Optical Characterization of the (Cd-Zn)S:CdCl₂ Thin Film Deposited by CBD Method

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ABSTRACT

Thin films of (Cd-Zn)S:CdCl₂ were deposited on glass substrates at 60°C for 60 minutes by Chemically Bath Deposition Method. The absorption coefficient (α) was determined from the absorption and transmission using (uv-vis spectrophotometer) at a normal incident of light in the wavelength of range (400-1000)nm. Using the relationship (αhν)^2 against hν, we find that the films have energy gap between (2.9ev-3.1ev) and (α≥10⁴ cm⁻¹) means the direct type of transmission, also we calculate (Refractive index , Extinction coefficient , real Dielectric constant, Imaging Dielectric constant). The dispersion parameters such as E₀ (single oscillator energy) and Eₐ (dispersive energy) have been discussed in terms of the Wemple-DiDomenico single-oscillator model. The values obtained by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells and piezoelectric devices.

Key words: thin film, chemical bath deposition, optical properties.

1. Introduction

There has been great interest of researchers in electro-optical properties of ZnS/CdS thin films prepared by CBD technique [1] because this technique is regarded as one of the simplest and most economical techniques for producing good quality nano-crystalline films [2]. Indeed this technique is very attractive because of being capable of depositing optically smooth, uniform and homogenous layers. Although a number of research papers have been published exhibiting electro-optical properties of CdS in different forms like powder, crystals, pellets, nanocrystallites and thin films [3], the information available on ternary CdₙZn₁₋ₙS system is very limited. It is well established that CdₓZn₁₋ₓS films possess properties between those of CdS and ZnS [4, 5]. Since their addition produces a common lattice in which band structure has a larger band gap than CdS, it makes the material more attractive for fabricating EL devices. Thin film studies of CdS and ZnS type materials are very important because of their wide technological applications e.g. ACTFEL panels, flat TV screen, sensitive photoconductor [6], IR detector [7], solar cell [8], light emitting devices [9] etc. These TFEL displays have found strong acceptance in medical and industrial control applications, where the need for wide view angle, longer life, wide temperature ranges and fast response time are critical.

CdₓZn₁₋ₓS films have been prepared in different forms like powders, crystals, pellets, nanocrystallites and thin films. Earlier workers used many sophisticated techniques like molecular beam
epitaxy [10], plasma chemical sputtering [11], metal organic chemical vapour deposition (MOCVD) [12] and metal organic vapor-phase epitaxy (MOVPE) [13] to produce thin films with adequate properties like high crystalline, low resistive and high transmittance. However, chemical deposition technique appears as an interesting technique for preparing ZnS/CdS thin films [1].

2. Experimental Details

2.1 Materials

The samples were prepared by vertically dipping the cleaned substrates of conducting glass plates of dimension 24 mm x 75 mm (with high transmission coefficient). The substrates were first washed with acetone, HCl, distilled water and by using ultrasonic cleaner. Such cleaned glass slides were dipped into a mixture of appropriate amounts of 1 M solutions of zinc acetate / cadmium acetate, thiourea and 30 % aqueous ammonia (All analytical reagent grade-99.9 % pure; mixture showed pH ~ 11). In addition appropriate amounts of 0.01 M solution of CdCl$_2$ were also mixed in the original mixture. Zn (CH$_3$COOH)$_2$ and Cd (CH$_4$COOH)$_2$ provided Zn and Cd respectively whereas Thiourea (NH$_2$)$_2$CS gave Sulphur for Cd$_x$Zn$_{1-x}$S films. The solutions of the compounds used were prepared in double distilled water and films were prepared at a constant temperature of 60$^\circ$C in a water bath. Films were prepared on around 60 % area of the glass slide. The deposition of films is based on precipitation followed by condensation. In the beginning when precipitation started, stirring was done. After that, depositions were made in the static condition and after deposition; films were washed with distilled water and then dried by keeping in open atmosphere under sun light until its moisture content reduces completely. Here subscripts to Zn and Cd represent the percentage composition in the solution and not the final compositions. In all the samples discussed here, the volumes of CdCl$_2$ and TEA used as activator and flux respectively were 2 ml each.

2.2 Optical Measurements

The optical absorption spectra of (Cd$_x$Zn$_{1-x}$)S:CdCl$_2$ thin films at room temperature were recorded by UV-Vis Spectrophotometer in the wavelength range 400nm-1000nm. The transmission of (Cd$_x$Zn$_{1-x}$)S:CdCl$_2$ thin film is influenced by varying concentration of Zn. It is noticed that the (Cd$_x$Zn$_{1-x}$)S:CdCl$_2$ thin film has higher transmission value in the visible range of the spectrum. The absorption edge is determined by the optical absorption method, which is simple and provides for the explanation of some features concerning the band structure of the films. Absorption coefficient is a ratio decreases in flux energy incident on the unit distance in dimensions diffusion wave in the media and absorption coefficient dependent on photon energy and prepared, the photo energy represent by relationship:

\[ E = h\nu \]  
\[ \alpha = \frac{2.303 A}{t} \]  
\[ t = \text{thickness of thin film}, A = \text{absorption} \]

The electrons transformation from valance band to conduction band vertically and without happening any change in value.

\[ \Delta k = 0 \]

The Absorption equation to the transition can be write in the form.

\[ a h\nu = A(h\nu - E_g)r \]

where \( E_g \) = optical energy gap, \( A \) = constant dependent on the (valance and conduction bands). \( r = 1/2 \) for allowed direct transition. The absorption coefficient \( \alpha \) at frequency \( \nu \) of radiation was calculated using the formula:

\[ \alpha(\nu) = \frac{2.303A}{d} \]
Where \( d \) is the film thickness and \( A \) is the optical absorbance. Also, \( \alpha(\nu) \) is related to the optical transmission \( T \) and reflection \( R \) as follows [29]:

\[
\alpha(\nu) = \frac{1}{d} \left\{ \frac{(1-R)^2}{2T} + \frac{(1-R)^2}{[(2T)^2+R^2]^{3/2}} \right\}
\]

(5)

And the refractive index was obtained from

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

(6)

Where \( k \) is the extinction coefficient which is related to the absorption coefficient and the wavelength as:

\[
k = \frac{\mu \lambda}{4\pi}
\]

(7)

On the other hand, the real and imaginary parts of dielectric constant of the films can also be estimated if the refractive index and extinction coefficient are known. The real and imaginary part of the dielectric constant can be expressed by the following relation:

\[
e_1 = n^2 - k^2
\]

and

\[
e_2 = 2nk
\]

### 3. Results and discussion

The transmission spectra of \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) \((x=.6, .7, .8)\) thin films of thickness \(\approx 1\)nm are shown in fig. (1). For \(x=0.6, 0.7 \& 0.8\) Zn contents the average transmission value is maximum for \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) films in the wavelength range 450-800nm range. It is noticed that \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) films has higher transmission value in the visible range of the spectrum.

The optical absorption edge is determined by the optical absorption method, which is simple and provides for the explanation of some features concerning the band structure of the films. The curves of \(\ln(\alpha \nu)\) versus \(\ln(h\nu - E_g)\) were plotted using the \(E_g\) values to determine the value of \(r\) and it was found about \(1/2\) from the slope of these curves. Therefore, \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) thin films appear to be a material which has a direct band gap. The variation of \((\alpha \nu)^2\) with \(h\nu\) for \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) thin film is shown in fig. 2. It has been observed that the plots of \((\alpha \nu)^2\) versus \(h\nu\) are linear over a wide range of photon energies which are indicating the direct type of transitions. The intercepts (extrapolation) of these plots (straight lines) on the energy axis give the energy band gaps. The direct band gaps for all the films were determined. With increasing Zn content the energy band gap of \((\text{Cd}_{x}\text{Zn}_{1-x})\text{S}:\text{CdCl}_2\) thin film increases.
The calculated values of refractive index $n$ and extinction coefficient $k$ were plotted as a function of wavelength, as shown in the fig. 3. We also calculated the real and imaginary part of the dielectric constant as it is directly related to the density of states within the energy gap of the films.

The real($\varepsilon_2$) and imaginary ($\varepsilon_1$) parts of the dielectric constant of the films are shown in figs. 4a and 4b respectively. It is seen that both, real and imaginary parts of dielectric constant decreases with increasing wavelength. It is seen that the values of real part is higher than that of the imaginary part. Increasing Zn content causes important changes in these optical constants.
TABLE: Direct energy band gaps and the optical constants for the (Cd$_{1-x}$Zn$_x$)S:CdCl$_2$ thin films

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$</th>
<th>$E_d$</th>
<th>$E_d$</th>
<th>$M_1$</th>
<th>$M_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:CdCl$_2$</td>
<td>2.8</td>
<td>3.99</td>
<td>11.93</td>
<td>2.989</td>
<td>0.1878</td>
</tr>
<tr>
<td>(Cd$<em>{0.6}$Zn$</em>{0.4}$)S:CdCl$_2$</td>
<td>2.92</td>
<td>4.4</td>
<td>12.59</td>
<td>2.861</td>
<td>0.1478</td>
</tr>
<tr>
<td>(Cd$<em>{0.7}$Zn$</em>{0.3}$)S:CdCl$_2$</td>
<td>3.0</td>
<td>3.5</td>
<td>15.89</td>
<td>4.539</td>
<td>0.3706</td>
</tr>
<tr>
<td>(Cd$<em>{0.8}$Zn$</em>{0.2}$)S:CdCl$_2$</td>
<td>3.09</td>
<td>4.4</td>
<td>12.59</td>
<td>2.861</td>
<td>0.1478</td>
</tr>
</tbody>
</table>

The single-oscillator parameter were calculated and discussed in terms of the Wemple-DiDomenico model. The dispersion parameters of various materials were investigated by using the model, as reported in [14, 17]. This model describes the dielectric response for transitions below the optical gap. This plays an important role in determining the behavior of the refractive index. The dispersion data of the refractive index can be described by a single-oscillator model [18],

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (hv)^2}$$

Where $E_0$ and $E_d$ are single oscillator constants ($E_0$ is the single-oscillator energy and $E_d$ is the dispersion energy which is a measure of the strength of interband optical transitions). By plotting $(n^2 - 1)^{-1}$ versus $(hv)^2$ and fitting a straight line shown in fig. 5,
$E_0$ and $E_d$ are determined directly from the gradient, $(E_0 E_d)^{-1}$ and the intercept $(E_0 / E_d)$, on the vertical axis. The values of $E_0$ increases with increasing Zn content. The $E_0$ and $E_d$ values for the $(\text{Cd}_{x} \text{Zn}_{1-x})\text{S}:\text{CdCl}_2$ thin films are given in the table. The oscillator energy $E_0$ is an average energy gap as pointed out in many references [19-22]. We found that $E_0$ value of the films is related empirically to the lowest direct band gap by $E_0 \approx 1.36 E_g$. This relation is in agreement with the relation ($E_0 \approx 1.4 E_g$) obtained with the use of single oscillator model [19].

The $M_{-1}$ and $M_{-3}$ moments of the optical spectra can be derived from the following relation:

$$E_0^2 = \frac{M_{-1}}{M_{-3}}$$

$$E_d^2 = \frac{M_{3}^1}{M_{-3}}$$

The values obtained are given in the table. It is seen that $M_{-1}$ and $M_{-3}$ moments have a tendency to increase with an increase in Zn content.

4. Conclusion

$(\text{Cd}_{x} \text{Zn}_{1-x})\text{S}:\text{CdCl}_2$ (x=0, x=.2, x=.3, x=.4) thin films have been deposited by CBD method on glass substrate at 60°C. Based on the optical investigation of the films, the following results were obtained. The maximum transmission value is obtained for $(\text{Cd}_{.7} \text{Zn}_{.3})\text{S}:\text{CdCl}_2$ film. The optical constants such as refractive index ($n$), extinction constant ($k$), real part of dielectric constant ($\varepsilon_1$) and imaginary part of the dielectric constant ($\varepsilon_2$) of the films, were calculated for the films. All of these constants decreases with wavelength. The optical absorption spectra of the films under study shows that the absorption spectra mechanism is due to direct transition. The optical dispersion ($E_0$ and $E_d$) using Wemple-Di-Domenico model were also analyzed. In conclusion we can state that the influence of Zn content on the optical properties of CdS thin films is noticeable.
References: