Growth and Characterization of CZTS Thin Films Synthetized by Electrodeposition Method for Photovoltaic Applications

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Abstract. In the present work we deposited CZTS absorber material using a one-step electrodeposition method on ITO glass substrates. We studied the effect of sulfurization temperature on structural, morphological and optical properties of CZTS thin films sulfurized in N2+H2S atmosphere at 350, 375, 400 and 425°C for 10 min respectively for 10 min. The films have been characterized by different techniques including X-ray diffractometer (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and UV-visible-NIR spectrophotometer. XRD patterns indicated kesterite CZTS with preferential orientation along (112) plane, the intensity of peaks increased with increase of sulfurization temperature signified the amelioration of the crystallinity with sulfurization temperature increased, the estimated crystallite size are in the range of 14.27-37.32 nm. Raman scattering experiments confirmed the presence of CZTS thin films by the characteristic peak at 336 cm⁻¹. SEM images showed the morphology of CZTS thin films improved with increasing of sulfurization temperature. UV-Visible-NIR spectrophotometer showed that the values of optical absorption coefficient are larger than 10⁴ cm⁻¹ and optical band gap energy of CZTS thin films decreased with increasing of sulfurization temperature ranging 1.56 and 1.66 eV. These results make the electrodeposited CZTS films a suitable material as absorber material in solar cells applications based thin films.

Keywords: CZTS, electrodeposition, sulfuration, thin films, gap energy.

1. Introduction

The first p Copper ternary and quaternary chalcogenide compounds are the most promising absorber materials for use in solar cells based thin films due to their high conversion efficiency [1, 2]. Copper zinc tin sulphur CZTS attracted considerable attention in recent years because there suitable properties for photovoltaic devices such as p-type conductivity direct band gap approximated to 1.5 eV and
optical absorption coefficient larger than $10^4$ cm$^{-1}$ ranging the visible spectrum [3]. The elements constituents of the quaternary CZTS thin films are non-toxic and abundant in the crust of the earth making them favourable replacements for copper indium gallium sulphur CIGS in which Zn and Sn substitutes In and Ga respectively. Wang et al achieved the champion conversion efficiency of 12.6% in 2014 for solar cells based Cu$_2$ZnSn(S,Se)$_4$ thin films prepared by spin coating technique using hydrazine based solution process in laboratory conditions [4]. The theoretical conversion efficiency reported by shockley–Queisser of CZTS films is about 32.2% [5]. Several methods employed to elaborate CZTS thin films such as pulsed laser deposition [6], chemical bath deposition [7], co-evaporation [8], electron beam evaporation [9], sputtering [10], spray pyrolysis [11], silar [12], spin coating [13], dip coating [14] and electro-deposition [15]. Among these methods, Electrodeposition is applied alternative for elaborate the thin films for solar cells applications. Non vacuum electrochemical deposition process is low cost and environmentally friendly industrial production, usually electrodeposition method can be devised into two categories are two steps process where the deposition of Cu-Zn-Sn followed by sulfurization for obtain CZTS thin films and single step is the deposition of copper (Cu), zinc (Zn), Tin (Sn) and sulfur (S) directly from electrolyte to prepare CZTS films.

Several groups presented in the literature have attempted the fabrication of CZTS films using electrodeposition method, Ennaoui et al prepared CZTS solar cells by one step electrochemical deposition of Cu-Zn-Sn followed by sulfurization using a gas combination of Argon with H$_2$S during 2h at 550°C, to show CZTS thin films. Secondary phases were formed with CZTS phase including ternary Cu$_2$SnS$_3$ and binary ZnS. The device obtained conversion efficiency of 3.4% [16]. Araki et al have produced CZTS thin films using electrodeposited CZT staked and precursors containing Cu-Zn-Sn. Sulfurization needed at 600°C duration 2h in an N$_2$ to result CZTS films with the best efficiency of 3.16% [17]. Scargg et al have synthetized thin films solar cells based CZTS absorber material by sequential electrochemical deposition of metallic precursor Cu/Sn/Cu/Zn stack onto Mo-coated soda lime glass substrates followed by annealing the stack with (H$_2$S + N$_2$) atmosphere for 2h at 575°C with 100 mg of sulfur (S) to get CZTS thin films. ZnS and Cu$_2$SnS$_3$ phases were showed with kesterite CZTS phase. The showed conversion efficiency of solar cell based electrodeposited CZTS of 3.2% [18]. Pawar et al prepared CZTS thin films by single step electrodepostion method followed by annealing at N$_2$+H$_2$S (95%/+5%) atmosphere at 550°C for 1h [19].

In this work we focus on the synthesis of CZTS thin films by single step electrodeposition method onto ITO coated glass substrates at 50 min to study the influence of sulfurization temperature in the range between 350 and 425°C by step of 25°C in the N$_2$+H$_2$S atmosphere during 10 min on the structural, morphological and optical properties of CZTS absorber material by XRD, Raman, SEM and UV–vis spectrophotometry, respectively. The some optical parameters were calculated to ameliorate the photovoltaic devises.

2. Experimental Details

Precursor solution for elaborate CZTS films were prepared from electrolytic solution containing of copper sulfate (0.02 M) CuSO$_4$, zinc sulfate (0.01 M) ZnSO$_4$, tin sulfate (0.02 M) SnSO$_4$ and sodium thiosulfate (0.02M) Na$_2$S$_2$O$_3$ using a single-step electrodeposition method. Electrodeposition was carried out potentiostatically in a three-electrode cell configuration where the reference electrode was Ag/AgCl and the counter electrode, a platinum wire, and ITO coated glass substrate were used as a working electrode. The ITO substrates were ultrasonically cleaned with acetone and ethanol for 20 min, rinsed with distilled water and subsequently dried. The 0.2 M trisodium citrate was used as a complexing agent. The PH of the solution was adjusted to 4.5 by adding tartaric acid. The applied potential was used fixed at -1.05 V, during the deposition the bath temperature were maintained 25°C without magnetic stirrer. All the samples were deposited at 50 min, subsequently the as deposited samples were sulfurized in N$_2$+H$_2$S atmosphere at 350, 375, 400 and 425°C for 10 min.

The structural properties were determined using X-ray diffractometer (XRD) using CuK$\alpha$ radiation ($\lambda = 1.54060$ Å) scanning angle (20°-60°) and Raman scattering experiments in the frequency range of
0-1000 cm⁻¹. The morphological properties were characterized by field-emission scanning electron microscopy (FESEM), UV-Visible-NIR spectrophotometer were used employed to control the optical properties.

### 3. Results and discussion

#### 3.1. Structural properties

Figure 1 shows the X-ray diffraction of annealed CZTS thin films. All samples indicate the peaks corresponding to the CZTS thin films situated about 28.32°, 29.51° and 56.21° respectively for (112), (103) and (312) planes. The preferential direction of (112) plane and peaks corresponding to the CZTS thin films confirmed the existence of kesterite CZTS phase of all films matched by (JCPDS-26-0575). The intensity of (112) peak increased with increasing of annealing temperature which prove that the crystallinity of the films ameliorate when the CZTS is annealed at 425°C. The intensity of peaks is better to the obtained by Chtouki et al [20]. The extra peaks are indicating to presence of secondary phases SnS at 24.15 according to (JCPDS 01-083-1758) and Cu₂Sn₃S₈ at 34.33° and 75.45° according to (JCPDS 27-0197). Other peaks corresponding to the (ITO) glass substrates observed at various films according to (JCPDS-00-006-0416). Figure 2 indicates the sample annealed at 425°C for clarified the X-ray diffraction peaks.

The crystallites size (D) of electrodeposited CZTS thin films is calculated using Debye Scherrer formula (1) [21], where k is the shape factor (k=0.94), θ is Bragg diffraction angle, λ is the wavelength of the X-ray diffractometer and β is the full-width at half maximum of the peak. “D” expressed using formula (1). Dislocation density value shows the quantity of defects in the structure. Higher dislocation density values show minor crystallinity for the thin films. The dislocation density (℅) is defined as the dislocation lines per unit volume of the crystal and expressed from the crystallite size using formula (2) [22]. The micro-strain (s) of the films was calculated by using the relation (3) [23]. Crystallite size, dislocation density and micro-strain were tabulated in the Table 1. The crystallite size of the samples annealed at 350, 375, 400 and 425°C is 14.27, 29.52, 30.58 and 37.22 nm respectively, the dislocation density of CZTS thin films is decreased with sulfurization temperature increased from 4.9×10¹⁶ to 0.72×10¹⁶ (Lines/m²), These behaviours indicate the decreasing of the defect in a electrodeposited CZTS absorber layers with sulfurization temperature increased. These values are close to the reported by Rondiya et al for CZTS thin films prepared by RF sputtering method [24].

\[
D = \frac{k \lambda}{\beta \cos \theta} \tag{1}
\]

\[
\text{℅} = \frac{1}{D} \tag{2}
\]

\[
s = \frac{\beta}{4 \tan \theta} \tag{3}
\]

Raman scattering measurements was used to confirm the presence of CZTS phase because of benary ZnS and ternary CuₓSn₃ have similar two theta values to CZTS phase. Raman spectra of all samples showed in Figure 3. Only single peak located at position 336 cm⁻¹ is corresponding to the kesterite CZTS thin films, this Raman peak obtained by several authors reported by various elaboration methods [24, 25]. The intensity of Raman peak increases with sufruziation temperature increased, this behavior confirmed the results obtained in the (XRD). No other binary and ternary phases were identified in the Raman shift range from 0 and 1000 cm⁻¹, including ZnS (Raman peak about 356 cm⁻¹) [26], Cu₂Sn₃S₈ (Raman peaks about 297 cm⁻¹, 352 cm⁻¹ and 374 cm⁻¹) [27], Cu₂S (Raman peak about 475 cm⁻¹) [28], SnS₂ (Raman peak about 315 cm⁻¹) [29], Cu₃SnS₄ (Raman peaks about 318 cm⁻¹, 348 cm⁻¹, and 295 cm⁻¹) [30].
Figure 1. XRD patterns of the electrodeposited CZTS thin films at sulfurized at various temperatures

Figure 2. XRD patterns of the electrodeposited CZTS thin films at sulfurized at various temperatures
Table 1. Microstructural information of CZTS thin films with (112) plane

| Annealing Temperature (°C) | Crystallite size D (nm) | Dislocation density $\bar{d}$ x 10$^{16}$ (Lines/m$^2$) | Micro-strain $\times 10^{-2}$ $\varepsilon$ |
|---------------------------|------------------------|---------------------------------------------------------|------------------------------------------|
| 350                       | 12.27                  | 4.91                                                    | 0.74                                    |
| 375                       | 29.52                  | 1.14                                                    | 0.50                                    |
| 400                       | 30.58                  | 1.06                                                    | 0.48                                    |
| 425                       | 37.22                  | 0.72                                                    | 0.40                                    |

Figure 3. Raman scattering measurements of CZTS thin films sulfurized at different temperatures

3.2. Morphological properties

The CZTS thin films formation rely on nucleation, coalescence and growth phenomena, and this depending on several growth parameters such as Thickness, annealing temperature, deposition time, concentration of precursors. In fact, the temperature plays a major role for CZTS growth, behaving as kinetic energy for the substrates to enhance the ability to diffuse the incident atoms into the substrate surface. Generally, the adatoms (adsorbed atoms) move on the surface until finding the best nucleation centers and creation the clusters, which are developing by the temperature effect.

Figure 4 shows the CZTS film growth process by controlling the sulfurization temperatures. At low temperature the substrate is not totally covering by the material and the shape of clusters are not stable demonstrating the insufficient temperature (energy) for grain formation and crystallization of CZTS phase, by increasing temperature from (a) to (c) the nucleation enhances and the coalescence starts. There where, the produced clusters agglomerate via cluster-cluster interaction, controlling the form of particles and resulting small particles in semi-granular form as seen in the Figure (c). These clearly shows the effect substrate temperature which influences the film morphology by modifying the
growing mechanism through a control of the interaction taking place at the CZTS solution–substrate interface. The final state is the crystallization of CZTS films as shown in Figure (d) with the appearance the tetragonal form of particles.

Figure 4. SEM images of CZTS thin films growth at (a) 350°C, (b) 375°C, (c) 400°C and (d) 425°C

3.3. Optical properties

The transmittance and absorbance data of CZTS thin films were examined by UV-visible spectrophotometer. The wavelength of incident light is ranging from 400 and 1050 nm. The Figure 5 exhibits the transmittance as a function of the wavelength $\lambda$, the transmittance of the annealed films increase with annealing temperature increased in the visible region, in the wavelength between 400 and 700 nm the transmittance of radiation is lower than 30% and after 800 nm the transmittance of the samples is shifted, this behaviour shows that the absorption of photon energy is changing in the high wavelength of incident light (800-1050 nm). Figure 6 shows the absorbance spectra of CZTS thin films versus the wavelength $\lambda$, the maximum absorbance of the films annealed at 350, 375, 400 and 425°C is 1.45, 1.51, 1.65 and 2.12, respectively. The suitable absorbance of the samples annealed at
425°C is due to more absorption of photon energy from CZTS thin film. These results are near to reported in the literature for an absorber material for photovoltaic applications [31, 32].

Using the measured transmittance data the absorption coefficient (α) of the samples annealed at different temperature was calculated followed the relation (4) [33].

\[ \alpha = \frac{2}{d} \ln \left( \frac{1}{T} \right) \]  

(4)

where d is the thickness of the films. The optical absorption coefficient of all annealed CZTS thin films showed in the Figure 7 present the values great than \(10^4\) cm\(^{-1}\), this values are in agreement literature for CZTS absorber materiel for solar cell applications [34, 35].

The direct band gap of CZTS absorber layer was calculated using Tauc’s relation [36]:

\[ (\alpha h\nu)^2 = C(h\nu - E_g)^2 \]  

(5)

where C is a constant, \(E_g\) is the optical band gap energy, \(h\nu\) is the incident photon energy and \(\alpha = \frac{2}{d} \ln \left( \frac{1}{T} \right)\) because of CZTS thin films has the direct allowed transition. Figure 8 presents the graph of optical band gap energy (\(E_g\)) for electrodeposited CZTS thin films and inset Figure 8 indicate the \((\alpha h\nu)^2\) versus \(h\nu\) of the films annealed at different temperature. The band gap was determined by extrapolating the linear part of the plot versus photon energy \(h\nu\) to \((\alpha h\nu)^2=0\). The obtained gap energies are 1.66, 1.64, 1.60 and 1.56 eV for CZTS growth at 350, 375, 400 and 425°C respectively. The gap energy of CZTS thin film annealed at 425°C is suitable for photovoltaic applications [37]. The optimum band gap energy of CZTS thin films is 1.5 eV, the shift of band gap is due existence of secondary phases observed in the XRD patterns. With increase in the sulfurization temperature the optical band gap energy is deviated to low energies, when the sulfurization temperature increased more energy is applied to improve the crystallinity of the material, which naturally decreases the band gap of CZTS absorber layer. The intensity of X-ray diffraction peaks of electrodeposited CZTS thin films increased with increasing of sulfurization temperature leading the enhancement of FESEM images quality and reducing of band gap energies, this behaviour is reported by previously study [38, 39].
Figure 6. Absorbance data versus wavelength $\lambda$ for CZTS absorber material

Figure 7. Optical absorption coefficient $\alpha$ of CZTS thin films as a function of wavelength $\lambda$. 
Refractive index ($n$) is an essential parameter in optical communication and representation of the optical devices. The refractive index ($n$) can be calculated from the reflectance ($R$) coefficient following the relation (6) [40]. Extinction coefficient ($k$) signifies the amount of absorption of electromagnetic wave in a semiconductor material due to inelastic scattering phenomena. The extinction coefficient can be determined from the absorption coefficient ($\alpha$) using the relation (7) [41]. Real part ($\varepsilon_r$) of dielectric constant related to slowing down of speed of light in the medium. Imaginary part ($\varepsilon_i$) of the dielectric constant defined by the correlation of the interaction of matter with the electric field vector. Real and imaginary dielectric constants are essential intrinsic properties of a material. The real and imaginary dielectric constants can be calculated using the equations (8) and (9) [42].

\[
\begin{align*}
\alpha &= \frac{2\pi n \sin \theta}{\lambda} \\
\beta &= \frac{2\pi k \sin \theta}{\lambda} \\
\varepsilon_r &= \frac{\alpha}{\beta} \\
\varepsilon_i &= -\frac{\alpha}{\beta}
\end{align*}
\]

where “$R$” is reflectance, “$n$” is refractive index “$k$” is extinction coefficient, “$\varepsilon_r$” is real dielectric constant and “$\varepsilon_i$” is imaginary dielectric constant. The refractive index increases with the sulfurization temperature increase in the wavelength range of 400 and 1050 nm. According to Figures 9 and 10, the high values of refractive index of the electrodeposited CZTS absorber material with different sulfurization temperature can be attributed to the enhancement in the crystallinity of the films [44]. A film with high density gives rise to a high refractive index. The values of refractive index are in the range of 1.51-7.27, these values are comparable by Babichuk et al for CZTS thin films [43]. The decreasing of refractive index with increasing of wavelength $\lambda$ signifies the normal dispersion behaviour. The extinction coefficient increases with increasing of sulfurization temperature in the wavelength range of 400-800 nm, from the 800 to 1050 nm we observe the deviation of extinction.

Figure 8. Determination of optical band gap by extrapolation method from the variation of $(ah)^2$ versus $h\nu$ for CZTS absorber layer.
coefficient behaviour in which the films annealed at 350 and 375°C have the values greater than the films annealed at 400 and 425°C respectively, this deviation indicate the changing of extinction coefficient behaviour between 800 and 1050 nm. The values extinction coefficient is obtained to be between 0.03 and 0.09 since “k” is directly relational to the absorption coefficient. The found values of extinction coefficient are comparable by Bakr for CZTS deposited by spray pyrolysis method [44]. Figures 11 and 12 showed that the values of the real and imaginary parts dielectric constants. The real dielectric constant increase with increasing of sulfurization temperature, this behaviour is close to the behaviour of the refractive index, because the real part depends a lot on refractive index compared to extinction coefficient. The imaginary dielectric constant increase with sulfurization temperature increased in the visible region (400-800 nm), after 800 nm we indicate the shift in the behaviour of imaginary dielectric constant in which the CZTS thin films annealed at 350 and 375°C have the values superior than the films annealed at 400 and 425°C respectively. The values of real and imaginary dielectric constants are in the range of 2.51-55.85 and 0.10-1.33 respectively. The optical parameters are used to develop and improve the photovoltaic devices [45].

Figure 9. Refractive index as a function of wavelength $\lambda$ for CZTS thin films with various temperatures
Figure 10. Extinction coefficient as a function of wavelength $\lambda$ for CZTS thin films with various temperatures

Figure 11. Real dielectric constant as a function of wavelength $\lambda$ for CZTS absorber material
Conclusion
CZTS thin films were deposited using single step on ITO glass substrates by electrodeposition method. The obtained samples were sulfurized in N$_2$+H$_2$S atmosphere at 350, 375, 400 and 425°C for 10 min for study influence of sulfurization temperature on the properties of CZTS thin films. The obtained films show a kesterite phase with the preferential orientation along (112) plane. Crystallites size was found to be between 14.27 and 37.22 nm, the Cu$_2$Sn$_3$S$_8$ and SnS secondary phases were observed in X-ray diffraction patterns with CZTS phase. Raman peak of all CZTS thin films was observed at 336 cm$^{-1}$confirming the existence of the kesterite CZTS structure. FESEM images indicated a surface of CZTS thin films morphology ameliorated with sulfurization temperature increased in the range of 350-425°C. The sample annealed at 425°C has good surface morphology for photovoltaic applications. The optical parameters are calculated using transmittance and absorbance data. The optical band gap energy was found to decrease with sulfurization temperature increased in the range of 1.56-1.66 eV. The best optical band gap of 1.56 eV is obtained for the sample annealed at 425°C. The values of refractive index, extinction coefficient, real and imaginary dielectric constants are increase with sulfurization temperature increased.

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