EFFECT OF THICKNESS ON STRUCTURAL, MORPHOLOGICAL, AND OPTICAL PROPERTIES OF COPPER (Cu) DOPED ZINC SELENIDE (ZnSe) THIN FILMS BY VACUUM EVAPORATION METHOD

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ABSTRACT

Effect of thickness on structural, optical and morphological properties of 2% copper (Cu) doped zinc selenide (ZnSe) thin films, grown onto chemically and ultrasonically cleaned glass substrate by thermal evaporation method in high vacuum (~10⁻⁶ Torr) were studied. Films of 100, 200, 300 and 400 nm thickness were prepared at 200°C substrate temperature where annealing temperature and annealing time was fixed at 100°C and 1 hour respectively. The X-ray diffraction (XRD) exhibited polycrystalline nature indicating the zinc-blende structure with a preferential orientation along the (111) plane of cubic phase. The grain size was found to be 19.27 nm. Dislocation density and microstrain were also found as 2.691 × 10⁻³ nm⁻² and 1.85 × 10⁻³ respectively. Atomic Force Microscopy (AFM) study confirmed the growth of grains and their distribution over the entire surface of the films. All the films were characterized optically by UV-VIS-NIR spectrophotometer in the photon wavelength ranging from 300 to 1000 nm. The optical transmittance and reflectance were utilized to compute the absorption coefficient, extinction coefficient and band gap energy of the films. The calculated band gap energy was found to increase (2.99 to 3.94 eV) with varying thickness. The maximum transmittance was found to be 87.65% for the 400 nm film.

Key words: Thermal evaporation, Cu-doped ZnSe films, XRD, Optical properties, AFM

INTRODUCTION

The growth of II-VI compound semiconductors has attracted considerable attention due to their novel physical properties and wide range of applications in optoelectronic devices. II-VI compound semiconductors are of interest as high-refractive index materials in multilayer optical coatings since they all have low absorption over a broad wavelength range. This group of semiconductor films have significant roles in wide variety of commercial electronics applications as well as in the development of semiconductor device physics. Among these materials, ZnSe thin films have attracted considerable attention over the years owing to their wide range of application in various optoelectronic devices and as window material for thin film heterojunction solar cells (Adachi 2009, Rumberg et al. 2000). ZnSe is also used as a buffer layer in thin film solar cells (Abu Sayeed and Rouf 2018). Zinc Selenide (ZnSe) is a wide band gap (2.7 eV) n-type semiconductor with attractive properties like optical transmittance, uniformity, low resistivity, mechanical hardness, high electrical conductivity and stability to heat treatment for which ZnSe can be also applied to solid-state gas sensors, sensing arrays, solar cells, photovoltaic cells, touch sensitive screens and thin film transistors (Shaaban et al. 2018, Hassanien and Akl 2018, Rajesh Kumar et al. 2018, Imran et al.)

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Copper is a material with very high thermal and electrical conductivity and it is very cheap (Riveros et al. 2001). It has been reported that optical and electrical properties of ZnSe enhances with Cu doping (Hussein et al. 2019, Ali et al. 2005). It has no obvious role in biological processes and common compounds are not toxic. It is most notably used as a conductor of heat and electricity, as a building material, and as a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement (Tersoff 1984).

There are a number of reports on the different structural, optical and electrical properties of ZnSe polycrystalline thin films prepared by various technique such as Chemical vapor deposition (CVD) (Hsu et al. 1992), Laser assisted evaporation (LAE) (Islam et al. 2004), Metal organic chemical vapor deposition (MOCVD), Electro deposition (ED) (Nweze and Ekpunobi 2014), Photochemical deposition (PD) (Kumaresan et al. 2002), Chemical bath deposition (CBD) (Lokhande et al. 1998), and thermal evaporation (TE) (Miah et al. 2010). Vacuum evaporated ZnSe thin films were prepared by Isam et al. (2015) by varying substrate temperature from 373 K to 573 K keeping thickness constant at 300nm. Structural and optical properties of those films were studied. Optical and morphological studies of thermally vacuum evaporated ZnSe thin films were also studied (Ion et al. 2013).

Cu doped ZnSe thin films of different thicknesses were grown by vacuum evaporation method and the different micro structural parameters of these films were determined from their XRD spectra. Different optical properties and surface morphology by AFM were also studied. In this present work, the effect of thickness of vacuum evaporated Cu doped ZnSe films is investigated to optimize the growth condition for a good quality film which will be suitable for optoelectronic devices.

EXPERIMENTAL DETAILS

The samples were prepared by thermal evaporation method. EU-300 model was used as a vacuum coating unit to fabricate the thin films. Glass slides were used as substrates which were cleaned chemically and ultrasonically. Powder form of ZnSe and Cu were used as source material. The rate of evaporation for ZnSe thin film was 0.2 nm/sec measured in situ by the FTM5 quartz crystal thickness monitor (Edwards, UK). Copper doped (2%) zinc selenide thin films of various thicknesses (100, 200, 300 and 400 nm) were prepared keeping substrate temperature at 200°C. These samples were annealed for 1 hour by keeping the temperature constant at 100°C. A PHILIPS PW 3040 X' Pert PRO X-ray diffraction system was used to get X-ray data for the samples. The powder diffraction technique was used with a primary beam power of 40 KV and 30 mA for Cu – Kα radiation. A UV-3100 (UV-VIS-NIR recording spectrophotometer) was used to investigate the optical properties of thin films. All the data of the samples were analyzed using “XPERT HIGHSCORE” computer software. For surface morphology Nanosurf (Acoustic Enclosure 100) was used.

RESULTS AND DISCUSSION

Structural Properties

Structural properties were investigated by X-ray diffraction (XRD) method. XRD pattern of Cu doped ZnSe thin films deposited at the substrate temperature of 200°C is shown in Fig. 1. The2θ scans of 100, 200 and 300 nm films were between 10° and 60°. The films of thickness of 100 and 200 nm were amorphous. The effect of the amorphous background glass substrate contributed prominently for the random orientation of the crystallites up to the
thickness of 200 nm that resulted in the formation amorphous Cu doped ZnSe thin films (Das et al. 2016). A prominent peak was found at $2\theta = 27.06^\circ$ for 300 nm film after annealing the film at 100°C for 1 hour. This 2\theta value corresponds to (111) plane and indicates a preferential orientation along (111) direction and the phase is cubic which is in good agreement with several reports (Mahalingam et al. 2007, Arslan et al. 2017). The (111) plane is the close packing direction of zinc blende structure. The zinc selenide thin film is face centered cubic (fcc) structure. No other peak was observed besides these which indicates single phase cubic structure of the films (Kalita et al. 2000, Ashraf et al. 2011).

The crystallite size (D) was calculated using the following Scherrer formula,

$$D = \frac{k\lambda}{\beta \cos \theta}$$

And the interplanar distance (d) was calculated using following equation represented as

$$2d \sin \theta = n \lambda$$

The lattice constant (a) was calculated using the equation

$$a = d\sqrt{(h^2 + k^2 + l^2)}$$

The value of Microstrain ($\varepsilon$) was calculated from the equation

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

And dislocation density ($\delta$) was calculated by the equation

$$\delta = \frac{1}{D^2}$$

where, \(\lambda\) is the wavelength of X-ray used as 0.15406 nm for CuKα line, \(k\) is 0.9, \(\beta\) is full width at half maxima (FWHM), \(\theta\) is diffraction angle and \(n\) is positive integer.

The value of different parameters corresponding to the one peak are given below (Table 1).

### Table 1. Values of different parameters of different film thickness of XRD

<table>
<thead>
<tr>
<th>Parameters Name</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size</td>
<td>19.27 nm</td>
</tr>
<tr>
<td>Interplanar distance</td>
<td>0.33 nm</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>0.5716 nm</td>
</tr>
<tr>
<td>Microstrain</td>
<td>$1.85 \times 10^{-3}$</td>
</tr>
<tr>
<td>Dislocation density</td>
<td>$2.69 \times 10^{-3}$ nm$^{-2}$</td>
</tr>
</tbody>
</table>

From Table 1, it can be observed that values of the parameters are well matched with those reported in earlier works (Kissinger et al. 2009, Isam et al. 2015)

![Fig. 1. XRD patterns of 2% Cu doped ZnSe thin films of different thicknesses deposited at substrate temperature of 200°C](image)

**Morphological Properties**

Atomic force microscopy (AFM) was used to determine the surface morphology of 200 nm, 300 nm and 400 nm thick films. The topography of the surfaces in 2d and 3d images are shown in Figs. 2, 3 and 4. There are some white spots in the 2D images of films. The spots indicate that there exists comparatively large grain on the surface of the films (Ion et al. 2013).
Fig. 2. AFM images for Cu doped ZnSe thin films of 200 nm thickness (a) 2D image, (b) 3D image.

Fig. 3. AFM images for Cu doped ZnSe thin films of 300 nm thickness (a) 2D image, (b) 3D image.

Fig. 4. AFM images for Cu doped ZnSe thin films of 400 nm thickness (a) 2D image, (b) 3D image.
The average roughness values of the films are provided in Table 2.

**Table 2. Variation of line and surface roughness with thickness**

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>Line roughness (nm)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>10.22</td>
<td>7.83</td>
</tr>
<tr>
<td>300</td>
<td>11.68</td>
<td>12.36</td>
</tr>
<tr>
<td>400</td>
<td>13.24</td>
<td>12.96</td>
</tr>
</tbody>
</table>

From table 2, it can be seen that average roughness of the films is quite small. So the films are quite smooth. Values in the table also indicate that as film thickness increases the value of roughness increases. So roughness depends on film thickness (Arslan et al. 2017).

**Optical Properties**

For transmittance (T\%) at normal incidence and reflectance (R\%) at near-normal incidence of light on the films, expressions for the multiple reflected systems have been given by Heavens (Heavens 1991) and Tomlin (Tomlin 1968). The simplified expressions are expressed as

\[
\frac{1+R}{1-R} = \frac{1}{T} \left[ \frac{1}{\sinh^2 \alpha_1 + \sinh^2 \alpha_1} \right] \left[ \frac{1}{1 - \sinh^2 \alpha_1 - \sinh^2 \alpha_1} \right]^{1/2}
\]

Where \( n_1 \) and \( n_2 \) are refractive indices of the film and substrate respectively, \( k_1 \) is the extinction co-efficient of the film, \( n_2 \) = 1.45, \( \alpha_1 = 2 \pi k_1 d / \lambda \) and where \( \lambda \) is the wavelength of light and \( d \) is the thickness of the film. Equations (1) and (2) are solved for \( k_1 \) and \( n_1 \) utilizing a computerized iteration process. The absorption co-efficient, \( \alpha \) is then calculated using \( \alpha = 4 \pi k_1 \lambda / \lambda \). Fig. 5 shows the variation of transmittance with photon wavelength varying from 300 nm to 1000 nm of Cu doped ZnSe thin films of different thicknesses such as 100, 200, 300 and 400 nm prepared at a constant substrate temperature of 200°C. It is observed that maximum transmittance (87.65\%) in the visible region is obtained for the thickness 400 nm.

The films of thickness 400 nm also shows good

**Fig. 5.** (a) Variation of transmittance with wavelength for Cu doped ZnSe thin films of different thickness deposited at substrate temperature of 200°C, (b) Variation of reflectance with wavelength for Cu doped ZnSe thin films of different thicknesses deposited at substrate temperature of 200°C
interference pattern which indicates better homogeneity and good quality as shown in Fig. 5(a). It can also be seen that all the films show good transmittance in the visible and infrared region.

The higher transmittance in the visible and infrared regions makes it a strong candidate for use in optoelectronic devices (Lokhande et al. 1998). The spectra also reveal wide transmission range covering 400 nm – 1000 nm. This makes the material useful in manufacturing optical components, windows, mirrors, and lenses for high power IR laser. Here the optical transmittance increases as the film thickness increases (Khairnar et al. 2012, Okereke and Ezenwa 2011).

The variation of reflectance with photon wavelength (range: 300 – 1000 nm) of the Cu doped ZnSe thin films of different thicknesses prepared at a constant substrate temperature of 200°C is shown in Fig. 5(b). The reflectance spectra show interference pattern with distinct peaks and valleys. The reflectance decreases for all the samples in the visible region. It is observed that minimum reflectance (12.03%) at wavelength 630 nm is obtained for the film thickness of 400 nm. The variation of absorption co-efficient $\alpha$ with photon energy of ZnSe thin films of different thicknesses 100, 200, 300 and 400 nm prepared at 200°C substrate temperature is shown in Fig. 6.

![Variation of absorption coefficient with photon energy for Cu doped ZnSe thin films of different thickness deposited at substrate temperature of 200°C](image)

**Fig. 6:** Variation of absorption coefficient with photon energy for Cu doped ZnSe thin films of different thickness deposited at substrate temperature of 200°C.
It is observed that $\alpha$ is maximum for 300 $nm$ film. For the film of 400 $nm$, absorption coefficient becomes constant at high values of photon energy which indicates that the film will never absorb more energy after that level. As observed from the Fig., the feature of the behavior of $\alpha$ versus $h\nu$ can be attributed to free carrier absorption which increases with the increase of the photon energy due to inter band transition of electron from the valence band to the conduction band as reported by El-Nahass et al. (2011). All the films have high absorption coefficient ($\sim 10^5$ $cm^{-1}$) above the fundamental absorption edge. The high absorption coefficient and nearly optimum band gap energy of this material is favorable for solar photovoltaic application (Reichelt and Jiang 1990).

In Fig. 7(a), $(\alpha h\nu)^2$ is plotted against photon energy $h\nu$ to find the value of band gap energy of the thin films of different thicknesses at constant substrate temperature 200$^\circ$C. The linear dependence shown by $(\alpha h\nu)^2$ with photon energy indicates that the transmission is direct (Tomlin 1972). The direct band gap energies of the films were determined by extrapolating the straight portion to the energy axis (Fig. 7b).

It can be observed from Fig. 7(b), that the values of band gap energies of the samples of different thicknesses of 100, 200, 300 and 400 $nm$ were 3.94, 3.79, 2.99 and 3.13 eV respectively. Initially the optical band gap decreases with increase in the film thickness but in case of 400 $nm$ film band gap increases. Higher band gap energy is found when the film thickness is 100 $nm$. This clearly indicates the dependence of optical band gap on thickness of the films. This can be attributed to the improvement in the films crystallinity. Decreasing of the band gap is related to the grain size effect. The bulk ZnSe possesses an optical band gap of 2.7 eV. In the present work the band gap value is seen to be higher than that of bulk material. This may be due to presence of Cu in the films and formation of very small crystalline size on the thin films. It is obvious that film of small thickness is more strained, have small size crystallites and weak orientation which together lead to highly absorbing film (Okereke and Ezenwa 2011).

![Fig. 7.](image-url)
CONCLUSION

It can be concluded that 2% copper doped zinc selenide thin films fabricated by thermal evaporation method have good surface morphology, good crystalline quality and high transparency in visible region. X-ray diffraction analysis showed that the films are of cubic structure with preferred orientation along (111) plane. Surface morphology of the films was carried out by Atomic Force Microscopy (AFM), which showed that line roughness and surface roughness varied between 10 to 13 nm and 7 to 13 nm respectively and this indicated good quality of the thin films. Cu doped ZnSe film of thickness 400 nm showed highest transmittance in visible region and has an average transmittance value of 80% in the Near Infrared (NIR) region. The film of thickness 400 nm showed maximum transmittance 87.65% around the wavelength of 650 nm among the thickness varying films. Film of thickness 100 nm showed maximum optical band gap of 3.94 eV. Optical band gap decreases gradually with the increase of film thickness. The calculated band gaps were found to vary from 2.99 to 3.94 eV. The results obtained in this work are in good agreement with those obtained by other researchers for the same materials. However, data on 2% copper-doped ZnSe thin films were not available before. Therefore, it may be concluded that, 2% Cu-doping gives better structural and optical properties with variable thickness.

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REFERENCES


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