Structural and Optical Properties of the New Absorber Cu$_2$ZnSnS$_4$
Thin Films Grown by Vacuum Evaporation Method

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Abstract

This work studies dependences of structural and optical properties on the substrate temperature of Cu$_2$ZnSnS$_4$ thin films deposited onto glass substrates by thermal evaporation method. The thicknesses of the films were in the range 500-600 nm. Their structure and composition are studied by X-ray diffraction, scanning electron microscopy, dispersive X-ray spectroscopy, optical reflectance and transmittance measurements. The variations of the Microstructural parameters, such as crystallite size ($\langle L \rangle$), dislocation density ($\langle \delta \rangle$), stacking fault probability ($\alpha$) and strain ($\varepsilon$), with substrate temperature were investigated. The results show the crystallite sizes increase as the substrate temperature increases. The variation of the dislocation density and the stacking fault probabilities and strain decrease as the substrate temperature increases. Optical measurements show that all the CZTS thin films have relatively high absorption coefficient between $10^4$ and $10^5$ cm$^{-1}$ with p-type conductivity.

1. Introduction

In order to avoid the problems related to CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) like the use of the rare elements In, Ga and toxic ones such as Se, some research groups have turned their attention to alternative absorber compounds with similar...
properties. With an absorption coefficient of $10^4 \text{cm}^{-1}$ and band gap energy close to 1.45 eV [1]. The quaternary semiconductor Cu$_2$ZnSnS$_4$ (CZTS) is a relatively new photovoltaic material and is expected to be interesting for environmentally amenable solar cells, as its constituents are nontoxic and abundant in the Earth’s crust [2]. The quaternary compound, Cu$_2$ZnSnS$_4$ (CZTS), shows properties that make it a good candidate to replace CIGS. The CZTS thin films show p-type conductivity, a band gap of 1.44–1.51 eV that is ideal to achieve the highest solar-cell conversion efficiency and relatively high optical absorption of $1 \times 10^4 \text{cm}^{-1}$ [3]. However, the highest conversion efficiency of CZTS reported so far is 7% [4,5], demanding further improvement for practical applications. Several research groups have reported the fabrication of CZTS crystals by using iodine vapor transport method [6,7], the one-pot synthesis of colloidal nanoparticles [8,9] and modified Bridgman method [10]. CZTS thin films have been fabricated using various physical and chemical vapor deposition techniques, such as thermal evaporation of the elements and binary chalcogenide [11], spray method [11,13], sulfurization of precursors [14], rf sputtering [11,15], hybrid sputtering [16], co-evaporation [17], pulsed laser deposition (PLD) method [18-20], Photochemical deposition [21], electrodeposition [22,23], electroplating techniques [24], Soft chemistry methods [25] and Sol-gel deposited precursors with post sulfurization processing [26]. In this study, CZTS was synthesized using simple horizontal Bridgman method in order to prepare a solid bulk compound CZTS target material for physical vapor deposition. It is expected in the near future that the synthesized powders could also be used as a starting powder for preparing CZTS thin films by using vacuum thermal evaporation technique. The influences of substrate temperature on the structural properties of thin films are very important. Many reports on the effect of substrate temperature of various materials have been published [27,28]. As is well known from the literature, no work providing a detailed explanation of the effect of substrate temperature on the properties of CZTS thin films deposited by thermal evaporation method has been reported so far. Furthermore, substrate temperature of thin films can be used to modify the crystallinity and structural parameters of thin films. Therefore, in the present paper, we have investigated the effect of substrate temperature on the structural and optical properties and microstructural parameters of CZTS thin films.

2. Experimental methods

2.1. Film preparation

Cu$_2$ZnSnS$_4$ thin films were deposited on a Corning 7059 with a 0.7 mm thick glass substrate by thermal evaporation method of the CZTS powder in a high vacuum system. The chamber was evacuated to a pressure of under $10^{-6}$ Torr before deposition. A tungsten crucible was used. The distance between the crucible and the substrate was approximately 10-12 cm. Thermal evaporation sources were used which can be controlled either by the crucible temperature or by the source powder. The substrates were kept at temperature of RT, 70, 125, 150 and 200°C, respectively. The mass of the introduced powder was not changed to yield the same film thicknesses.

2.2. Film characterization

Film thickness was measured by interference fringes method [29] and was in the range 500-600nm. The crystal structure of the deposited films was identified by X-ray diffraction (XRD). XRD patterns of the films were obtained using a D8 Advance diffractometer with monochromatic high-intensity CuK$_\alpha$ radiation $\lambda = 0.1506\text{nm}$. The microstructure was observed by scanning electron microscopy technique (SEM), using Philips XL 30 equipment. The chemical composition of the films has been assessed by an energy dispersive X-ray spectrometer (EDAX). The optical transmittance and reflectance of the CZTS thin films was measured with an UV-VIS-NIR spectrophotometer (Shimadzu UV3100F) in the wavelength range of 300-1800nm. The hot probe method measurements were carried out in order to determine the conduction types of the samples.
3. Results and discussion

3.1. Structural properties

Fig. 1 displays the X-ray diffraction patterns for Cu₂ZnSnS₄ thin films prepared at different substrate temperature. The different peaks are indexed and the values of interplanar spacing d are calculated and compared with standard 2 theta and d values (2003 JCPDS database No: 26-0575). Table 1 presents the calculated 'd' values and the corresponding indices, respectively. The peak intensity increases with substrate temperature and the X-ray spectra are polycrystalline in nature. Also, the X-ray diffractions patterns indicate that the films deposited at RT were amorphous whereas for higher temperatures, the amorphous background was diminished and diffraction peaks (112) and (220) of Cu₂ZnSnS₄ appeared. The peaks intensity and sharpness increased with increasing substrate temperature. This confirms that crystallinity of the films improves with increasing substrate temperature.

![X-ray diffraction patterns of Cu₂ZnSnS₄ thin films deposited at different substrate temperature.](image)

Table 1. Structural information obtained from XRD patterns for Cu₂ZnSnS₄ thin films with different substrate temperature that compared with JCPDS-No: 26-0575. (Ref. 2003 JCPDS database).

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>hkl</th>
<th>2θ (°)</th>
<th>d-spacing d_{hkl} (nm)</th>
<th>Lattice parameters (nm)</th>
<th>FWHM (°)</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>a=b</td>
<td>c</td>
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<tr>
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<td>112</td>
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<td>0.3302</td>
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<tr>
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<td>46.35</td>
<td>0.1957</td>
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</table>
3.2. Elemental composition

Energy dispersive X-ray analysis (EDAX) was employed to determine the elemental composition of Cu2ZnSnS4 thin films deposited at different substrate temperature. The concentrations of Cu, Zn, Sn and S were obtained by EDAX at three different zones on the surface of each sample and the corresponding average values are shown in Fig. 2. The squares, circles, triangles and stars in the figure indicate Cu, Zn, Sn and S at % in different substrate temperature Cu2ZnSnS4 thin films. We present in Table 2 the Cu/Zn+Sn and 2Cu+4(Zn+Sn)/3S ratio against substrate temperature of Cu2ZnSnS4 thin films deposited at different substrate temperature. It is clear that films become more stoichiometric with increasing substrate temperature. Scanning electron microscopy was also used to observe the microstructure of the CZTS films. Fig. 3 shows the scanning electron micrographs (SEM) of Cu2ZnSnS4 films deposited at room temperature RT and at 200°C, with a thickness of about 600 nm. Particles growth was distributed at the surface and the distribution become more homogeneously at higher substrate temperature. The crystallite sizes were found in nanoscale and estimated at about 50-125 nm and all CZTS thin films exhibit p-type conductivity.

The effects of the strain ($\varepsilon$) and crystallite sizes ($L$) on the FWHM can be expressed by the following equation (Williamson–Hall method) [30-32]:

$$\beta \left( \cos \frac{\theta}{\lambda} \right) = \frac{1}{L} + \varepsilon \left( \sin \frac{\theta}{\lambda} \right)$$

Where $\beta$ is the measured FWHM (in radians), $\theta$ is the Bragg angle of the peak, $\lambda$ is the X-ray diffraction wavelength, $L$ is the effective crystallite size, and $\varepsilon$ is the effective strain.

The dislocation density ($\delta$), defined as the length of the dislocation lines per unit volume of crystal, is evaluated using the formula, [33-35]:

$$\delta = \left( \frac{n}{L^2} \right)$$

Where $n$ is a factor that equals unity when the dislocation density is minimum and $L$ is the crystallite size.

The stacking fault probabilities were calculated from the shift of the peaks of the X-ray lines of the films with reference to the 2003 JCPDS database No: 26-0575, using the relation between the stacking fault probability $\alpha$ and the peak shift $\Delta(2\theta)$ proposed by Warren and Warekois [37]:

$$\alpha = \left[ \frac{2\pi^2}{45 \sqrt{3} \tan \theta} \right] \Delta(2\theta)$$
Fig. 3. SEM photographs of Cu₂ZnSnS₄ thin films deposited at (a) RT and (b) 200°C.

Table 2. Cu/(Zn+Sn) and 2Cu+4(Zn+Sn)/3S ratio against substrate temperature for Cu₂ZnSnS₄ thin films.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Cu/(Zn+Sn)</th>
<th>2Cu+4(Zn+Sn)/3S</th>
</tr>
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<tbody>
<tr>
<td>RT</td>
<td>1.32</td>
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</tr>
<tr>
<td>70</td>
<td>1.28</td>
<td>1.27</td>
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<tr>
<td>200</td>
<td>1.16</td>
<td>1.14</td>
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</table>

In fig. 4, $\beta(\cos\theta/\lambda)$ is plotted versus $(\sin\theta/\lambda)$ for CZTS deposited at different substrate temperature. The effective crystallite size that has taken the strain into account can be estimated from the extrapolation on the plot shown in Fig. 4. The slope of the fitted line indicates the presence of strain in the CZTS crystal lattice. Table 3 presents the crystallite size (L), strain ($\epsilon$), dislocation density ($\delta$) and stacking fault probabilities ($\alpha$). Fig. 5 plots the variation of the crystallite size (L) and strain (\(\epsilon\)) with the substrate temperature of the films. Fig. 6 plots the variation of dislocation density (\(\delta\)) and stacking fault probabilities (\(\alpha\)) with substrate temperature. The crystallite size increases with substrate temperature of the films and strain decreases with substrate temperature of the films, as shown in Figure 5. The increase in the crystallite size may be caused by a columnar grain growth in the structure.

Fig. 4. Williamson-Hall plots of Cu₂ZnSnS₄ thin films deposited at different substrate temperature.
Table 3. Microstructural parameters of Cu$_2$ZnSnS$_4$ thin films deposited at different substrate temperature.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Crystallite size L (nm)</th>
<th>Strain $\varepsilon \times 10^{-3}$</th>
<th>Dislocation density $\delta \times 10^{14}$(lin.m$^{-2}$)</th>
<th>Stacking fault probability $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70</td>
<td>50</td>
<td>15</td>
<td>4.00</td>
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<td>125</td>
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<tr>
<td>150</td>
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<td>125</td>
<td>1.5</td>
<td>0.64</td>
<td>0.0220</td>
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</tbody>
</table>

Fig. 5. The crystallite size and lattice strain against substrate temperature for Cu$_2$ZnSnS$_4$ thin films.

Fig. 6. Dislocation density and stacking fault probability against substrate temperature for Cu$_2$ZnSnS$_4$ thin films.

3.3. Optical properties

Figs. 7 and 8 show the reflectance and transmittance spectra of CZTS thin films grown at different substrates temperatures.

Fig. 7. Optical reflectance spectra of Cu$_2$ZnSnS$_4$ thin films deposited at different substrate temperature.

Fig. 8. Optical transmittance spectra of Cu$_2$ZnSnS$_4$ thin films deposited at different substrate temperature.
The optical reflectance of these films varies over the range 20-40% and the transmittance is over 80% in the visible region and the fundamental absorption edges have been clearly observed for all samples. A decrease in transmittance with substrate temperature is observed when Temperature is more than 150°C. This decrease in transmittance is due to the increase in crystallinity of films which results in higher scattering of light. The ripples in transmittance and reflectance spectra are attributed to optical interference effects.

The absorption coefficient $\alpha$ of CZTS thin films can be calculated from the following relation [38]:

$$\alpha = \frac{1}{d} \ln \left( \frac{(1-R)^2}{T} \right)$$

Here $T$ is the transmittance, $R$ is the reflectance and $d$ is the film thickness.

Fig. 9 shows the absorption coefficients $\alpha$ (hv) versus the photon energy (hv) for CZTS thin films added at different substrate temperatures. It can be seen that all the films have relatively high absorption coefficients between $10^4$ cm$^{-1}$ and $10^5$ cm$^{-1}$ in the visible and the near-IR spectral range. It is also noted that the absorption coefficient increases with growing substrate temperature.

Fig. 9. Absorption coefficient spectra of Cu$_2$ZnSnS$_4$ thin films deposited at different substrate temperature.

4. Conclusion

The relationships between substrate temperature of Cu$_2$ZnSnS$_4$ thin films and structural and optical properties are studied. The higher substrate temperatures of CZTS develop more perfect microstructures. The crystallite sizes increase as the substrate temperature of the films increases. The variation of the dislocation density and the stacking fault probabilities and strain decrease as the substrate temperature increases. Stresses in the layers and the dislocation density decrease because the stresses that have built-up in the layers are released as the substrate temperature increases. All the CZTS thin films have relatively high absorption coefficient between $10^4$ and $10^5$ cm$^{-1}$ with p-type conductivity.

References

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