STUDY OF OPTICAL PARAMETERS OF CHEMICAL BATH DEPOSITED Cd_{1-x}Zn_xS THIN FILMS

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Abstract. The Chemical Bath Deposition Method (CBD) was employed for deposition of Cd_{1-x}Zn_xS (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) thin films. The chemically deposited Cd_{1-x}Zn_xS thin films were characterized by using UV-Visible spectrophotometer. Transmission spectra show the blue shifting of absorption edge as the Zn content increased. The x = 0.8 composition shows maximum 78 % transmittance. The reflection in the blue portion of the incident spectrum was decreased as the Zn content increased. The \((\alpha h\nu)^2\) versus photon energy \((h\nu)\) curves shows tuning of band gap with Zn content. The observed band gap was 3.9 eV in the x = 0.8 composition. The effect of composition on refractive index, absorption index and other optical dispersion parameters were also investigated. The calculated values of average excitation energy \(E_o\) approximately obey the empirical relation \(E_o=1.2 E_g\) obtained from single oscillator model.

1. Introduction

Now solar cell devices plays vital role in converting solar energy into usable form. The selection of window material is often important in the fabrication of low cost, high efficiency solar cell devices. Cadmium sulphide (CdS) is a low direct band gap \((E_g= 2.42\) eV) n-type semiconductor and widely used as window layer material in solar cell devices (Tuttle J.R. et al., 1996 [1]). CdS absorbs blue portion of solar radiations and decrease the current density of solar cells (Chavhan S.D. et al., 2008 [2]). Addition of Zn to widely used CdS window material improves the electrical and optical properties. The CdZnS provides the wider band gap and higher optical transmittance as compared to CdS. The wider band gap and higher optical transmittance are essential requisite in solar cell applications (Chavan S.D. et al., 2005 [3]). The CdZnS is II-VI compound semiconductor potentially used as window material for fabrication of p-n junction without lattice mismatch in CdTe or CuIn_xCa_{1-x}Se_2 solar cell devices (Ilican S. et al., 2007 [4]).

The knowledge of optical parameters such as optical band gap, reflectivity, optical transmittance, refractive index and dielectric constants etc. are essential prerequisite in using the suitable material for device applications.

A number of thin film deposition techniques are available. Of the most, Chemical Bath Deposition (CBD) is practically attractive because of its simplicity in comparison with other techniques, requiring vacuum conditions and complex instrumentations. Production of large surface area CdS thin films by easy and low cost techniques for industrial use, is still of great importance (Rakhshani et al., 1998 [5]). CBD is fast, simple, inexpensive, non-vacuum and suitable for mass production.
The objective of the present study is to synthesize Cd\textsubscript{1-x}Zn\textsubscript{x}S thin films by using chemical bath deposition technique (CBD). The prepared thin films are characterized by using UV-Visible spectrophotometer to study the effect of Zn content on the optical properties and optical constants like refractive index, extinction coefficients and dielectric constants etc. of Cd\textsubscript{1-x}Zn\textsubscript{x}S thin films.

2. Experimental

In order to prepare Cd\textsubscript{1-x}Zn\textsubscript{x}S thin films, the aqueous solution of Cadmium Chloride CdCl\textsubscript{2}, Zinc Chloride ZnCl\textsubscript{2} and thiourea NH\textsubscript{2}CSNH\textsubscript{2} were used as the precursor solutions. The stock solutions of CdCl\textsubscript{2} (0.05 M), ZnCl\textsubscript{2} (0.05 M) and NH\textsubscript{2}CS-NH\textsubscript{2} (0.1 M) were prepared. The experimental solutions with different volume proportions were taken in reaction beaker for deposition of Cd\textsubscript{1-x}Zn\textsubscript{x}S thin films as shown in following Table 1.

<table>
<thead>
<tr>
<th>Composition x</th>
<th>CdCl\textsubscript{2}, ml</th>
<th>ZnCl\textsubscript{2}, ml</th>
<th>NH\textsubscript{2}CS-NH\textsubscript{2}, ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>0.2</td>
<td>8</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>0.4</td>
<td>6</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>0.6</td>
<td>4</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>0.8</td>
<td>2</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>1.0</td>
<td>0</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

The pH of the solution was adjusted to 11 by adding the aqueous NH\textsubscript{3}. The reaction beaker was kept in temperature bath, maintained at constant 80 °C. Glass substrates were cleaned by 24 hr immersion in chromic acid, rinsed with acetone and distilled water.

All the chemicals and reagents used were of analytical grade. 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 30 minutes.

The pH of the precursor, reaction temperature, rotation speed and dipping time of the substrate were kept constant throughout the experiment at optimized values. The thin, uniform Cd\textsubscript{1-x}Zn\textsubscript{x}S films were obtained at the end of the reaction process. The prepared Cd\textsubscript{1-x}Zn\textsubscript{x}S thin films were rinsed with deionized water to remove the loosely bound particles and annealed at 100 °C. The synthesized Cd\textsubscript{1-x}Zn\textsubscript{x}S films are characterized by using UV-Visible spectrophotometer.

Two different methods were used for thickness measurements: the “Weighting difference method” and the “Optical interference fringes method”. The weighting difference method gives an approximate value for thickness of the prepared films. A digital balance with accuracy of (= 0.1 x 10\textsuperscript{-3} gm) was used for weighting the bulk content of deposited material on the substrate (Nathera A. et al., 2012 [6]).

The optical band gap was determined by using relation (Jauc J., 1974 [7]):

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^n,$$

(1)

where $A$ is the energy independent constant; $E_g$ is the optical band gap; $n$ is the constant which can determine types of optical transitions. The wavelength dependence of optical constants
such as extinction coefficients \( k \), refractive index \( n \), real and imaginary parts of dielectric constant \( \varepsilon_1 \) and \( \varepsilon_2 \) were calculated using following relations (Abeles F., 2007 [8]):

\[
\frac{n}{1 - R} + \left\{ \frac{4R}{(1 - R)^2} - k^2 \right\}^{1\!\!2},
\]

(2)

where \( R \) is the reflectance; and \( K \) is extinction coefficient,

\[ k = \frac{\alpha \lambda}{4\pi}, \]

(3)

where \( \alpha \) is absorption coefficient.

3. Results and discussion

Absorbance data of Cd\(_{1-x}\)Zn\(_x\)S thin films was recorded by using UV-Visible spectrophotometer (Systronics Double Beam 2201).

Figure 1 is the plot of transmission versus wavelength. The transmission curves show the blue shifting of absorption edge (approximately from 450 – 350 nm). From Fig. 1, it is clear that, the optical transmittance is maximum in the visible region (450 - 800 nm) and found increased from 5 to 78 % with Zn content. In the composition \( x = 0.8 \), the observed transmittance was 78 %.

![Fig. 1. Percent transmittance plotted versus wavelength for Cd\(_{1-x}\)Zn\(_x\)S thin films.](image)

Figure 2 shows the variation of optical reflection with wavelength. The reflection is found decreased from 0.02 to 0.005 (a.u.) in the visible and near infrared region. It supports the antireflection property of the Cd\(_{1-x}\)Zn\(_x\)S thin films. In the compositions \( x = 0.8 \) and 1.0, the optical reflectance was significantly decreased in the blue portion of the incident spectrum. Blue shifting of absorption edge indicate the decrease in optical absorption in the blue portion of the solar spectrum. (Borse S.V. et al., 2007 [9]).

The variation of film thickness with composition \( x \) is displayed in Table 2. Thickness of the films was found decreased from 6.63 to 1.13 \( \mu m \).
The annealing effect shows that, band gap of CdS (Cd$_{1.0}$Zn$_{0.0}$S) is 2.47 eV which is larger than 2.42 eV of the bulk CdS material. The variation of band gap with Zn content was shown in Table 2. The band gap was increased with Zn content from 2.427 to 3.9 eV. In the composition x=0.8, the band gap was found to be 3.9 eV.

The dispersion of incident photon energy plays the important role in determining the optical property of the material. The knowledge of variation of refractive index helps to investigate the average excitation energy ($E_o$) and dispersion energy ($E_d$) of the deposited material.

The variation of refractive index ($n$) and extinction coefficient ($k$) with wavelength of the Cd$_x$Zn$_{1-x}$S films are presented in Figs. 4 and 5 respectively.

The refractive index of the deposited films significantly changes with the film composition. In the low wavelength region the values of refractive index for deposited films are higher and then decreased after 350 nm. The effect of Zn content of the deposited Cd$_{1-x}$Zn$_x$S films on $n$ and $k$ was clearly illustrated from Figs. 4 and 5.

The extinction coefficient ($k$) shows similar nature of variation, however the $k$ has less value as compared to $n$. The observed values of $n$ and $k$ at wavelength 450 nm were presented in Table 2.
The investigation of complex dielectric constant is very important as it provides information about electronic structure of the deposited material onto the substrate. The dielectric constant is given as, \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \), where, real \( \varepsilon_1(\omega) \) and imaginary \( \varepsilon_2(\omega) \) parts of dielectric constant are related to the \( n \) and \( k \) values respectively. The \( \varepsilon_1 \) and \( \varepsilon_2 \) were calculated using formulas:

\[
\varepsilon_1 = n^2 - k^2, \quad (4)
\]

\[
\varepsilon_2 = 2nk. \quad (5)
\]
From the Figs. 6 and 7, it is concluded, that both $\varepsilon_1$ and $\varepsilon_2$ decrease from 0.45 to 0.025 and 2.4 to 1.2 respectively. The observed values of $\varepsilon_1$ and $\varepsilon_2$ at wavelength 450 nm were presented in Table 2.

The variation of $\varepsilon_1$ as a function of wavelength follows the similar behavior as $\alpha$ whereas the variation of $\varepsilon_2$ follows the behavior of $k$. The extinction coefficient ($k$) and $\varepsilon_2$ are related to absorption coefficient $\alpha$ and hence the thickness of the deposited thin films. The change of Zn content in Cd$_{1-x}$Zn$_x$S thin films causes the important change in dielectric constants.
Fig. 7. Plot of imaginary part of dielectric constant ($\varepsilon_2$) versus wavelength of Cd$_{1-x}$Zn$_x$S thin films.

The approximate relation between refractive index $n$, average excitation energy for electronic transition ($E_0$), the dispersion energy ($E_d$) and incident photon energy ($h\nu$) was described by Wemple and DiDomenico (Wemple S.H., 1971 [10]) means of single oscillator:

$$n^2 - 1 = \frac{E_d E_0}{(E_0^2 - (h\nu)^2)}.$$  \hfill (6)

Plot of $(n^2-1)^{-1}$ against $(h\nu)^2$ gives the oscillator parameters $E_0$ and $E_d$ which are determined by fitting a straight line to the points and shown in Fig. 8.

Fig. 8. Plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ of Cd$_{1-x}$Zn$_x$S thin films.

The values of $E_0$ and $E_d$ can be directly determined from the gradient $(E_0 E_d)^{-1}$ and intercept on vertical axis, $(E_d/E_0)$. The values obtained for dispersion parameters, $E_0$ and $E_d$ are displayed in Table 3. Caglar M. et al. (2006) [11] and Illican S. (2006) [12] reported that the oscillator energy $E_0$ was related to lowest direct band gap empirically by $E_0 = 1.2 E_g$. The
calculated values of \( E_o \) satisfies the empirical relation approximately obtained from single oscillator model.

\[
\text{Table 3. Variations of oscillator parameters with composition.}
\]

<table>
<thead>
<tr>
<th>Composition of Cd(_{1-x})Zn(_x)S film</th>
<th>( E_o ), eV</th>
<th>( E_d ), eV</th>
<th>( M_1 )</th>
<th>( M_3 ), (eV)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.72</td>
<td>23.1</td>
<td>6.71</td>
<td>0.49</td>
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<tr>
<td>0.2</td>
<td>4.082</td>
<td>25.9</td>
<td>6.31</td>
<td>0.38</td>
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<tr>
<td>0.4</td>
<td>4.08</td>
<td>26</td>
<td>6.32</td>
<td>0.38</td>
</tr>
<tr>
<td>0.6</td>
<td>4.378</td>
<td>22</td>
<td>5.0</td>
<td>0.26</td>
</tr>
<tr>
<td>0.8</td>
<td>5.17</td>
<td>14.78</td>
<td>2.89</td>
<td>0.118</td>
</tr>
<tr>
<td>1.0</td>
<td>5.26</td>
<td>14</td>
<td>2.66</td>
<td>0.096</td>
</tr>
</tbody>
</table>

The moments \( M_1 \) and \( M_3 \) of the optical transitions can be obtained from relationships:

\[
\left( E_o \right)^2 = \frac{M_1}{M_3}, \tag{7}
\]

\[
\left( E_d \right)^2 = \frac{M_3}{M_3}. \tag{8}
\]

The calculated values of \( E_o \), \( E_d \), \( M_1 \), \( M_3 \) were found decreased with Zn content. As compared with values reported (Ilican S. et al., 2006), the obtained values of \( E_o \), \( E_d \), \( M_1 \), \( M_3 \) are found higher. This may be because of technique of deposition. The values of moments of optical transitions are tabulated in Table 3. Table 3 shows the decreasing trend with Zn content.

The compositional and structural studies are the future scope of the work, to confirm the initial and final content of elements.

4. Conclusions
The transparent Cd\(_{1-x}\)Zn\(_x\)S thin films have been synthesized by low cost simple Chemical Bath Deposition Technique. It was concluded that, Zn content changes the optical properties of the Cd\(_{1-x}\)Zn\(_x\)S thin films. The film of composition \( x = 0.80 \) and 1.0 gives maximum 78% transmittance. The maximum transmittance and low reflection property indicate that the prepared thin films are antireflective. The band gap shows the increasing trend with Zn content. The film composition \( x = 0.8 \) shows maximum 3.9 eV band width. The variation of \( \varepsilon_1 \) as a function of wavelength follows the similar behavior as \( n \) whereas the variation of \( \varepsilon_2 \) follows the behavior of \( k \). The values of \( E_o \), \( E_d \), \( M_1 \), \( M_3 \) decreased with concentration of Zn. The calculated values of average excitation energy \( E_o \) approximately obey the empirical relation obtained from single oscillator model.

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References