Study of Physical Characteristics of Zinc Selenide Thin Film

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Abstract - Zinc Selenide (ZnSe) film has been grown on well cleaned glass substrate by thermal evaporation technique under vacuum (5 x 10^-6 mbar). The physical characteristics of ZnSe film such as compositional, structural and optical properties were examined using energy dispersive X-ray analysis (EDAX), X-ray diffractometer and UV-Visible spectrophotometer respectively. The EDAX study shows that the ZnSe film is almost stoichiometric. Polycrystalline nature of the film was observed from XRD analysis. It is revealed that deposited film has zinc blende system along with some amorphous phase present in ZnSe film and a preferred (3 1 1) orientation. The grain size and lattice strain have been calculated by Williamson-Hall (W-H) plot. Other relevant structural parameters (dislocation density and internal stress) have been calculated. The value of corrected lattice parameter has been determined using Nelson-Riley error function. The optical parameters (optical band gap, Urbach energy and extinction coefficient) have been found for the wavelength region (300 nm - 1100 nm) by absorption spectra.

Keywords- EDAX; XRD; absorption spectra; ZnSe thin film.

I. INTRODUCTION

The group of II-VI compound semiconductors has extensive attention because of their novel properties and many applications. ZnSe has relatively wide band gap, high transparency over wide spectrum range and low value of resistivity which offers an important numbers of optoelectronic applications such as blue and green light emitting diode, LASERs, photodetectors and ultrasonic transducers. It is also applicable for window layer for thin film solar cell [1-4]. ZnSe has either a cubic structure with lattice parameter a = 5.668 Å or hexagonal structure with lattice parameter a = 3.820 Å and c = 6.628 Å [5]. The performance of optoelectronic devices is highly sensitive to the structural properties of the film. Also structural properties such as grain size, lattice constant, crystal phase and orientation depend upon preparation technique and deposition condition [6].

In this paper, ZnSe thin film was prepared by thermal evaporation technique which is easy and conventional method for low costs and large area applications. It is very simple and practicable as compared to other method in industrial production line [7]. The physical characteristics of ZnSe film such as compositional, structural and optical properties were studied.

II. EXPERIMENTAL PROCEDURE

The ZnSe film was deposited on well cleaned glass substrate using thermal evaporation technique under vacuum pressure at 5 x 10^-6 mbar by using HIND HVAC coating unit (Model: 15F6D). The glass substrate was first cleaned by chromic acid and later on by boiling water and acetone before inserting substrate in the vacuum chamber. The film thickness and deposition rate are 7374 Å and 2-5 Å/s respectively which was measured by quartz crystal monitor.

The quantitative compositional analysis of ZnSe thin film was carried out by energy dispersive X-ray analysis (EDAX). The structural properties of ZnSe film was recorded by X-ray diffractometer (Rigaku, Japan) with Ni-filter CuKα radiation at λ=1.541 Å in the 2θ range 20°-60°. The optical transmittance, absorption and reflectance measurement of the ZnSe film as a function of wavelength was recorded using UV-Visible spectrophotometer (CARY 300, Varian, Australia) in the wavelength range of 300nm - 1100 nm.

III. RESULT AND DISCUSSION

A. Compositional Properties

The chemical composition of the ZnSe film at thickness 7374 Å was determined by energy dispersive x-ray analysis (EDAX) is shown in Fig.1. The peaks of Zn and Se were found which is indicated that the source material is pure and equal proportion. The result of chemical composition of deposited ZnSe thin film is shown in Table 1.
Typical EDAX results shows that the atomic contents percentage of element Zn and Se is found to be 54.4 and 45.6 respectively which showing that the film is almost nearer to stoichiometric. The prepared film had a Se rich composition with an average Zn/Se weight ratio of 0.99 which is good in agreement with the value obtained from other workers [8, 9]. This is due to the vapour pressure of Se is higher than that of Zn and their sticking coefficient are also different.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Net Int.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SeL</td>
<td>50.34</td>
<td>45.63</td>
<td>1,545.4</td>
<td>6.24</td>
</tr>
<tr>
<td>ZnK</td>
<td>49.66</td>
<td>54.37</td>
<td>315.6</td>
<td>10.76</td>
</tr>
</tbody>
</table>

### TABLE I. WEIGHT AND ATOMIC PERCENT OF SE AND ZN FOR ZNSe THIN FILM.

The structural properties of deposited ZnSe thin film were studied by X-ray diffraction method. The XRD spectra of thermally deposited ZnSe thin film of thickness 7374 Å on the cleaned glass substrate is shown in Fig.2.

**B. Structural properties**

The structural properties of deposited ZnSe thin film were studied by X-ray diffraction method. The XRD spectra of thermally deposited ZnSe thin film of thickness 7374 Å on the cleaned glass substrate is shown in Fig.2.

The XRD spectra revealed that the film had three peaks at nearly 20 is equal to 26.98°, 44.96° and 53.24° respectively which correspond to the (1 1 1), (2 2 0) and (3 1 1) reflection which agreed with standard value taken from the JCPDF data file no. 02-0479. Also, it shows that ZnSe film is poly crystalline with cubic zinc blende structure. The other peak observed in XRD pattern due to the amorphous glass substrate and some amorphous present in ZnSe thin film.

### TABLE 2. COMPARISON BETWEEN STANDARD D-VALUE AND OBSERVED D-VALUE OF ZNSe THIN FILM

<table>
<thead>
<tr>
<th>Standard d-value (Å) (JSPDF No.: 02-0479)</th>
<th>Observed d-value (Å)</th>
<th>plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.28</td>
<td>3.30</td>
<td>(1 1 1)</td>
</tr>
<tr>
<td>2.84</td>
<td>-</td>
<td>(2 0 0)</td>
</tr>
<tr>
<td>2.00</td>
<td>2.01</td>
<td>(2 2 0)</td>
</tr>
<tr>
<td>1.72</td>
<td>1.72</td>
<td>(3 1 1)</td>
</tr>
<tr>
<td>1.41</td>
<td>-</td>
<td>(4 0 0)</td>
</tr>
</tbody>
</table>

The lattice parameter (a) of cubic ZnSe film was calculated by following relation [10]:

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}
\]

Where h, k and l is miller planes. The value of lattice parameter is found to be 5.701 Å.

The corrected value of lattice parameter is estimated from Nelson-Riley error function [11];

\[
f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\sin^2 \theta}{\theta} \right)
\]

Where \( \theta \) is angle of diffraction.

The lattice constant is found to have slightly changed in the values for different orientation of the same film. This is due to source of error in the measurement of 2θ. Nelson-Riley plot for ZnSe thin film have been plotted for different lattice parameter against the error function as shown in Fig. 3. The corrected value of lattice parameter is estimated from the intercept at f(θ)=0. The corrected lattice parameter
is 5.679 Å which are closed to bulk ZnSe lattice parameter 5.667 Å (JSPDF No.: 02-0479). However significant change shows that crystallite of film is under strained due to change in nature and concentration of local defects [12].

The entire broadening of diffraction profile is to be due to simultaneous contributions from both particle size (D) and lattice strain (ε) which is calculated by Williamson–Hall method for Cauchy nature of broadened profile [13];

\[ \beta \cos \theta = \frac{\lambda}{D} + 4\varepsilon \sin \theta \]

Where \( \beta \) is full width at half of the maximum (FWHM) and \( \lambda \) is wavelength of incident X-ray.

The Williamson–Hall plot of ZnSe thin film \( \beta \cos \theta \) versus \( \sin \theta \) is linear in nature as shown in Fig.4. Using the least square fit, the intercept and slope of this plot gives the value of grain size and lattice strain which were found to be 28.67 nm and 1.453 x 10^{-3} respectively.

The average dislocation density (\( \delta \)) of ZnSe films is found to be 1.34 x 10^{15} m^{-2} by following expression [14];

\[ \delta = \frac{15\varepsilon}{aD} \]

Also the average internal stress is defined by [14]

\[ \sigma = Y\varepsilon \]

and it is 0.098 x 10^9 Pa.

Where Y is young modulus of bulk ZnSe (67.2 x 10^9 Pa) [15].

C. Optical Properties

The transmittance and reflectance spectra as a function of wavelength which were determined from absorption spectra by following expression [16];

\[ T = \frac{1}{10^\alpha} \quad \text{and} \quad A + T + R = 1 \]

Where A, T and R is absorption, transmittance and reflectance respectively. The nature of absorption, transmittance and reflectance spectra of ZnSe thin film within the range of 300nm -1100 nm are shown in Fig.5.

The absorption spectra as a function of wavelength of ZnSe film exhibits sharp absorption edge corresponds to forbidden energy gap. The shape of absorption spectra for ZnSe thin film shows that deposited ZnSe has stoichiometric composition [17, 18]. The transmittance spectra showed a sudden increase in transmittance near to fundamental absorption region. The maximum transmittance is 74% - 84% in wavelength more than 600 nm and a low transmittance in visible region (≤ 500 nm). The transmittance spectra have two main regions: the fundamental absorption region and the interference oscillation region. The nature of transmittance curve is oscillating type indicates that the prepared ZnSe film has good optical quality and homogeneity with uniform thickness [19].

The absorption coefficient (\( \alpha \)) can be expressed by following expression;

\[ \alpha = \frac{2.303A}{t} \]

Where A is absorption and t is film thickness.

The value of absorption coefficient is high in order of 10^4 cm\(^{-1}\). Thus, ZnSe film is highly suitable for photo sensors and solar cells. The fundamental absorption edge which corresponds to the direct transition between valance band to conduction band can be used to determine the optical
band gap of ZnSe film. The absorption coefficient ($\alpha$) and photon energy ($h\nu$) was related with Tauc’s relation [20];

$$a h\nu = A (E_g - h\nu)^{1/2}$$

Where $E_g$ is optical band gap, $A$ is constant and $\alpha$ is absorption coefficient.

The plot of $(\alpha h\nu)^2$ versus photon energy of ZnSe thin film is shown in Fig.6. The value of optical band gap has been determined by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The value of optical band gap of ZnSe thin film is found to be 2.50 eV.

For lower absorption coefficient value, the absorption is depending exponentially on photon energy according to Urbach relation [21];

$$\alpha = \alpha_e \exp \left( \frac{h\nu}{\Delta} \right)$$

Where $\Delta$ is Urbach energy.

From the above relation, the Urbach energy was calculated by inverse of slope of the linear part of the curve In $\alpha$ versus $h\nu$ as shown in Fig.7. The Urbach energy was found 130.41 meV. The value of Urbach energy is lower (in order of meV) represented that ZnSe thin film has lower density of localized defect states [22].

When electromagnetic radiation is passed through the ZnSe film, a part of energy is lost by absorption and scattering process which is known as extinction coefficient. The extinction coefficient ($k$) of ZnSe thin film was calculated using following relation [22];

$$k = \frac{\alpha \lambda}{4\pi}$$

The variation in the extinction coefficient ($k$) against wavelength curve is as shown in Fig.8. The lower value of extinction coefficient in visible and infrared region is clearly the indication of excellent surface smoothness of ZnSe thin film [23]. Also, the value of $k$ has higher at strong absorption region due the coupling of electron of ZnSe thin film to the oscillating electric field [24]. The oscillatory behaviour of the extinction coefficient appears due to the variation in the absorbance in grain boundaries [16].
D. CONCLUSION

The outcome of compositional, structural and optical properties of the thermally deposited ZnSe can be summarised as follows:

From the energy dispersive X-ray analysis (EDAX), the average atomic ratio of Zn and Se is found to be 54.4 and 45.6 respectively and having ratio 1.19 showing that thermally deposited film have purity form and almost stoichiometric.

From X-ray diffraction, it is found that the film is polycrystalline in nature. The lattice parameter and grain size of the film was calculated. The corrected value of lattice constant is found to be 5.679 Å. This due to the lattice misfit of the film with substrate and presence of defects.

From the optical study, it is found that the deposited ZnSe film on glass substrate is highly transparent. The direct optical band gap and Urbach energy will be making suitable for window layer for solar cell and optoelectronics devices. The lower value of Urbach energy and extinction coefficient is indicated that ZnSe thin film has good surface smoothness and lower defects.

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REFERENCES