The Influence of Se Concentration on Optical Properties of Thermal Evaporated Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$Thin Films

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ABSTRACT

Thin CZT(S, Se) films were deposited onto glass substrates by thermal evaporation in vacuum 5 x 10$^{-3}$ mbar. Films of thickness 750 nm were prepared at 413K. The optical properties of the films were as convinced by UV-VIS spectrophotometer (photon wavelength ranging between 200 and 1100 nm). Influence of Se concentrations of the films on the optical properties was studied with keeping other deposition parameters fixed. Maximum transmittance decreased with the increase of S concentration. Optical transmittance, reflectance and thickness of the films were utilized to compute the extinction coefficient and optical band gap energy of the films using a computerized process. The nature of the optical transition has been direct allowed with average optical band gap energies ranging between 1.31 eV and 1.62 eV. The optical band gap energy has a tendency to increase with the increase of the S concentration. The optical constants were investigated as a function of Se concentrations. The extent and nature of transmittance and optimized band gap of the material ensure to utilize it for photovoltaic applications.

Keywords: Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ alloys and thin films, thermal evaporation, optical properties

1. INTRODUCTION

Recently there has been a lot of research on CZT(S, Se) in thin film form for its possible applications in UV light emitters, gas sensors, and transparent electronics and solar cells. Several groups have already done much research on CZT(S,Se) by use of various film growth techniques, including Thermal evaporation [1], RF/DC magnetron sputtering [2], chemical bath deposition [3], pulsed laser deposition [4], sol-gel [5] and spray pyrolysis [6]. Although lots of works have been done on CZT(S,Se), it still requires carrying out intensive research to study its fundamental properties in order to obtain better quality films[7]. In optoelectronic device applications, knowledge of the optical parameters such as transmittance and absorption coefficient of semiconductors as well as their electrical properties is necessary for designing appropriate heterostructures [8].

Concerning its significant interest in recent research world, our aim is to have a systematic study on CZT(S,Se) thin film based on vacuum evaporation technique. In this study, CZT(S, Se) thin films of different S concentrations were prepared. Optical properties of the prepared films were investigated by using an ultraviolet-visible (UV-Visible) spectrophotometer. The influence of S concentrations on optical properties was investigated.

2. EXPERIMENTAL DETAILS

The preparation of Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ alloys from source materials Cu, Zn,Sn,Se and S [CZT(S, Se)] with purities of 99.999% and different concentration of Se (x=0.0,0.25,0.50,0.75 and1.0) were done in cleaned evacuate tube with a certain heating process in furnace. The glass substrates were first cleaned by deionized water (DIW) at room temperature (298K) to remove contamination. After the cleaning process, all of the substrates were cleaned in an ultrasonic cleaner for 10 min with ethanol alcohol. The samples were again dipped in DIW. The last step of clean was drying the substrates. Thin Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ films with different Se concentration (x=0.0,0.25,0.50,0.75 and1.0) were prepared on glass substrate by using thermal evaporation technique in a vacuum of 5 x 10$^{-3}$ mbar through different individual evaporation sessions. The evaporator system is Edwards 306. The glass substrate maintained at substrate temperature 413K during the deposition. The molybdenum boat was heated using 1.0 A direct current for 10 minutes to melt the CZT(S, Se) and placed at a distance of 15 cm from the glass substrate. The current was increased slowly to 4.0 A for all of the CZT(S,Se) evaporated. The substrate was removed when the chamber was cool.

Optical properties of the prepared films such as transmittance, absorption coefficient, optical energy gap, refractive index, extinction coefficient, dielectric constants real and imaginary, were investigated as a function of Se concentration by using an ultraviolet-visible (UV-Visible) spectrophotometer in the range 200 - 1100 nm and computerized program.

3. RESULTS AND DISCUSSION
The transmittance versus wavelength behavior of the films was surprising in that the optical absorption edge shifted when the deposition conditions were varied. Data for five samples deposited using substrate temperatures of 413 K and each of film thicknesses was estimated by atomic weight and density for preparation of the near stoichiometric CZT(S,Se) films. The optical properties of the fabricated CZT(S,Se) sample were evaluated by the measurement of the transmittance spectra at room temperature. The absorption coefficient can be calculated from the following expression [9]:

\[ T = (1 - R)^2 = \alpha \]  

(1)

where T is the transmittance, R is the reflectance, \( \alpha \) is the absorption coefficient and t is the film thickness.

Transmittance was measured starting from 1100 nm which reaches to a minimum value at 300 nm of photon wavelength. The variation of transmittance spectra for thin Cu2ZnSn(Se1-xSx)4 films with different concentrations of x(0, 0.25, 0.50, 0.75 and 1.0) were studied as a function of photon wavelength (500 - 1100 nm) which are represented in Fig. (1). The films were dark and uniform to the naked eyes. This is evident from the transmittance curves. Maximum transmittance obtained from this study is 55% at 1050 nm of photon wavelength for thin Cu2ZnSn(Se1-xSx)4 films with thickness of 750 nm. The transmittance was found to decrease with the increase of Se concentration except for sample with x=0.75, the transmittance had lower value. Sharp absorption edge was obtained between (750-900) nm of photon wavelength. The obtained result confirms well with the result of other workers [5],[6].

![Figure 1 Dependence of optical transmittance on wavelength for thin Cu2ZnSn(Se1-xSx)4 films at different Se concentrations.](image)

The optical parameters such as absorption coefficient (\( \alpha \)) and optical band gap were determined from conventional methods. The value of absorption coefficient for strong absorption region of thin film for thickness (t) and absorbance (A) is calculated using the following equation [10].

\[ \alpha = \frac{1}{t} \ln \frac{A}{t} \]  

(2)

Figure (2) showed the optical absorption coefficient of the prepared thin CZTS films as a function of wavelength (\( \lambda \)). The absorption coefficient is larger than 10^4 cm^{-1} in the visible region, which is consistent with those reported in earlier published results [7],[11], and therefore, the film is considered to be a suitable material for photovoltaic solar energy conversion.

![Figure 2 Dependence of absorbance coefficient on wavelength for thin Cu2ZnSn(Se1-xSx)4 films at different Se concentrations.](image)

The optical absorption spectra for the CZT(S,Se) thin films were recorded in the wavelength range of 200-1100 nm. The optical absorption data was analyzed using the following classical relation of optical absorption in semiconductor near band edge [12].

\[ (\alpha h\nu) = A(\nu) - E_g \]  

(3)
where $E_g$ is the separation between bottom of the conduction band and top of the valence band, $h\nu$ is the photon energy and $r$ is a constant. The value of $r$ depends on the probability of transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. Thus, if the plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ is linear, the transition is direct allowed. Also the value of absorption coefficient in the present case is of the order of $10^4$ cm$^{-1}$, which supports direct band gap nature of the deposited CZT(S,Se) material. Extrapolation, of the straight line to zero absorption coefficient ($\alpha=0$), leads to estimation of band gap energy ($E_g$) values. Figure (3) showed variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) for as-deposited precursor film. The optical band gap energy of the as-deposited CZTS thin film was change from 1.62 eV to 1.31 eV depending on the Se concentrations. These results are in agreement with that shown by other researchers [13]-[16]. These values are quite close to the optimum band gap energy for thin film solar cell. The values of optical energy gap at various Se concentrations are tabulated in Table (1).

![Figure 3](image1.jpg)

**Figure 3** Dependence of optical transmittance on wavelength for Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ thin films at different Se concentrations.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$E_g$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.31</td>
</tr>
<tr>
<td>0.25</td>
<td>1.39</td>
</tr>
<tr>
<td>0.50</td>
<td>1.50</td>
</tr>
<tr>
<td>0.75</td>
<td>1.57</td>
</tr>
</tbody>
</table>

The extinction coefficient ($k$) can be calculated by using the relation [9]:

$$k = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (4)

The variation of extinction coefficient with wavelength of incident radiation for thin CZT(S, Se) films is shown in Fig. (4). Extinction coefficient is found to decrease with increasing wavelength for thin CZT(S, Se) films as a function of Se concentration. The increase in Se concentration caused shifted $k$ curve to higher wavelength.

![Figure 4](image2.jpg)

**Figure 4** Dependence extinction coefficient on wavelength for thin Cu$_2$ZnSn(Se$_x$S$_{1-x}$)$_4$ films at different Se concentrations.
The refractive index (n) is determined using the following equation [9].

\[ n = \left( \frac{1 + R}{1 - R} \right)^2 - \left( \frac{k^2 + 1}{k^2 - 1} \right)^{1/2} + \frac{1 + R}{1 - R} \] (5)

The variation of refractive index with wavelength of incident radiation for thin CZT(S, Se) films is shown in Fig. (5). Refractive index is found to decrease as a function of wavelength for CZT(S, Se) thin films. The peak of refractive index shifted to higher wavelength (lower photon energy) with increasing Se concentration. At higher wavelength of the incident photon, the refractive index tends to be constant. The decrease in the value of the refractive index with photon wavelength showed a normal semiconducting dispersion behavior of the material and higher IR activity. It is obvious that a remarkable variation is observed in both n and k values.

The dielectric constant which is another important optical parameter can be defined as:

\[ \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \] (6)

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary parts of dielectric constant can be calculated with using n and k values [9].

The real dielectric constant (\( \varepsilon_r \)) can be calculated as:

\[ \varepsilon_r = n^2 - k^2 \] (7)

while the imaginary dielectric constant (\( \varepsilon_i \)) can be calculated as:

\[ \varepsilon_i = 2nk \] (8)

The variation of the real and imaginary dielectric constants with wavelength (\( \lambda \)) are shown in Figs.(6 and7). It is clear from these figures that the real and imaginary parts of the dielectric constant showed a similar behavior. The peak of real and imaginary dielectric constants shifted to higher wavelength (lower photon energy) with increasing Se concentration. It is also clear that the values of the real part of dielectric constant are more than the imaginary part. The variation of the dielectric constant with wavelength indicates that some interactions between photons and electrons are produced in this range.

Figure 5 Dependence of optical transmittance on photon wavelength for thin \( \text{Cu}_2\text{ZnSn(Se,S)\text{S}_x\text{S}_{1-x})} \) films at different Se concentrations.

Figure 6 Plot of real part of dielectric constant vs. \( \lambda \) for thin \( \text{Cu}_2\text{ZnSn(Se,S)\text{S}_x\text{S}_{1-x})} \) films at different Se concentrations.
4. CONCLUSIONS

Thin CZT(S,Se) films were prepared by thermal evaporation technique from preparing Cu$_2$ZnSn(S$_1$Se$_x$)$_4$ alloys at different Se concentrations. The nature of the optical absorption for thin CZT(S,Se) films above the fundamental absorption edge is direct allowed optical transition. Optical energy gap decreased with increasing the concentration of Se. The peaks for all optical constant shifted to higher wavelength with increasing Se concentrations. The synthesis of pure thin Cu$_2$ZnSn(S$_1$Se$_x$)$_4$ films reported here in now provides an avenue for probing the effect of Se inclusion in mixed-chalcogenide thin films. The optical properties of the films could be changed by optimizing the growth parameters which is an important achievement for thin film technology. The results obtained from this study are interesting to be utilized in the field of optoelectronic technology.

REFERENCES

