Effect of molar concentration on structural, morphological and optical properties of CdS thin films obtained by SILAR method

K Manikandan*, P Mani1, P Fermi Hilbert Inbaraj1, T Dominic Joseph1, V Thangaraj2, C Surendra Dilip2 & J Joseph Prince1

1Department of Physics, University College of Engineering, Anna University, BIT Campus, Tiruchirappalli 620 024
2Department of Chemistry University College of Engineering, Anna University, BIT Campus, Tiruchirappalli 620 024

*E-mail: 1984manikandan@gmail.com

Received 2 March 2013; revised 24 June 2013; accepted 5 January 2014

Thin films of cadmium sulphide (CdS) were deposited on a glass plate by the SILAR method for 0.05, 0.10 and 0.15 M concentrations. The structural, optical and morphological properties of the films were characterized by X-ray diffraction (XRD), energy dispersive spectrum (EDS), UV-Vis spectrometry and atomic force microscopy (AFM) techniques. The XRD patterns of the films indicated that the crystalline natured films have hexagonal phases. The energy-dispersive spectrum (EDS) analysis confirms the compositions of cadmium and sulphur in CdS films. The direct band gap values in the range 2.32-2.24 eV were observed from the transmittance studies, the results infer that the band gap energy decreases with increasing molar concentration. The AFM studies show that the film is evenly coated and has uniform grain sizes.

Keywords: Thin film, CdS, SILAR, AFM, Band gap

1 Introduction

In solar cells, the thin film semiconductor materials with wide band gap energy preferentially used, hence research on such materials is needed for the current development1-3. Cadmium sulphide (CdS) thin film is widely considered for the solar cell applications. The CdS is used with several other semiconducting materials such as ZnS (Ref.4), Cu2S (Ref.5), PbS (Ref.6), SnS (Ref.7) and CdTe (Ref.8) due to its noticeable efficiency. The deposition of CdS films is done by several coating techniques viz., chemical bath deposition9-13 (CBD), spray pyrolysis14, spin coating15-18, close space sublimation19 and MOCVD (Ref. 20-21) as a window layer material for solar cell applications. However, all these techniques require sophisticated facilities like precise temperature control, high pressure, vacuum etc., In both principle and practice of the solution methods for the deposition of thin film, successive ionic layer adsorption and reaction (SILAR) method offers an extremely easy way22-25. The deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles. Moreover, it is relatively inexpensive, simple and convenient for large area deposition. This research work is focused to prepare ultra thin films of CdS with different concentration and study their structural, elemental, morphological and optical properties.

2 Experimental Details

The Successive Ionic Layer Adsorption and Reaction (SILAR) is an extension of the chemical bath deposition (CBD) and which overcomes the difficulties of CBD. The SILAR method is having sequential reactions at the substrate surface. Rinsing is an important method at each reaction, which enables the heterogeneous reaction between the solid phase and the insoluble ions in the solution. The glass plates were degreased with acetone and cleaned by concentrating HNO3 for 2 days, washed with a detergent solution, rinsed with distilled water and dried in an air. Cadmium sulphide thin films were prepared from the beakers containing aqueous solutions of cadmium nitrate [Cd(NO3)2·9H2O], sodium sulphide [Na2S]. The cadmium nitrate and sodium sulphide were kept at 1:1 molar ratio of all the concentrations. The film coating process is employed by following the method given in Table.1 and Fig. 1. Pre-cleaned glass plates were immersed in cationic precursor (cadmium nitrate) for 30 sec, so that Cd2+ ions present in the solution can be adsorbed on the glass plates. Then, the substrate is rinsed in distilled water for 30 sec, so that, the excessively adsorbed Cd2+ ions are rinsed away from the deposited layer which may result in saturated adsorbed layer of (Cd2+) cationic ions on the glass plate. The cation coated films were immersed in anionic precursor for 30 sec.
leading to adsorption so that, the anions S$_2^{-}$ from the
anionic sodium sulphide solution are introduced to the
system and a solid substrate is formed on the
interface. Hence, the cationic Cd$^{2+}$ ions can react with
the newly introduced anionic S$_2^{-}$ ions, un-reacted
sulphide ions were removed by rinsing them in
distilled water for 30 sec. Thus, a SILAR cycle is
comprised of these four parts. These operations were
repeated for 20 SILAR cycles in order to get an
adherent film. The resulted cadmium sulphide thin
film was annealed at 100°C for two hours in a hot air
oven.

3 Results and Discussion

3.1 Structural properties

The X-ray diffraction patterns of CdS thin films
deposited from various molar concentrations are
shown in Fig. 2. The patterns indicate that films are
nanocrystalline in nature. The observed broad hump
at 20 ~15°-38° and 38°-45° to exhibit in XRD pattern
is due to amorphous glass substrate$^{26}$. Figure 2 shows
that the CdS thin films are having hexagonal
(wurtzite) structure$^{27-29}$. All the films show three
diffraction peaks at angles 2θ ~ 24.80°, 31.18° and
43.70°. They are associated with (100), (200) and
(110) reflections of hexagonal (wurtzite) phase and
found to be matched with the standard hexagonal CdS
(JCPDS card No. 10-0454). No characteristics peaks
corresponding to impurity phases are detected. From
Fig. 2, it is seen that the intensity of the (100) peak
decreases gradually as the concentration increases. It
is also observed that there is a considerable mixture of
nanocrystalline phases for overlapping peaks which
indicates the decrease in full width half maxima
(FWHM) and increase in particle size with the
increasing concentration.

The grain size ($D$) of the CdS crystals formed in the
film during a deposition is calculated from the line
broadening of the (100) diffraction peak. According
to the Scherrer equation:

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad \ldots (1)$$

where $\lambda$ is the wavelength of Cu-Kα radiation
(0.15406 nm), $\beta$ the broadening of a diffraction peak
measured at full width and half of the maximum
intensity and $\theta$ is the diffraction angle. The calculated
average grain sizes of CdS thin films were estimated
to be around 250, 402 and 607 nm for 0.05, 0.10 and
0.15 M concentrations of CdS thin film, respectively.

<table>
<thead>
<tr>
<th>Table 1 — Optimised condition for CdS thin film deposition in SILAR method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start position</td>
</tr>
<tr>
<td>Dip length</td>
</tr>
<tr>
<td>Dip speed</td>
</tr>
<tr>
<td>Retrieval speed</td>
</tr>
<tr>
<td>Dip duration</td>
</tr>
<tr>
<td>Ex dip duration</td>
</tr>
<tr>
<td>No of cycles</td>
</tr>
<tr>
<td>No of dips</td>
</tr>
</tbody>
</table>

Fig. 1 — Schematic representations of SILAR deposition method

Fig. 2 — XRD patterns of CdS thin films for (a) 0.05 M
(b) 0.10 M (c) 0.15 M concentrations
also calculated from the diffractogram by using the formula

\[
\rho = \frac{1}{D^2}
\]  \(\ldots(2)\)

The value of micro strain (\(\varepsilon\)) was obtained using the relation:

\[
\varepsilon = \frac{\beta \cos \theta}{4}
\]  \(\ldots(3)\)

The calculated value of dislocation density was found to be 1.6780 \times 10^{13}, 2.7140 \times 10^{12} and 6.1879 \times 10^{12} line m\(^{-2}\) while for micro strains the values were calculated as 1.6345 \times 10^{-5} line m\(^{-2}\), 5.8471 \times 10^{-5} line m\(^{-2}\) and 8.828 \times 10^{-5} line m\(^{-2}\), respectively for the 0.05, 0.10 and 0.15 M concentrations. These observations indicate that the values are found to be decreasing with increasing concentration of the CdS thin film. It has been observed that the crystalline properties and the crystallite size have also increased with the increasing substrate molar concentrations. Since, the dislocation density and the micro strain of the films were decreased with increasing concentrations, the crystalline nature and the crystallite sizes were enhanced. These observations infer that the crystalline properties have improved with the increase in concentrations.

### 3.2 Elemental analysis

A representative energy-dispersive spectrum (EDS) is shown in Fig. 3 for the CdS thin film deposited by chemical solution methods (SILAR) at 0.10 M concentration. The expected elements Cd, S weight and atomic percentage were observed. The S/Cd at. ratio of CdS films is 0.8317. From Fig. 3, it is understood that the film exhibits better Stoichiometry. The identification of CdS film is presented at sulphur and cadmium element peaks exhibited at X-ray energy 2.3 and 3.15 eV, respectively.

### 3.3 Morphological analysis

Atomic force microscopy (AFM) measurements were performed to study the morphological characteristics of the CdS thin films deposited at different molar concentrations. Figures (4-6) show the AFM images of the CdS film with a scanning area of 25 \(\mu\)m\(^{2}\) for the 0.05, 0.10 and 0.15 M concentrations. The particles are randomly oriented...
and have different grain sizes. Average surface roughness ($R_a$), height and particle sizes of the deposits were observed in all the films. The CdS particles were randomly distributed on the surface of the films and their surfaces were homogeneous and the films are uniformly deposited in all the cases. The surface roughness ($R_a$) was increased with concentrations and observed as 5, 46 and 65 nm for the films of 0.05, 0.10 and 0.15 M, respectively. The results of average surface roughness ($R_a$), height and particle size were given in Table. 2.

### 3.4 Optical analysis

The optical absorption and transmittance properties of the deposited films have been studied in the wavelength range 200-800 nm. The variations of transmittance (%) and absorbance ($A$) of the material with wavelength are shown in Figs 7 and 8, respectively. The films were showing better absorption in the visible region and lower absorbance in the near-IR region. The increasing absorbance and decreasing transmittance properties were observed in the visible and IR regions with increasing molar concentrations. Figure 7 shows that as the wavelength increases, the absorbance of the films also increases and reaches a maximum at 298 nm wavelength invariantly for all the concentrations. The sharp shoulder peak and the cut-off wavelengths were observed using the formula 

\[
\text{Cut-off wavelength} = \frac{1}{n} \\
\text{shoulder peak} = \frac{1}{n+1}
\]
The transmittance spectrum is shown in Fig. 8. The transmittance is found to agree well with absorbance and shown at 298 nm wavelength. The optical densities 0.027, 0.108 and 0.119 are determined to the corresponding transmittance of 94%, 78% and 76% absorbance for the 0.05 M, 0.10 M and 0.15 M concentration, respectively.

\[ E_g = \frac{1240}{\lambda_{\text{max}}} \]  \hspace{1cm} (4)

Where \( \lambda_{\text{max}} \) is the wavelength of the absorption peak.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from \((Ahv)^2\) versus \((hv)\) with the relationship of near-edge absorption\(^{37}\):

\[ A = k(hv - E_g)^{n/2} \]  \hspace{1cm} (5)

where \( v \) is the frequency, \( h \) is Planck’s constant; \( k \) equals a constant while \( n \) carries the value of either 1 or 4. The values of \( n \) are 1 and 4 for the direct transition and indirect transition, respectively.

The optical absorbance of CdS thin films for the a) 0.05 M, b) 0.10 M and c) 0.15 M concentrations.

Fig. 8 — Transmittance spectrum of the CdS thin films for the (a) 0.05 M, (b) 0.10 M and (c) 0.15 M concentrations.

From Table 3, it is observed that as the concentration increases, the required absorption photon energy decreases, the photon energy difference (i.e. between higher energy band gap and lower the energy band gap) decreases and absorption coefficient also

![Table 3 — Optical properties of CdS thin film by UV-Visible spectrometer](image)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Absorbance (AU)</th>
<th>Wavelength (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05 M</td>
<td>0.10 M</td>
<td>0.15 M</td>
</tr>
<tr>
<td>Sharp shoulder peak</td>
<td>2.9296</td>
<td>1.7837</td>
<td>0.4793</td>
</tr>
<tr>
<td>Minimum peak of wavelength</td>
<td>0.1775</td>
<td>0.5901</td>
<td>0.5901</td>
</tr>
<tr>
<td>Cut off wavelength</td>
<td>0.095</td>
<td>0.4081</td>
<td>0.4668</td>
</tr>
</tbody>
</table>

Fig. 9 — Band gap analysis of the CdS films from transmittance spectrum for (a) 0.05 M, (b) 0.10 M and (c) 0.15 M concentrations.
increases. This increase in absorption coefficient is due to the increase in the particle size of the CdS grains and hence the photon energy decreases (Table 3).

4 Conclusions

CdS films were deposited by the SILAR technique using the equimolar and equivolume solutions of cadmium nitrate and sodium sulphide. The films with all the concentration are having dominant hexagonal peaks and show good appearance and fine grained deposition. These films have good optical properties and hence suitable for solar cell applications. The increase in molar concentration results into decrease in absorption photon energy and increase in absorption coefficient. This increase in absorption coefficient is due to the increase in the particle size of the CdS grains and hence, the required photon energy decreases which is harming with the results of AFM and XRD.

Acknowledgement

We thank Dr M Sivakumar, Coordinator, Department of Nanoscience & Technology of University College of Engineering, Anna University, Tiruchirappalli, for providing us AFM and UV-Visible spectra facilities. We also acknowledge Vellore Institute of Technology, Vellore-Tamil Nadu for providing XRD facilities for conducting this research.

References

18 Haiming Qin, Yue Zhao & Hong Liu, J Solid Chem, 194 (2011) 725.