Growth and characterization of CdS thin films by photochemical and chemical bath deposition

H. L. Pushpalatha¹ and R. Ganesha¹*

¹Department of Physics, Yuvaraja's College, University of Mysore, Mysore 570 005, Karnataka, India.

Abstract: Chemical solution deposition methods namely photochemical and chemical bath depositions are used to deposit cadmium sulphide (CdS) thin films on insulating glass substrates. In photochemical deposition (PCD), the deposition occurs by light induced reactions in the chemical solution. A substrate is immersed in the deposition solution and irradiated with ultraviolet light. Then the compound is formed in the solution due to photochemical reactions and deposited in the irradiated region of the substrate. The reactions occur only in the irradiated region, and the deposition process can be easily controlled by turning on/off the light. While in chemical bath deposition (CBD), the deposition occurs by chemical reaction promoted by thermal energy. The films obtained by both methods are characterized by XRD, UV-Visible spectrophotometer, Photoluminescence and Raman measurements. A comparative analysis is presented.

Key words: CdS thin film; chemical solution deposition; photochemical deposition; chemical bath deposition; UV photons.

1. Introduction

CdS due to its wide band gap (2.42 eV), photoconductivity, and high electron affinity, is an excellent heterojunction partner for p-type cadmium telluride (CdTe), p-type copper indium diselenide (CuInSe₂) and/or Cu (In,Ga)Se₂ (CIGS)⁵. CdS has two crystal forms; the more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite).

2. Experimental

Fig. 1. Photographs of experimental arrangement of PCD

The Experimental details of deposition of CdS thin films by PCD¹ and CBD⁴ are reported earlier. The schematic diagram of PCD-CdS apparatus is reported earlier⁵. The photograph of PCD experimental set up is as shown Fig. 1. The high purity chemicals (Sigma Aldrich) were used without further purification. In obtaining
PCD-CdS thin films the chemicals used are 0.2 M cadmium sulfate (CdSO₄), 0.2 M sodium thiosulfate (Na₂S₂O₃) in acidic medium. But it is a UV light photon mediated process in aqueous chemical solution. In obtaining CBD-CdS thin films the chemicals used are 1 M CdSO₄, 1 M thiourea [(CSNH₂)₂] in an alkaline medium. The chemical reaction that leads to the formation of CdS films is thermal-energy mediated process in aqueous chemical solution.

3. Results

3.1 Structural studies

The X-ray diffraction (XRD) patterns of CdS thin films deposited by PCD (Fig. 1) and CBD (Fig. 2) are as shown. The peaks in Fig. 1 confirm the hexagonal structure and peaks in Fig. 2 confirms both cubic and hexagonal structure (mixed phase).

![Fig. 2. XRD of the PCD-CdS thin films](image)

![Fig. 3. XRD of the CBD-CdS thin films](image)

The lattice parameters for a cubic plane (eq. 1) and hexagonal plane (eq. 2) & (eq. 3) is calculated using the formula

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \\
a = 2 \times 3^{-0.5} d_{100} \\
c = 2 \times d_{002}
\]

(1)  
(2)  
(3)

where d is the interplanar distance. The lattice parameters are tabulated (Table-1).
Table-1: Lattice parameters for cubic and hexagonal planes.

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Phase</th>
<th>Observed</th>
<th>ASTM</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD</td>
<td>Cubic (a)</td>
<td>0.58076 nm</td>
<td>0.582 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexagonal (a) and (c)</td>
<td>0.4137 nm and 0.6752 nm</td>
<td>0.4136 nm and 0.6713 nm</td>
<td>1.631</td>
</tr>
<tr>
<td>PCD</td>
<td>Hexagonal (a) and (c)</td>
<td>0.4122 nm and 0.6480 nm</td>
<td>c/a=1.633</td>
<td>1.572</td>
</tr>
</tbody>
</table>

3.2 Optical studies

UV-Visible spectrophotometer

The transmission spectrum of CdS thin films as a function of wavelength grown by PCD (Fig. 4a) and CBD (Fig. 4b) are as shown. The transmittance (Fig. 4a) is found in the range of 47-75%. The actual transmittance of the films is reduced due to the scattering of light on the surface of the CdS film. In Fig. 4b, transmittance for wavelength above 500 nm is 40% and above 750 nm is more than 50%. Comparatively higher transmission is noticeable in Fig. 4a than Fig. 4b in the lower wavelength (higher energy) range (400 nm-500 nm) hence PCD-CdS can be better window for solar radiation in the solar cell.

![Fig. 4](image_url)

(a) Optical transmission spectrum of PCD-CdS thin films and (b) CBD-CdS thin films

The band gap of the films was calculated by plotting \((\alpha h\nu)^2\) against \(h\nu\) and the graphs are presented in the Fig. 5a and Fig. 5b. The band-gap values determined from the intercept of the straight-line portion of the \((\alpha h\nu)^2\) against \(h\nu\) graph on the \(h\nu\) axis were found to be 2.35 eV for both PCD and CBD CdS thin films.

![Fig. 5](image_url)

(a) Variation of \((\alpha h\nu)^2\) vs \(h\nu\) of PCD-CdS thin films and (b) CBD-CdS thin films
Photoluminescence (PL) analysis

The room temperature PL spectrum of the CdS thin films grown by PCD (Fig. 6a) and CBD (Fig. 6b) are as shown. Fig. 6a exhibits two broad emission bands at 2.26 eV and 2.97 eV. The green band at 2.26 eV is due to donor-acceptor transition.

Another peak located around 418 nm (2.97 eV) is larger than the band gap value becomes visible at room temperature. Fig. 6b exhibits two broad emission bands at 2.28 eV (green band) and 1.72 eV (red band).

Raman analysis

The Raman spectra of CdS thin films grown by PCD (Fig. 7a) and CBD (Fig. 7b) are as shown. The peaks can be identified as the multi-overtones of the longitudinal optical (LO) phonons. In the case of Fig. 7a, the wave number of first overtone (1LO) is 299 cm\(^{-1}\), second overtone (2LO) is 603 cm\(^{-1}\) and third overtone (3LO) is 978 cm\(^{-1}\). In the case of Fig. 7b, the wave number of first overtone (1LO) is 301 cm\(^{-1}\) and second overtone (2LO) is 602 cm\(^{-1}\).

Discussion

From the XRD analysis, in CBD-CdS films, mixed phase (polymorphism) is observed whereas in PCD-CdS films, stable hexagonal phase is observed which is preferred for solar cell applications. An optical band gap of 2.35 eV is obtained for both PCD-CdS and CBD-CdS thin films from optical studies. Photoluminescence studies confirm the presence of green band in both PCD and CBD indicating the evidence for the higher crystallinity of the CdS thin films. From the Raman spectra characteristic CdS peaks are obtained.

Conclusion

CdS thin films have been deposited successfully by PCD and CBD. CBD is the most widely used technique in the industry and in the research area for CdS thin films deposition. PCD a modified version of
CBD has better control over the deposition rate and allows for patterning by turning on/off the light source and masking. PCD-CdS offers better transmission to the solar radiation in the lower wavelength (higher energy) range (400 nm-500 nm) and hence is preferred for making more solar energy available for conversion. A detailed analysis of the x-ray photoelectron spectroscopy XPS (ESCA) that gives a greater insight into the chemical composition through peaks corresponding to excitation of different electronic energy levels and correlation of the calculated chemical shifts with PL data is in progress.

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References


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