STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CHEMICAL BATH DEPOSITED CdS THIN FILMS

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Thin films of CdS of different thickness have been prepared on glass substrates in various temperatures by Chemical bath deposition. The thickness of the deposited film is measured by employing quartz crystal monitor method. The optical properties have been studied. The variation of band gap values of CdS thin film samples were found to be in the range of 2.16 to 2.45 eV. Electrical resistivity measurements were carried out in four-probe vanderpauv geometry at room temperature. Resistivity of CdS thin films is about $10^8 \, \Omega \text{cm}$. The micro structural parameters such as grain size, dislocation density and strain have been evaluated. The lattice parameter values ‘a’ and ‘c’ have been determined and is found to be 4.101 Å and 6.68 Å respectively.

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1. Introduction

Chemical bath deposition is a well known deposition process for Chalcogenides such as Cd, Zn, Co, Hg, Pb sulphides and selenides [1-3]. The Chemical Bath Deposition (CBD) method, being less expensive than other thin film deposition methods allows for the manufacture of relatively low cost devices especially light detectors, light energy conversion cells and thin films field effect transistor [4-6]. CdS is an important semiconductor material with very narrow band gap (2.10 to 2.40eV). The CdS material exhibits hexagonal structure with a preferred orientation along (002), (116,312) and (316,332) directions [7-10]. In this paper we present the results of our studies on structural, optical and electrical studies of Chemical Bath Deposited CdS thin film.

2. Experiment

A simple Chemical bath deposition (CBD) method was employed to deposit CdS thin films on to glass substrates using thiourea as sulfide ion source and cadmium sulphate as cadmium ion source in Ammonia bath. For the preparation of CdS thin films, 110ml of water heated upto 70°C and glass substrates was inserted and 0.0623M Cadmium sulphate was added with slow stirring of the precipitated solution. Ammonia solution (NH₃) was then added. When adding ammonia solution, the temperature of precipitated solution was reduced. Then 0.3284M Thiourea was added slowly in the solution. After adding thiourea, the precipitated solution became a yellowish colour which indicates the production of Cadmium sulfide in the precipitated solution. Time taken for the growth of the Cadmium Sulfide on the glass substrates varied from 30 minutes to 45 minutes. Substrate cleaning plays an important role in the deposition of thin films.

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Commercially available glass micro slides were submerged into the chromic acid for upto 2 to 3 hours. Then the glass substrates are washed with detergent and finally rinsed with acetone before use. The films with different thickness were obtained by varying the deposition time period. The thickness of the CdS thin films are measured by using gravimetric method [11-14]. The thickness variation of successive film is in the range of 90 Å in CdSO₄ combination. The structural characteristics were found by using x-ray diffractometer (Model-SHIMADZU XRD-2000). The nature of the electrical properties was examined by four-probe vander pavu geometry at room temperature. The arrangement consists of PID controlled oven (Model PID-2000, Scientific Equipment and services, Roorkee, India).

3. Result and discussion

3.1 Structural analysis of CdS thin films.

The structural identification of Cadmium sulfide film was carried out using an x-ray diffractometer in the range of $2^\circ \leq 2\theta \leq 60^\circ$ and is shown in figure 1. The presence of sharp peaks in the x-ray diffraction pattern clearly shows that the prepared CdS compound is polycrystalline nature with hexagonal structure and the CdS thin film of thickness 1700 Å. The material exhibits hexagonal structure with a prepared orientation along (002), (116,312), (316,332) directions.

![Fig. 1. X-ray diffraction pattern of (a) the deposited CdS thin film prepared by Chemical bath deposited method and (b) the irradiate film subjected to a dose of $10^{17}$ ions/cm², using Cu Kα radiation.](image)

The lattice parameter values ‘a’ and ‘c’ have been determined and is found to be 4.101 Å and 6.68 Å respectively and the ‘d’ values also given in table 1. These results are found to be in good agreement with the reported results and also with ASTM data.
Table 1. Structural parameter values “a” and “c” for CdS compound.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>(hkl)</th>
<th>Observed d(Å)</th>
<th>ASTM d(Å)</th>
<th>“a” Observed</th>
<th>“c” Observed</th>
<th>“a” ASTM</th>
<th>“c” ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>(116,312)</td>
<td>1.749</td>
<td>1.743</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>(316,332)</td>
<td>1.332</td>
<td>1.327</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Structural parameters for CdS thin film.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>(hkl)</th>
<th>Lattice parameters (Å)</th>
<th>Grain size D x 10^{10} m</th>
<th>Dislocation δ x 10^{15} m lines/m²</th>
<th>Strain ε x 10^{-3}</th>
<th>FWHM in Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(002)</td>
<td>4.0902 6.7076</td>
<td>156.629</td>
<td>4.0762</td>
<td>1.9677</td>
<td>1.24</td>
</tr>
</tbody>
</table>

The lattice parameters ‘a’ and ‘c’ and the micro structural parameters grain size, dislocation density and strain have been calculated and are shown in table 2. From the table 3, thickness of the film was gradually increased with increasing deposition time. The thickness variation of successive film is in the range of 90 Å in CdSO₄ combination.

Table 3. Variation of film thickness with deposition time.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Composition of CdSO₄ in aqueous solution</th>
<th>Deposition Time Allowed (Mins)</th>
<th>Thickness observed in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0623</td>
<td>30</td>
<td>3333</td>
</tr>
<tr>
<td>2.</td>
<td>0.0623</td>
<td>45</td>
<td>3423</td>
</tr>
</tbody>
</table>

3.2 Optical properties of CdS thin films.

The optical band gap (Eg) values for chemically deposited CdS thin film samples determined by plotting curve between (hγ) and (zhγ)² gives the value of direct allowed energy gap of each samples shown in figure 2; by plotting curve between (hγ) and (zhγ)¹/² gives the value of indirect allowed energy gap of each samples shown in figure 3; by plotting curve between (hγ) and (zhγ)³/² gives the value of direct forbidden gap of each samples shown in figure 4; and by plotting curve between (hγ) and (zhγ)¹/² gives the value of indirect forbidden gap of each samples shown in figure 5.
Fig. 2. A plot \((\alpha h\gamma)^2\) as a function of photon energy \((h\gamma)\) for CdS thin film.

Fig. 3. A plot \((\alpha h\gamma)^{1/2}\) as a function of photon energy \((h\gamma)\) for CdS thin film.

Fig. 4. A plot \((\alpha h\gamma)^{3/2}\) as a function of photon energy \((h\gamma)\) for CdS thin film.
From the table 4, the variation by band gap values of CdS thin film samples were found to be in the range of 2.16 to 2.45 eV. These values were found to be lower than the reported CdS bath material and the single crystalline CdS films. The maximum direct energy gap (2.41), Indirect allowed energy gap (2.31), Direct forbidden energy gap (2.41), Indirect forbidden energy gap (2.30) were observed. The CdS has very narrow band gap (2.10 to 2.40 eV) at visible region, so it acts as a window layer.

Table 4. Variation by band gap values of CdS thin films.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Composition of CdSo₄ in aqueous solution</th>
<th>Direct allowed energy gap (eV)</th>
<th>Indirect allowed energy gap (eV)</th>
<th>Direct forbidden energy gap (eV)</th>
<th>Direct forbidden energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0623</td>
<td>2.32</td>
<td>2.25</td>
<td>2.33</td>
<td>2.16</td>
</tr>
<tr>
<td>2.</td>
<td>0.0623</td>
<td>2.41</td>
<td>2.31</td>
<td>2.41</td>
<td>2.30</td>
</tr>
</tbody>
</table>

3.3 Electrical properties of CdS thin films

The Chemical bath deposited CdS thin film was found to be nearly stoichiometric. CdS exhibits n-type conductivity. The nature of the charge carriers were measured by hot probe method. Conductivity is in the range of 10⁻⁸ ohm.cm⁻¹ as shown in figure 6. Increase in dosage leads to increase in conductivity upto 10⁻¹ ohm.cm⁻¹ as shown in figure 7. Conductivity can be controlled by deviations from the stiochiometry, resulting from sulphur vacancies of cadmium excesses.
For electrical characterization, ohmic contacts to the films were made with silver paste. Ohmic character of the contact was verified by I-V measurements. Resistivity measurements were carried out in four-probe vander pavu geometry at room temperature. Resistivity of CdS thin film is about $10^8 \, \Omega \cdot \text{cm}$. High resistivity is due to stoichiometric nature of film. From table 5, shows the variation of resistivity, mobility and carrier concentration with cadmium concentration in bath. It is found that, there is an increase in carrier concentration with Cd concentration.

**Table 5. Variation of resistivity, mobility and carrier concentration**

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Cd concentration in bath (mm)</th>
<th>Thiosulphate ion concentration in bath (mm)</th>
<th>pH</th>
<th>Resistivity ($\Omega \cdot \text{cm}$)</th>
<th>Mobility (cm²/VS)</th>
<th>Carrier concentration (Cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2</td>
<td>100</td>
<td>3.5</td>
<td>$1.70 \times 10^{-1}$</td>
<td>89.25</td>
<td>$4.62 \times 10^{17}$</td>
</tr>
<tr>
<td>2.</td>
<td>4</td>
<td>100</td>
<td>3.5</td>
<td>$1.61 \times 10^{-1}$</td>
<td>85.23</td>
<td>$4.43 \times 10^{17}$</td>
</tr>
<tr>
<td>3.</td>
<td>6</td>
<td>100</td>
<td>3.5</td>
<td>$9.16 \times 10^{-1}$</td>
<td>11.37</td>
<td>$5.83 \times 10^{18}$</td>
</tr>
<tr>
<td>4.</td>
<td>8</td>
<td>100</td>
<td>3.5</td>
<td>$5.12 \times 10^{-1}$</td>
<td>2.39</td>
<td>$5.18 \times 10^{19}$</td>
</tr>
<tr>
<td>5.</td>
<td>10</td>
<td>100</td>
<td>3.5</td>
<td>$5.21 \times 10^{-1}$</td>
<td>2.57</td>
<td>$4.70 \times 10^{19}$</td>
</tr>
</tbody>
</table>

**Fig. 6. Conductivity ($\sigma$) versus 1000/T characteristics for CdS thin films.**

**Fig. 7. Conductivity ($\sigma$) versus Dosage of CdS thin films.**
4. Conclusion

CdS bulk material is obtained by taking 99.999% of pure material. CdS thin film has been deposited on a well cleaned glass substrate by chemical bath deposition technique. X-ray diffraction reveals that the films are polycrystalline in nature with hexagonal phase. Variations of particle size, strain, dislocation density and full width half maxima with substrate temperature have been studied.

The CdS has very narrow band gap (2.10 to 2.40 eV) at visible region. CdS shows n-type conductivity. Its resistivity is about $10^8 \, \Omega \cdot \text{cm}$. Carrier concentration is found to improve with Cd concentration in bath. Conductivity is found to improve with dosage.

CdS exhibits characteristics compatible with window material for solar cells.

References