Characterization of CdS thin films deposited by the novel technique: Photochemical deposition using two different cadmium sources

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Abstract: Cadmium sulphide (CdS) thin films were deposited on glass substrates in aqueous medium by Photochemical deposition (PCD) using different cadmium (Cd) sources: cadmium sulphate (CdSO₄) and cadmium nitrate (CdNO₃). The substrate held in an aqueous solution containing thiosulfate ions (S₂O₃²⁻) and metal ions (Cd²⁺) ions is irradiated with UV light. The S₂O₃²⁻ absorbs the UV photons and release solvated electrons and sulphur (S) atoms which react with Cd²⁺ to form CdS. Deposition of CdS using Cd(NO₃) by PCD is reported for the first time. Characterization of the films by XRD, SEM and AFM is presented.

Key words: II–VI semiconductor; thin film; photochemical deposition; XRD; AFM; SEM.

1. Introduction

CdS is a II–VI metal chalcogenide compound semiconductor with a direct band gap 2.42 eV. CdS thin films can be deposited by several methods. A new aqueous solution growth method viz. photochemical deposition that allows better controllability developed in 1997 by Masaya Ichimura, Goto and Arai is used¹.

1.1 Photochemical reaction mechanism

The mechanism of CdS formation in PCD is as follows¹. When UV light is passed through the acidic solution (pH=3.6) containing ionized CdSO₄ and Na₂S₂O₃, elemental sulphur S is released from S₂O₃²⁻ ion:

\[ S_2O_3^{2-} + hv \rightarrow S + SO_3^{2-} \]  \hspace{1cm} (1)

In the presence of UV light S₂O₃²⁻ ions liberate electrons:

\[ 2S_2O_3^{2-} + hv \rightarrow S_4O_6^{2-} + 2e^- \]  \hspace{1cm} (2)

Similarly electrons are also generated when S₂O₃²⁻ ion combines with SO₃²⁻ (sulphite ion) in the presence of UV light:

\[ SO_3^{2-} + S_2O_3^{2-} + hv \rightarrow S_3O_6^{2-} + 2e^- \]  \hspace{1cm} (3)

The S₂O₃²⁻ ions act as a reducing agent to form S₄O₆²⁻ (tetrathionate) ion or S₃O₆²⁻ (trithionate) which supplies electrons for the reduction of Cd²⁺ ions. Cd²⁺ ions combine with elemental S in the presence of electrons to form CdS only on the illuminated region:
\[
\text{Cd}^{2+} + S + 2e^- \rightarrow \text{CdS}
\]  

(4)

2. Experimental

A schematic diagram of PCD is as shown in Fig. 1. Experimental details of deposition and characterization of CdS thin film using CdSO\(_4\) (Cd source) are reported earlier\(^2\). The experiment was repeated with identical growth conditions\(^2\) using 50 mL of 0.2 M CdNO\(_3\) (Cd source) solution and 75 mL of 0.2 M Na\(_2\)S\(_2\)O\(_3\) solution.

![Schematic PCD-apparatus](image)

Fig. 1. Schematic PCD-apparatus

3. Results and discussion

3.1 Structural studies

The X-ray diffraction (XRD) patterns of CdS thin-films using CdSO\(_4\) (Fig. 2a) and CdNO\(_3\) (Fig. 2b) as Cd sources are as shown. The intensity of peaks in Fig. 2a is almost double the intensity of peaks in Fig. 2b. The peaks (100), (002), (101), (102), (110), (103), (004), (104), (211) and (105) confirm the hexagonal structure in both cases. The peaks exhibited by the films are in conformity with reported in the literature\(^1\). Fig. 2a reveals better crystallinity through quite a good number of sharp peaks while Fig. 2b with a few peaks. The average grain size calculated using Debye-Scherrer formula in the case of Fig. 2a is around 90 nm and in the case of Fig. 2b is around 50 nm.

![XRD of the CdS thin films deposited using (a) CdSO\(_4\) source (b) CdNO\(_3\) source](image)

Fig. 2. XRD of the CdS thin films deposited using (a) CdSO\(_4\) source (b) CdNO\(_3\) source
3.2 Morphological studies

Scanning Electron Microscopy (SEM)

The SEM micrographs of CdS thin films using CdSO$_4$ source (Fig. 3a) and CdNO$_3$ source (Fig. 3b) are shown at 50 kx magnification. Fig. 3a and Fig. 3b exhibit grains with grain-size 107 nm and 80 nm throwing light on the dependence of grain-size on the choice of Cd source.

![Fig. 3. SEM of PCD-CdS thin films deposited using (a) CdSO$_4$ source (b) CdNO$_3$ source](image)

Atomic Force Microscopy (AFM)

AFM picture (Fig. 4a) of CdS thin films (using CdSO$_4$ source) and (Fig. 4b) (using CdNO$_3$ source) are as shown. Scan-area is 5 µm × 5 µm. Fig. 4a provides the values of rms roughness Rq = 121 nm, average roughness Ra = 96.1 nm and the Z-max is 1.7 µm. Fig. 4b provides the values of Rq = 36.7 nm, Ra = 29.9 nm and Z-max is 417.7 nm. From the roughness values of the films it is clear that the roughness is more in the former indicating that the roughness of the film is thickness-dependent.

![Fig. 4. AFM of CdS thin films deposited using (a) CdSO$_4$ source (b) CdNO$_3$ source](image)

Discussion

The order of grain-size given by SEM is comparable to that derived from XRD data. Fig. 3a shows densely deposited CdS with good surface coverage on the substrate (ion-by-ion mechanism) over which loosely adherent clusters of grains (cluster-by-cluster mechanism). Fig. 3b exhibits loosely adherent clusters distributed sparingly on the dense CdS film deposited with uniform surface-coverage. This indicates comparatively higher deposition-rate in Fig. 3a than in Fig. 3b. In Fig. 4a, grains of relatively larger size are
distributed over the surface while in Fig. 4b islands of clusters comprising of smaller grains are observed.

**Conclusion**

PCD is gaining importance as a novel technique for deposition of compound II-VI semiconductor thin films offering better controllability. Although deposited under identical growth conditions, rate of deposition and hence thickness, roughness of the film and crystallinity are observed to be more for the film deposited using CdSO$_4$ as Cd-source than using CdNO$_3$ as Cd-source with unique morphological features. Reports on CdS thin films deposition using CdSO$_4$ as Cd-source are available in literature. In this paper we are reporting deposition of the CdS thin films using CdNO$_3$ as Cd-source for the first time.

**References**


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