Study of structural, Morphological and Electrical Properties of Cd$_x$Zn$_{1-x}$S Thin Films

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Abstract: The Cd$_x$Zn$_{1-x}$S (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) were prepared by using Chemical Bath Deposition (CBD) Technique. The prepared Cd$_x$Zn$_{1-x}$S thin films were characterized by X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM). The structural and morphological properties have been investigated. XRD pattern exhibits the hexagonal crystal structure of Cd$_x$Zn$_{1-x}$S. The dark electrical resistivity measurement was carried out in the temperature range 298 to 383 K by using two point probe method. The dark resistivity measurement shows that the prepared Cd$_x$Zn$_{1-x}$S thin films have high resistivity. The dark resistivity at room temperature was found to be of the order of $\geq 10^8$ $\Omega$ cm for pure CdS and $\geq 10^9$ $\Omega$ cm for Cd$_x$Zn$_{1-x}$S thin films. The dark resistivity was observed increased with Zn content.

Keywords – Chemical Bath Deposition, Cd$_x$Zn$_{1-x}$S thin films, Electrical resistivity, Structural properties, and morphological properties.

I. INTRODUCTION

Thin films are crystalline or non-crystalline and play vital role in all optoelectronic devices. They have been used as electroplated films for decoration and protection [1]. In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other optoelectronic devices with much interest shown in the use of CdS window layer in solar cell architecture. However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of solar cells [2].

The Cd$_x$Zn$_{1-x}$S films have more advantages for application in solar cell because they also offer a wider band gap (larger than 2.5 eV) as compared to the CdS films [3]. The higher band gap of ternary CdZnS has led to less window absorption loss, which makes it an effective replacement for CdS in thin film solar cell systems [4].

The limited reports were found on study of electrical properties of Cd$_x$Zn$_{1-x}$S system therefore the attempt have been made to synthesize the Cd$_x$Zn$_{1-x}$S thin films to study the structural and electrical properties.

There are many report on the deposition of CdZnS thin films with different concentration of Zn$^{+2}$ deposited by using different deposition techniques [5-8]. A number of thin film deposition techniques are used for deposition of the thin films. Chemical Bath Deposition Technique (CBD) is a simple technique in which no high quality substrates are required; also it is a non vacuum system. The method is more suitable for large area coatings. Therefore, in present research work an attempt was made to deposit the Cd$_x$Zn$_{1-x}$S thin films by CBD technique.

II. EXPERIMENTAL

In order to prepare Cd$_x$Zn$_{1-x}$S thin films, cadmium chloride (CdCl$_2$), zinc chloride (ZnCl$_2$) and thiourea (NH$_2$CSNH$_2$) were used as Cd$^{+2}$, Zn$^{+2}$ and S$^{+2}$ ions respectively. The stock solutions of CdCl$_2$ (0.25M), ZnCl$_2$ (0.25M) and NH$_2$CSNH$_2$ (0.3M) were prepared. The experimental solutions with different proportion were taken in reaction beaker for deposition of Cd$_x$Zn$_{1-x}$S thin films as shown in table1.

Table 1 The experimental solution with different proportion in chemical bath

<table>
<thead>
<tr>
<th>Composition x</th>
<th>CdCl$_2$ (ml)</th>
<th>ZnCl$_2$ (ml)</th>
<th>NH$_2$CSNH$_2$ (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>2</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>0.4</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>6</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>0.8</td>
<td>8</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>
The pH of the solution was adjusted to 11 by adding the aqueous NH$_3$. The reaction beaker was kept in temperature bath, maintained at 80° C. Glass substrates were cleaned by 24 hr immersion in chromic acid, rinsed with acetone and distilled water. The experimental glass substrates were mounted on substrate holder and immersed in the reaction beaker. The substrate holder was rotated at slow speed (45 rpm) by means of DC geared motor for 25 to 27 minutes. The thin, uniform Cd$_x$Zn$_{1-x}$S films were obtained at the end of the reaction process.

**Mechanism Cd$_x$Zn$_{1-x}$S Thin Film Formation:** The method which is used to prepare cadmium Zinc sulphide (CdZnS) includes the reaction of Cd$^{2+}$, Zn$^{2+}$ ions and S$^{2-}$ ions were found in solution from thiourea as:

\[ \text{(NH}_2\text{CS)} + \text{OH}^– \rightarrow \text{SH}^+. + \text{CN}_2\text{H}_2 + \text{H}_2\text{O} \quad \text{(1)} \]

\[ \text{SH}^+. + \text{OH}^– \rightarrow \text{S}^{2-} + \text{H}_2\text{O} \quad \text{(2)} \]

Dissolving CdCl$_2$ and ZnCl$_2$ in water made both cadmium and zinc ions available in the solution and formation of complexes of those ions as: In case of NH$_3$ as complexing agents, the Cd$^{2+}$ and Zn$^{2+}$ exist predominantly in the form of ion complex. The rates of ZnS and CdS formation are determined by the concentration of Zn$^{2+}$ and Cd$^{2+}$ provided by [Zn(NH$_3$)$_4$]$^{2+}$ and [Cd(NH$_3$)$_4$]$^{2+}$, and the concentration of S$^{2-}$ from the hydrolysis of SC(NH$_2$)$_2$, respectively. The general reaction can be expressed as:

\[ \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+. + \text{OH}^- \]

\[ [\text{Zn(NH}_3)_4]^{2+} \rightarrow \text{Zn}^{2+} + 4 \text{NH}_3 \]

\[ [\text{Cd(NH}_3)_4]^{2+} \rightarrow \text{Cd}^{2+} + 4 \text{NH}_3 \]

\[ [\text{Cd} (\text{NH}_3)_4]^{2+} + [\text{Zn} (\text{NH}_3)_4]^{2+} + \text{S}^{2-} + \text{NH}_3 \rightarrow \text{Cd}_x\text{Zn}_{1-x}\text{S} + \text{Remaining product.} \quad \text{-------(3)} \]

The prepared Cd$_x$Zn$_{1-x}$S thin films were rinsed with deionized water to remove the loosely bound particles and annealed at 100 °C. The synthesized Cd$_x$Zn$_{1-x}$S films are subjected to different characterizations to study the effect of Zn content on structural, morphological, compositional, electrical properties.

Film thickness is an important parameter in the study of the film properties. Amongst different methods for measuring the film thickness, the weight difference method is simple and convenient and thickness ‘t’ is measured using the relation (4).

\[ t = \frac{m}{A \rho} \quad \text{-------(4)} \]

where, m is the mass of area A of the substrate and material in the bulk form.

**III. RESULTS AND DISCUSSION**

**Structural study :**

The chemically deposited Cd$_x$Zn$_{1-x}$S (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) films were characterized by X-ray diffractometer. The XRD pattern was presented in fig. 1. The XRD spectra of the Cd$_x$Zn$_{1-x}$S films exhibit the hexagonal crystal structure with preferential orientations at (100), (002), (101), (203), (102), (110), (200) and (004) planes, at $\theta = 25.31, 26.75, 29.59, 31.20, 37.9, 52.10$ and $55.60$. The observed diffraction patterns are in good agreement with the standard JCPDS card data: 49-1302. Rajathi S. et al. (2012) and Kumar T. et al., (2009) reported similar hexagonal structure of Cd$_x$Zn$_{1-x}$S [9, 10]. As Zn content in the composition was increased, XRD peaks corresponding to (100), (101), (203), (102), (110) and (200) reflections significantly disappeared and only (002) was found significant. The (002) peak gives the lattice matching to the chalcogenide semiconductor such as CuInGaSe2 and CuIn(SexS1-x)2 which are used in solar cell devices for better solar cell efficiency [11]. In the composition x=0.4 and X=0.2 the polycrystalline nature of prepared Cd$_x$Zn$_{1-x}$S thin films was increased with Zn content. However in the film composition x=0.0 (ZnS) shows amorphous crystal structure with broad hump at 26.70° due to glass substrate. In the x=0.0 composition the film exhibits (100) and (002) reflection at an angle of diffraction 20=34.32 and 36.144 respectively which was well fitted with JCPDS card No. 12-0688 of ZnS.
The average grain size calculated by using scherrer’s relation (5):

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (5) \]

Where \( \lambda = 1.54 \text{ Å} \), \( \theta \) is the angle of diffraction and \( \beta \) the full width at half maximum. The variation of average grain size verses composition (x) was shown in table 2 and presented in fig. 2. The average grain size for \( x=0.2 \) composition was observed to be 4.19 nm.

The values of lattice constants \( a \) and \( c \) are calculated from XRD data by using relation (6).

\[ \frac{1}{d^2} = \frac{4}{3} (h^2 + hk + k^2)/a^2 + 1/c^2 \quad (6) \]

The variation of lattice constant with composition (x) was shown in fig. 3 and displayed in table 2.
3.2 Morphological study

In order to investigate the effect of Zn content on the surface morphology of the prepared Cd\textsubscript{x}Zn\textsubscript{1-x}S thin film the selected film were scanned by using Scanning electron microscopy (SEM Model: Quanta 200 ESEM). The SEM micrographs five different Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films were presented in fig. 4 (A through E). All the films were scanned at 15 KX magnifications. The micrograph shows that the films deposited cover the whole substrate with uniform surface morphology.

SEM image of Cd\textsubscript{1.0}Zn\textsubscript{0.0}S (fig. 4 A) shows the porous fibrous network consisting of regularly arranged matrix over which regular shaped fine particles systematically distributed. The larger size spherical granules were observed on the scan image due to aggregation of spheroid structure of S\textsuperscript{2-} ions.

The effect of increase of Zn content in Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films clearly understood from the improvement in the microstructure of the surface morphology from figures 4 (A through E). The micrograph of Cd\textsubscript{0.0}Zn\textsubscript{1.0}S shows spherical granules of ZnS particles irregularly distributed over the substrate. The SEM study confirms that even low Zn content was effectively changes the microstructure Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films.

### Table 2: Film Thickness, Grain Size, Lattice constant and optical band gap of different composition of Cd\textsubscript{x}Zn\textsubscript{1-x}S

<table>
<thead>
<tr>
<th>Composition of Cd\textsubscript{x}Zn\textsubscript{1-x}S film</th>
<th>Thickness μm</th>
<th>Grain Size nm</th>
<th>Lattice Constants nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>1.13</td>
<td>24</td>
<td>4.1017</td>
</tr>
<tr>
<td>0.2</td>
<td>1.67</td>
<td>4.82</td>
<td>4.110</td>
</tr>
<tr>
<td>0.4</td>
<td>2.13</td>
<td>17</td>
<td>4.114</td>
</tr>
<tr>
<td>0.6</td>
<td>2.13</td>
<td>15.8</td>
<td>4.115</td>
</tr>
<tr>
<td>0.8</td>
<td>2.43</td>
<td>16.6</td>
<td>4.0911</td>
</tr>
<tr>
<td>1.0</td>
<td>2.63</td>
<td>18.5</td>
<td>4.121</td>
</tr>
</tbody>
</table>

Fig. 4 The SEM micrographs of Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films [A) for x=1.0, B) for x=0.8, C) for x=0.4, D) for x=0.2 and E) for x=0.0]
4. Electrical characterization of Cd$_x$Zn$_{1-x}$S thin films

In order to study the electrical characterization of Cd$_x$Zn$_{1-x}$S thin films, dc two point probe technique was used. The dark electrical resistivity measurement was carried out in the temperature range 298 to 383 K. The dark resistivity measurement shows that the prepared Cd$_x$Zn$_{1-x}$S thin films have high resistivity. The dark resistivity at room temperature, was found to be of the order of $\geq 10^5$ $\Omega$ cm for pure CdS and $\geq 10^6$ $\Omega$ cm for Cd$_x$Zn$_{1-x}$S thin films. The plot of dark resistivity at different temperature was shown in fig. 5. The plot shows that the resistivity decreased with temperature. The decrease of resistivity with increasing temperature shows that the prepared Cd$_x$Zn$_{1-x}$S thin films are semiconducting. The variation of resistivity at room temperature verses composition (x) was shown in figure 6. It was observed from fig. 6 that resistivity at room temperature increased with Zn content of the films. The similar findings were reported by S. Jiyon et al.,(2005) in their work [12]. The variation $(\log \rho)$ with $(1000/T)$ (K$^{-1}$) has shown in fig. 7.

![Fig. 5 Electrical resistivity plotted verses temperature (K)](image)

![Fig. 7 The variation $(\log \rho)$ plotted verses $(1000/T)$ (K$^{-1}$)](image)

The thermal activation energy estimated from the slopes of the curve in fig. 7 and by using relation (7).

$$\rho = \rho_0 \exp (-\Delta E / KT) \ldots (7)$$

The activation energy was found to be in the range of 0.215 to 0.336 eV. Similar finding were reported by different researchers for CdS thin films [13,14]

**Thermoemf Measurement of Cd$_x$Zn$_{1-x}$S Films.**

The thermoemf of the prepared thin films was measured by using two point probe method in the temperature range 298 K to 383 K with the interval of 10 K. Fig. 8 shows the variation of thermoemf plotted as function of temperature difference.
It is observed that thermoemf increases with a temperature difference. This may be attributed to increase the mobility of charge carriers and carrier concentration with increase in temperature. From the sign of the terminal connected towards hot end the sign of predominant charge carriers can be deduced. In this case the hot end is connected to the positive terminal, the films shows n-type conductivity.

IV. CONCLUSION

The Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films prepared by simple chemical deposition exhibits hexagonal crystal structure. The crystallinity of Cd\textsubscript{x}Zn\textsubscript{1-x}S was observed increase with Zn Content. In the x=0.2 composition grain size observed was 4.19 nm. Incorporation of Zn ions in the CdS, only (002) peak was found significant which gives the lattice matching to the chalcogenide semiconductors used in solar cell devices. The SEM study confirms that even low Zn content was effectively changes the microstructure Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films. The dark resistivity at room temperature was found to be of the order of ≥10\textsuperscript{5} Ω cm for pure CdS and ≥10\textsuperscript{6} Ω cm for Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films. The effect of Zn doping increases the dark resistivity of CdS thin films. The decrease of resistivity with increasing temperature shows that the prepared Cd\textsubscript{x}Zn\textsubscript{1-x}S thin films were semiconducting. The activation energy was found to be in the range of 0.215 to 0.336 eV. The TEP measurement concluded that the prepared Cd\textsubscript{x}Zn\textsubscript{1-x}S films show n-type conductivity.

ACKNOWLEDGEMENTS

The corresponding Author is acknowledges to UGC India, for providing financial assistant under Minor Research Project , Prof Khairnar , Director School of Physical Sciences, SRTM University, Nanded, India, for providing XRD and other Laboratory Facilities.

REFERENCES

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