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ABSTRACT

Cu_2SnS_3 thin film have been synthesized by solid state reaction under vapour sulphur pressure at 530 °C, during 6 h, via a sequentially deposited copper and tin layers Cu/Sn/Cu…Sn/Cu/Sn. The structure and the composition were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Electron Probe Micro Analysis (EPMA). X-ray diffraction revealed that as the deposited film crystallizes in the cubic structure and the crystallites exhibit preferential 111 orientation of the grains. Moreover, EPMA analysis confirmed that the obtained film is stoichiometric. The SEM study shows the presence of spherical particles of ≈100–120 nm diameters. The optical absorption coefficient and band gap of the film were estimated by means of transmission and reflection optical measurements at room temperature. A relatively high absorption coefficient in the range of 10^4 cm^{-1} was indeed obtained and the band gap value is of the order of 1.1 eV. On the other hand, the electrical conductivity of Cu_2SnS_3 film prepared in the present experiment is suitable for fabricating a thin film solar cell based on not cheaper and environmental friendly material.

1. Introduction

In recent years, there has been a great deal of interests in the research of nontoxic semiconductors both from a fundamental as well as technological point of view. Cu–Sn–S systems are members of the I–IV–VI group of semiconductors which attracted some attention because of their interesting properties [1–6] and their potential applications as small band semiconductors and as suitable candidate for nonlinear optical materials and in photovoltaic cells [7–11]. Many of semiconducting multicomponent phases have been reported in this system, such as Cu_4SnS_4 [12], Cu_2SnS_3 [9,13–15], $Cu_4Sn_7S_{16}$ [9], $CuSn_{3.75}S_8$ [16], Cu_3SnS_4 [17]. Cu_2SnS_3 ternary semiconducting material is one of the most promising semiconductor materials which can be used in solar cells due to its band gap close to that expected for photovoltaic solar energy conversion and its high absorption coefficients [15]. The preparation of Cu_2SnS_3 has been reported in micro- as well as in nanocrystalline forms [5,18–20]. The only attempts in thin films were by using the spray pyrolysis technique [15], or by evaporation of the powdered Cu_2SnS_3 [21]. However, the films prepared by Kuku et al. [21] were deficient in copper. So, even double evaporation technique involving Cu_2SnS_3 and copper could not provide stoichiometric films of Cu_2SnS_3. Nevertheless, not much has been explored in finding other alternative ways to deposit single phase Cu_2SnS_3 thin film [17,22].

The aim of this study is to establish the optimized experimental conditions needed to prepare stoichiometric Cu_2SnS_3 films using a solid state reaction. It has been achieved by annealing, in sulphur atmosphere, of sequentially deposited of copper/tin sandwich layers. The films have been characterized by X-ray diffraction (XRD), microprobe analysis and scanning electron microscopy (SEM). The electrical and optical properties of the film have also been investigated.

2. Experimental details

The optimized Cu_2SnS_3 film was deposited by a sequential thermal evaporation onto glass substrate. The working pressure was maintained at about 10^{-4} Pa.

2.1. The deposition of Cu_2SnS_3 thin film was accomplished in two stages

In the first stage, four bi-evaporated layers of Cu/Sn were grown using two separated crucibles containing high purity Cu and Sn and which were mounted horizontally, each of them being at a corner of an equilateral triangle, while the sample holder was situated at the third one. The crucible-to-substrate distance was adjusted to 10 cm.

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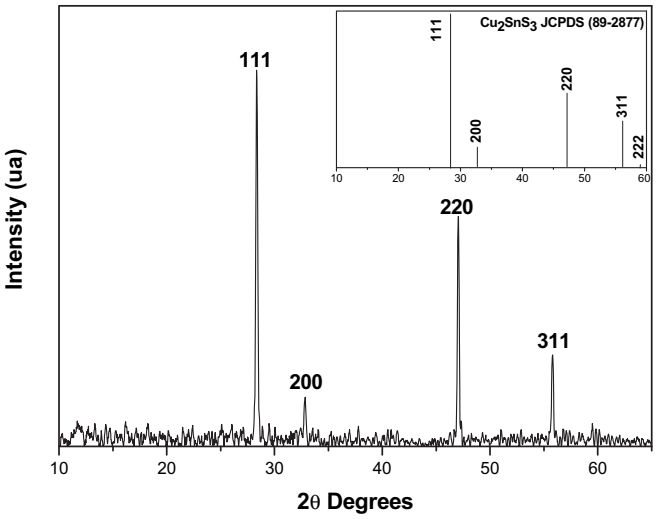

Fig. 1. X-ray diffraction pattern of Cu_2SnS_3 thin film obtained at 530 °C.

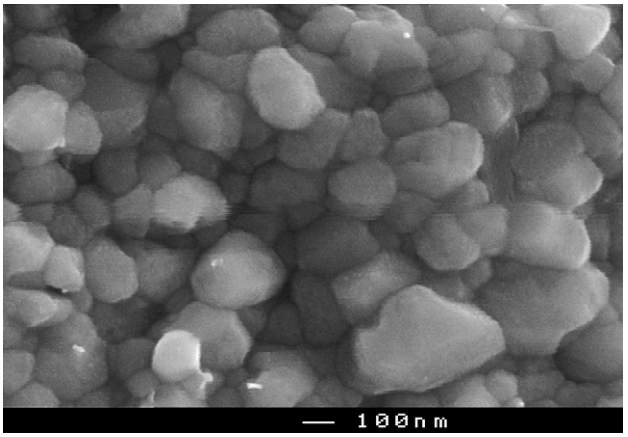

Fig. 2. SEM micrographs of Cu_2SnS_3 thin film obtained at 530 °C.

The substrate temperature during the deposition of Cu was maintained at 150 °C and they were subsequently cooled down to room temperature for the deposition of the Sn layer. The thicknesses of each layer of: Cu and Sn were approximately 100 and 60 nm respectively.

In the second stage, the simple is sealed in glass tube under a vacuum of 10^{-2} Pa with sulphur bulk and it was submitted to a thermal annealing in sulphur environment at 530 °C for 6 h.

The XRD of the sample was recorded by using a Siemens D500 powder diffractometer with Cu Kα radiation. The average crystallite size (t) corresponding to (hkl) reflections has been calculated by using the Scherrer's equation as follows:

$$t = \frac{K\lambda}{\beta\cos\theta}$$

Where, the constant K is a shape factor and has been taken equal to 0.9, λ is the wavelength of the X-ray, $\beta_{2\theta}$ is the FWHM corresponding to the Bragg's angle θ.

The surface topography and the composition of prepared film have been obtained using a JEOL F-6400 and a JEOL F-5800 LV respectively. The optical characteristics were determined with SHIMADZU 3100S UV/VIS spectrophotometer in the range of 300–1800 nm. Finally, the electrical parameters, including conductivity and conductivity type, were determined by the two probes and hot point probe techniques respectively.

3. Results and discussion

3.1. X-ray diffraction

It was noted that the original white colour of Sn at the surface of the Cu/Sn metallic precursor changed to grey colour when sulphurized. Such grey colour is expected for Cu_2SnS_3 films. Fig. 1, shows the X-ray diffractogram of the deposited film annealed at

Table 1
Ratio of I_{hk1}/I_{111} for Cu_2SnS_3 thin films and powder.

I_{hkl}/I_{111}	530 °C	JCPDS (89-2877)
I_{200}/I_{111}	0.135	0.128
I_{220}/I_{111}	0.617	0.485
I_{311}/I_{111}	0.243	0.298

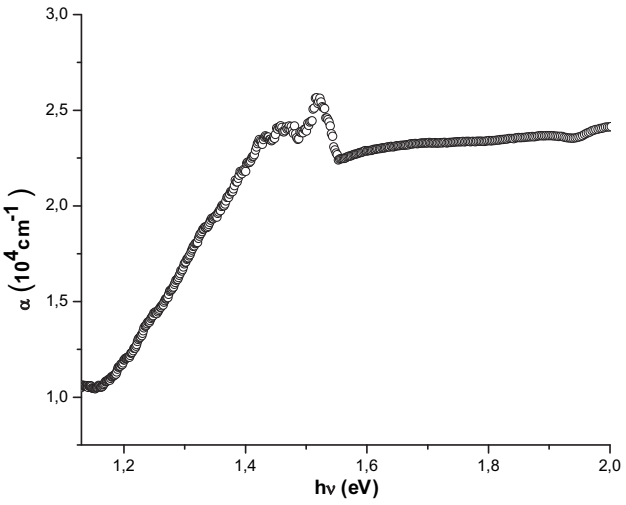

Fig. 3. Variation of absorption coefficient (α) with wavelength for Cu_2SnS_3 thin film.

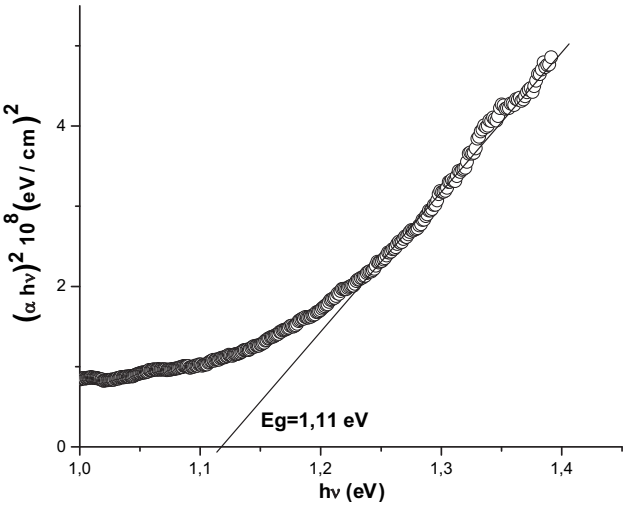

Fig. 4. $(\alpha h\nu)^2$ vs. hν for the films of Cu_2SnS_3 obtained at 530 °C.

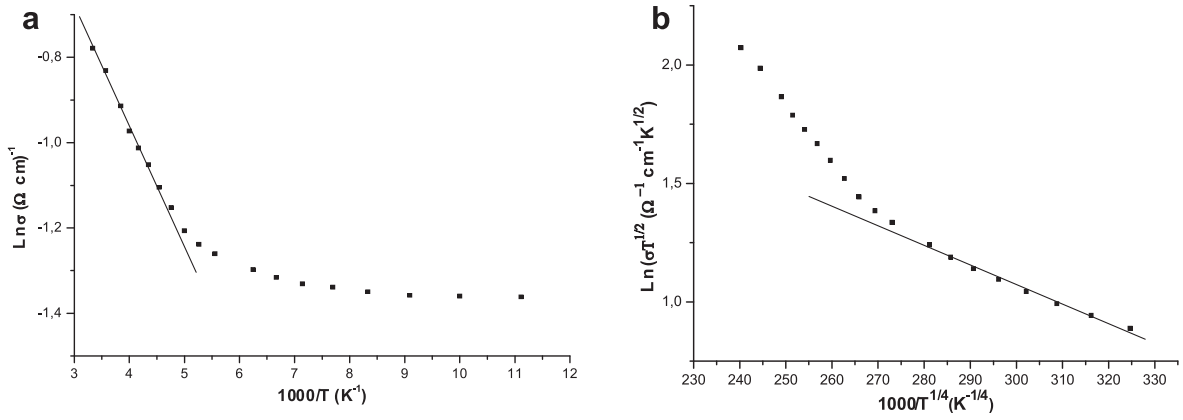

Fig. 5. a. Plot of ln σ vs. 1000/T for the Cu_2SnS_3 thin film. b. Replot of the data in Fig. 5a as ln ($\sigma T^{1/2}$) vs. $1000/T^{1/4}$.

530 °C for 6 h. All the observed diffraction peaks can be indexed to a single phase of Cu_2SnS_3 with lattice constants very close to the cubic phase (a = 5.430 nm) according to JCPDS file [23]. EPMA analysis of the film shows Cu:Sn:S atomic ratios to be 2:1:3 in conformity with the identified phase by XRD. It is clear from the diffractogram in Fig. 1 that the 111 diffraction peak is of most intense. The other peaks observed in the diffractogram correspond to 200, 220 and 311 directions. The diffraction peak intensity ratios of I_{hkl}/I_{111} have been calculated and the results are compared in Table 1 with those of a Cu_2SnS_3 reference polycrystalline powder. It can be seen that the ratios I_{hkl}/I_{111} for the film annealed at 530 °C are very close to the reference values. When the sequential deposition was modified with Sn as first layer the ternary compound was not obtained and we obtain a sample with a CuS phase and a low Sn content due to the strong tendency of Sn evaporation during the Cu deposition.

The size of the crystallites in the film relative to the *hkl* directions and calculated using Scherrer's equation lies in 35–45 nm domain.

3.2. Scanning electron micrograph

A scanning electron micrograph of the film annealed at 530 °C under sulphur pressure is shown in Fig. 2. It can be seen that the film is homogeneous with no visible cracks or holes. The grains of Cu_2SnS_3 exhibit spherical shape with diameters lying in the range of 200–300 nm. The grain sizes measured by X-ray are smaller than that statistically estimated from SEM. The discrepancy can be attributed to the fact that the grains visualized by SEM are constituted of more than one crystallite. Such observations have been observed in many cases [24,25]. The thickness of the deposited film is about 0.9 μm.

3.3. Optical properties

The optical absorption coefficient (α) of Cu_2SnS_3 film has been calculated using the well known expression [26]:

$$\alpha_\lambda = \frac{1}{t}\left(\frac{(1-R_\lambda)^2}{T_\lambda}\right)$$

It was found that α value was about 10^4 cm^{-1}, Fig. 3.

Fig. 4 shows a characteristic plot of the variation in $(\alpha h\nu)^2$ with photon energy $h\nu$ near the fundamental edge. As we can see, for optically measured film we found a linear dependence indicating an allowed direct transition with:

$$\alpha\, h\nu = A\left(h\nu - E_g\right)^{1/2}$$

Where E_g is the band gap, A a constant. The gap energy was estimated by extrapolating $(\alpha h\nu)^2$ vs. $h\nu$ to zero to be equal to 1.11 eV.

This value is in good agreement with the reported data on bulk polycrystalline as well as for the Cu_2SnS_3 films prepared either by spray and reported in our previous work [15] or by other methods [5,20,22]. Such value of the band gap is quite close to the optimum band gap for solar cells, which makes it a very promising absorber material in future solar cells.

3.4. Electrical properties

Fig. 5 exhibits the variation of electrical conductivity of Cu_2SnS_3 thin film sulphurized at 530 °C with the inverse of absolute temperature. From the plot, we find that the conductivity of the film increases with increase of temperature indicating the semiconducting behavior of the sample. The increase of conductivity is gradual near the room temperature range. Similar observations have been reported previously [27,28].

The presence of two regions with different slopes in the plot suggests that there are two types of conduction mechanism present in Cu_2SnS_3 film deposited by a solid state reaction of Cu, Sn and S. The point of inflection is found to be around 238 K. In the temperature region below 238 K, the conduction is due to a variable range hopping mechanism following Mott's law: [29]

$$\sigma \propto T^{-1/2}\exp\left[-(T_0/T)^{1/4}\right]$$

Whereas, in the temperature region above 238 K, the electrical conductivity varies linearly with temperature. Data can be fitted to Arrhenius's law:

$$\sigma \propto \exp(-E_a/kT)$$

and it is attributed to a thermal excitation of charge carriers. These results seem to agree well with those observed in such chalcopyrite as: $CuInS_2$, $CuInSe_2$ [30]. The activation energy E_a is around 25 meV.

The results reveal that the films are stable and p-type conductivity of the sample has been checked by the hot point probe technique.

4. Conclusion

The purpose of our work was to gain experience with a new preparation technique of Cu_2SnS_3 thin film achieved by sulphurization of a metallic precursor constituted of sequentially deposited

Cu/Sn/…Cu/Sn multilayer and annealed under sulphur pressure for 6 h at 530 °C. Structural, morphological, optical and electrical properties of the optimized sample have been investigated. The obtained results show that this is a promising starting point for future investigations of Cu_2SnS_3 non toxic thin film instead of CIS and CIGS, classical materials in the fabrication of high performance photovoltaic devices.

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