film deposited on glass substrate with H₂S atmosphere revealed that the grains are more spherical in shape and are homogeneously distributed over the whole surface in comparison to the CdS film deposited on glass substrate without H₂S atmosphere. The average grain sizes are observed to be increased in CdS films deposited with H₂S atmosphere. The average roughness also increases in vacuum evaporated CdS films deposited with H₂S atmosphere. The average grain size & roughness of CdS films deposited without and with H₂S atmosphere comes out 12 nm (grain size) & 2.39219 nm (roughness) and 65nm (grain size) 12.1064 nm (roughness) respectively. CdS film with H₂S atmosphere show cluster of particles with highly dense structure with high packing density and have advanced surface and typical columnar structure with highly dense grains.
Figure 4.13: (i) 2D and (ii) 3D AFM images of vacuum evaporated CdS thin film deposited without H$_2$S atmosphere of an area 1000 x 1000 nm orders.

Figure 4.13: (iii) Histogram distribution of AFM image of vacuum evaporated CdS thin film deposited without H$_2$S atmosphere of an area of 1000 x 1000 nm orders.
Figure 4.14: (i) 2D and (ii) 3D AFM image of vacuum evaporated CdS thin film deposited with H$_2$S atmosphere of an area 1000 x 1000 nm orders.

Figure 4.14: (iii) Histogram distribution of AFM image of vacuum evaporated CdS thin films deposited with H$_2$S atmosphere of an area 1000 x 1000 nm orders.


### 4.7 Elemental Analysis by XPS:

X-ray Photoelectron Spectroscopy measurements have been carried out for the vacuum evaporated CdS thin films deposited without and with H\textsubscript{2}S atmosphere, using a Perkin Elmer 1257 model, operating at an average base pressure of $\sim 1.3 \times 10^{-8}$ torr at 300 K with a nonmonochromatized MgK\textalpha\ line at 1253.6 eV, and a hemispherical sector analyzer capable of 25-meV resolution. The overall instrumental resolution was about 0.3 eV. Pass energy for general scan and core level spectra kept at 143.05 eV and 71.55 eV respectively.

XPS survey spectra acquired in the range of 0-1150 eV are shown in figure 4.15. Corrections due to charging effects were taken care of by using C 1s as an internal reference and the Fermi edge of a gold sample. Peak areas were obtained by integrating the appropriate signal after data analysis. During photoemission studies, small specimen charging was observed which was later calibrated by assigning the C 1s signal at 285 eV. Few peaks are impurity peaks which are marked with (*). Sharp peaks of C 1s (285 eV), O 1s (532 eV), Cd (3d\textsubscript{5/2}), and Cd (3d\textsubscript{3/2}) at 405 and 412 eV respectively; The core level XPS spectra of Cd, C, S and O have shown symmetric profiles depicting uniform bond structure and emphasize that with and without H\textsubscript{2}S atmosphere exist in same phase. The core level spectra figure 4.16 (i) of Cd (3d) shows two distinct Cd(3d\textsubscript{5/2}) and Cd(3d\textsubscript{3/2}) states for CdS 405.65 and 412.4 eV and with H\textsubscript{2}S it shows at 405.35 and 412.15 eV respectively. The separation of the states in without and with H\textsubscript{2}S atmosphere is 6.75 and 6.8 eV, respectively, which is due to spin-orbit splitting. The slight shift in binding energies are due to variation from site to site substitution H\textsubscript{2}S gas. Figure 4.16 (iii) shows S (2p) and 2S (2s) core level spectra. The peaks with and without H\textsubscript{2}S atmosphere are observed that sulphure contributions is increase in with H\textsubscript{2}S atmosphere CdS films. Figure 4.16 (iv) shows O (1s) core level spectra. The peaks with and without H\textsubscript{2}S
atmosphere are observed at 532.75 and 532.3 eV are the contributions from surface oxygen of CdS films. Our results agree very Survey scan spectra of CdS films without and with H₂S atmosphere.

Figure 4.15: XPS survey scan spectra of vacuum evaporated CdS thin film deposited without and with H₂S atmosphere recorded with a photon energy of MgKα line at 1253.6 eV.
Counts (10^3 arb. units)

(a) CdS without H\textsubscript{2}S atmosphere

(b) CdS with H\textsubscript{2}S atmosphere

(i) Cd\textsubscript{3d\textsubscript{5/2}}

(ii) C\textsubscript{1s}

(iii) S\textsubscript{2s}, S\textsubscript{2p}
Figure 4.16: Core level XPS spectra of (i) Cd 3d (ii) C 1s (iii) S (2p & 2s) and (iv) O 1s, vacuum evaporated CdS thin films deposited without and with H\textsubscript{2}S atmosphere.

The observed C and O peaks can be attributed to the adsorption of these elements on the surface of the microstructure due to the exposure to the atmosphere. It is clearly seen from survey scan spectra and core level spectra of CdS thin films that after introducing H\textsubscript{2}S atmosphere the films is indicating better stoichiometry condition, better crystallity and growth in compared to without H\textsubscript{2}S atmosphere. This is manifest by increase in the Cd (3d) and S (2p) peak in survey scan spectra.

4.8 I-V Measurements:

Figure 4.17 (i) & (ii) shows I-V measurement of vacuum evaporated CdS films deposited without and with H\textsubscript{2}S atmosphere. Both contacts were of vacuum deposited aluminum on the same side of the sulphide films with the gap of same side about 1mm between them. Both these contacts being blocking, only their reverse characteristic would be observed whatever be the polarity of applied voltage. For high metal-semiconductor barrier the reverse tunneling current also become appeasable for high contact barrier and is given by the expression [41]
Figure 4.17: I-V Measurement of vacuum evaporated CdS thin films deposited without and with H₂S atmosphere.
\[ I(\text{tunneling}) \propto \frac{1}{\sqrt{V}} \]

This would be in addition to the normal reverse Schottky barrier current given by the following expression [42].

\[ j_{\text{rev}} = \frac{1}{4} n e v \exp \left( -\frac{\Phi_m - \chi_s}{kT} \right) \]

Where \( J \) is current density, \( n \) is the concentration of charge, \( v \) is the velocity of charge carriers, \( \Phi_m \) is the metal work function and \( \chi_s \) electron affinity of semiconductor. In this system at least one contact will always be act as a blocking contact. Under reverse bias tunneling mechanism could also predominate the current flow across the blocking electrode. Therefore the under reverse bias the current will be the sum of the reverse diffusion current and the tunneling current and its depends on the voltage and could be higher.
References:

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