Structural, morphological and optical properties of copper-tin-sulfide thin film synthesized by spin coating technique

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Abstract. Copper-tin-sulfide, thin films were fabricated by the sol-gel method on soda lime glass. The structural, morphological and optical properties of these thin films were studied by x-ray diffraction, scanning electron microscopy, and ultraviolet-visible spectroscopy. X-ray diffraction studies revealed the formation of the Cu_3SnS_4 phase for annealed thin films at 350°C and 400°C in argon atmosphere for one hour. The scanning electron microscope study revealed a good surface for solar cells. The optical transmission measurements showed that the band gap of these films decrease from 0.97 eV to 0.82 eV after annealing.

1. Introduction

Copper indium gallium selenide (CIGS), CdTe and copper indium selenide Cu_2InSe_2 (CIS) thin films absorbers are used today in commercial thin film photovoltaic devices. High conversion efficiency of approximately 21.7 % was achieved in CIGS-based cells [1]. The high cost and scarcity of indium (In), gallium (Ga) and tellurium (Te) besides the toxicity of cadmium (Cd) and its environment impact limit the large scale production of CIS, CIGS and CdTe photovoltaic panels that can compete with the silicon technology. Copper tin sulfide (CTS) is potential candidate for low-cost thin film solar cells, because of its suitable direct band gap between 0.82 and 1.7 eV [10,11], large absorption coefficient over 10^4 cm^{-1} and the abundance and non-toxicity of its elements [12]. Several techniques were used or the deposition CTS thin films, namly sputtering [2], chemical bath deposition (CBD) [3], spray pyrolysis [4], electro-deposition [5], pulsed laser [6], co-evaporation [7], sol-gel [8], sulfurization [9], etc. However, most of these techniques require a sulfurization step. In the present article, we propose the synthesis of Cu_3SnS_4 thin films by the sol-gel process without any further sulfurization. The sol-gel is a versatile, potentially low-cost technique that can be used to deposit CTS thin films.

2. Experimantal

2.1. Sample preparation

The copper tin sulfide thin films were deposited by the spin coating technique on soda lime glass substrates. The substrate was first cleaned by successive ultrasonic bath of water, acetone and water respectively during 15 min and dried in an oven. The precursor solution consisted of 2 M copper (II) chloride $CuCl_2.H_2O$; (>99% from Sigma Aldrich), 1.3 M tin (II) chloride dehydrate $SnCl_2.2H_2O$; (98% from Sigma Aldrich) and 8 M thiourea H_2NCSNH_2; (>99% from Sigma Aldrich) added in a solvent mixture composed of dionized water/ethanol (v/v 30:70). The mixture was then stirred at 40°C during 40 min to yield a clear and homogenous solution. The resultant solution was then spin-coated using an SPI the spin coater Model P6700 onto glass substrate at 4000 rpm for 30 s followed by solvent-drying at 100°C for 5 min. The deposition step was repeated three times in order to achieve a suitable thickness. Subsequently, the films were annealed at two temperatures of 350°C and 400°C in an Argon atmosphere for one hour using a tubular furnace.

2.2. Characterization

The structural, morphological and optical properties were studied. The crystalline structure was analysed by X-ray diffraction using copper a CuKα radiation (λ=1.5418 A°) and an X'Pert difractometer (PANalytical, Almelo, The Netherlands). Sample morphology and uniformity were determined by a scanning slectron microscope (SEM) (TESCANVGA 3) at the center of analysis and characterization, Cadi Ayyad University. The elemental composition of the films was examined by an energy dispersive spectroscopy (EDS). The optical properties were measured on a UV-Vis- NIR double beam spectrophotometer (Shimadzu, Tokyo, Japan).

3. Resultats and Discussions

3.1. Structural charcterization

The X-ray diffraction (XRD) patterns of thin films deposited on soda lime glass substrate are shown in figure 1. These patterns contain three diffraction peaks indicating that these films are polycrystalline in nature. Only the peaks characteristic of the Kuramite phase of CTS can be observed in this case. The major XRD peaks are located at 2θ = 28.5 °, 47.4° and 56.5 °. Figure 1 shows that the films exhibit a high intensity peak at 2θ = 28.5 °, suggesting a preferred growth in the (112). The other peaks of this phase are also present with relatively lower intensity. We also note that annealing the samples at 400°C improved the intensity of the peaks and reduces their width. This suggests that annealing has improved the crystallinity of our films. Table 1 shows that the observed d-spacing values of our sample are in good agreement with the values the tetragonal (I -42m) Cu_3SnS_4 phase (JCPDS 33-0501 standard). The lattice parameters corresponding to tetragonal crystal structure were calculated using the relation [13] :

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}}} \quad (1)$$

Where (hkl) are the Miller indices and d is the interplanar distance. The lattice parameter values are a= b = 5.42 A°, c = 10.86 A°. The d_{hkl} is the interplanar distance which is determined by Bragg's Law [14]:

$$d_{hkl} = \frac{n\lambda}{2sin\theta} \quad (2)$$

Where n is a positive integer, λ =1.541 Å is the radiation wavelength and θ is Bragg's angle of the (hkl) planes associated to the structure.
The evaluated lattice parameters are in close agreement with the JCPDS 33-0501. The ratio of c/2a, which is almost equal to one, shows that the phase is tetragonal.
The full width at half maximum (FWHM) of the (112) diffraction peak for the thin films annealed at 350 °C and 400°C, allows to estimate the grain size D by using Scherrer's formula [15] :

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

Where λ is the X-ray wavelength and β is the FWHM of the (112) peak and θ is the corresponding Bragg diffraction angle. The estimated crystallite sizes are 7.5 nm and 9 nm for the films annealed at 350°C and 400 °C respectively.
Furthermore, the lattice strain effect can be calculated using the following equation (Williamson- Hall method) [16]:

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (4)$$

The dislocation density Ψ was calculated using the Williamson and Smallman formula [17]:

$$\Psi = \frac{1}{D^2} \quad (5)$$

The number of crystallites N per unit surface is determined using the following relation [18]:

$$N = \frac{t}{D^3} \quad (6)$$

Where t is the film thickness, which was estimated to 1400 nm. It is clear from Table 2 that with the increase of the annealing temperature, the crystallite size of CTS films increases while strain, dislocation density and number of crystallites decrease.

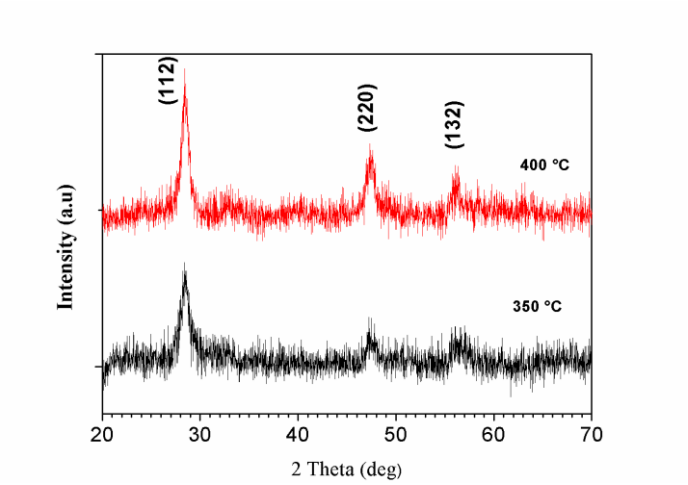

Figure 1. XRD patterns of the Cu_3SnS_4 (CTS) thin films annealed at 350°C and 400°C in argon gas for one hour.

Table 1. Comparison between observed d spacing values of Cu_3SnS_4 and JCPDS References.

2θ (°)	hkl	d-spacing (Å)			Compounds
		Observed values		JCPDS Ref	
		350°C	400°C		
28.5	112	3.13070	3.13361	3.13000	Cu_3SnS_4
47.4	220	1.91774	1.9286	1.91400	Cu_3SnS_4
56.5	132	1.62689	1.64030	1.64000	Cu_3SnS_4

Table2. Summary of calculations from Debye Scherer formula and results of Williamsone Hall analysis for lattice strains.

Samples	FWHM(◦)	D(nm)	$\Psi(nm^{-2})$	$N(nm^{-2})$	$\varepsilon(10^{-3})$
350°C	0.0191	7.5	0.017	3.317	0.018
400°C	0.0161	9	0.012	1.920	0.015

3.2. Morphological characterization

Figure 2 shows SEM surface micrographs for samples annealed at 350°C and 400°C in argon atmosphere for one hour. Annealing at 350°C (figure 2a) resulted in grains having almost the same size. For 400°C (figure 2b), there is appearance of small grains and beginning of formation of crystallization. As it can be seen in the SEM images of Figure 2 (c,d,e and f), the surface of the annealed thin films is homogenous with no cracks or pinholes, which is suitable for photovoltaic applications. The compositional analysis of the films is investigated by the energy dispersive spectroscopy. The quantitative elemental analysis is carried out for Cu, Sn and S (Table 3). The atomic ratio S/(Cu+Sn) is close to that of the Cu_3SnS_4 stoichiometric. The weak Cu/Sn ratio indicates that there are phases that are not yet crystallized. In fact the EDS detects all the phases while the XRD detects only the crystalline phases.

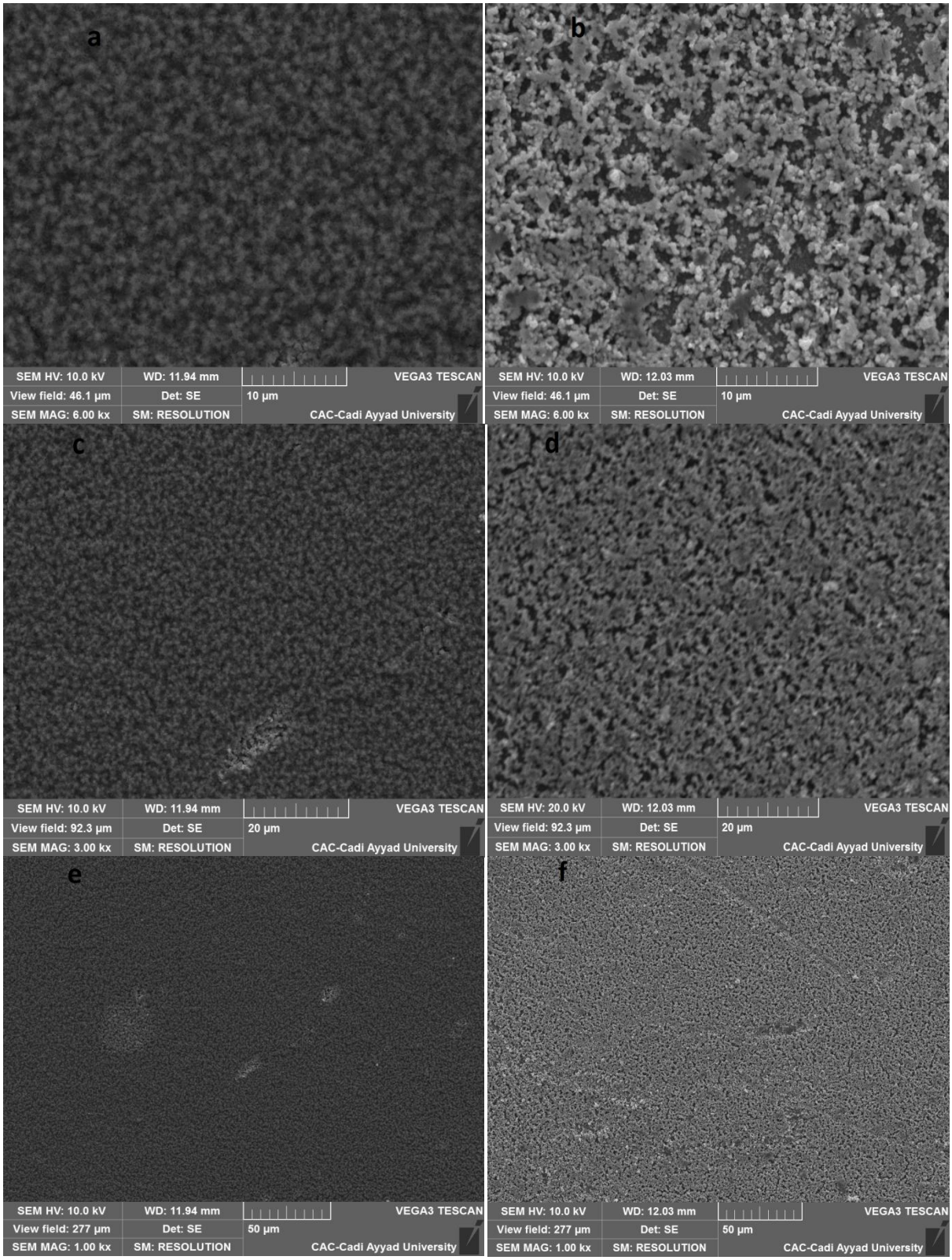

Figure 2. SEM micrographs of Cu_3SnS_4 absorbers annealed for (a), (c) and (e) at 350°C; and for (b), (d) and (f) at 400°C respctivily.

Table 3. Composition ratios of the annealed films from EDS.

Temperature (°C)	Atomic percent			Atomic ratios	
	Cu	Sn	S	Cu/Sn	S/(Cu+Sn)
350	24.97	26.73	48.30	0.73	0.93
400	21.26	24.15	54.58	0.38	1.20

3.3. Optical characterization

The absorption coefficient α was calculated from the transmittance T using the approximation $T = e^{-\alpha d}$, which is valid in the high-absorption region of the spectrum. Where, d is the film thickness which is estimated to be 1.4 µm. The optical gap (Eg) was evaluated from the plot of $(\alpha h\upsilon)^2$ against photon energy ($h\upsilon$). This plot should be linear near the absorption edge in the case of a direct band gap semiconductor, which is the case for our films (Figure 3). The optical gap is obtained by extrapolating the linear region of this plot to $h\upsilon = 0$. Hence, by using this method, we found that the band gap is 0.97 eV at 350°C and 0.82 eV at 400°C [10]. These results are in good agreement with the reported values.

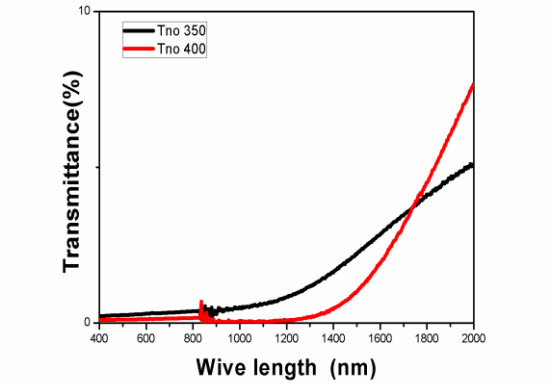

Figure 3. Optical transmittance as a function of photon energy of the CTS film annealed at 350 °C and 400 °C.

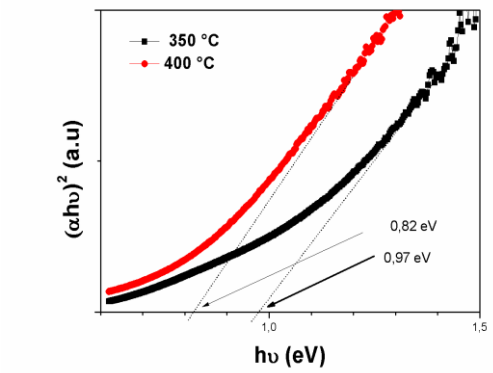

Figure 4. Square of the product of the absorption coefficients and photon energies of the annealed thin films as a function of photon energy.

4. Conclusion

The copper tin sulfide thin films were successfully synthesized by spin coating without sulfurization. The effects of annealing at 350°C and 400°C temperature for 1 hr on the structural, morphological and optical properties of the CTS thin films were investigated. The X-ray diffraction result shows that the obtained layer was composed by Cu_3SnS_4 Kuramite phase and has a (I-42m) tetragonal structure with (112) preferential orientation. The prepared films showed a good homogeneity for photovoltaic applications. The deposited films showed high optical absorption coefficient with a band gap between 0.82 eV and 0.97 eV.

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