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Substrate effect temperature on Cu_2ZnSnS_4 thin films deposited by ultrasonic technique

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Abstract

Cu_2ZnSnS_4 (CZTS) thin films are a potential candidate for absorber layer in thin film solar cells. CZTS films were deposited by spray ultrasonic technique. An aqueous solution composed of copper chloride, zinc acetate, tin chloride and thiourea like precursors is sprayed on heated glass substrates at various temperatures. The substrate temperature was changed from 280°C to 360°C in order to investigate its influence on CZTS films properties. The DRX analyses indicated that Cu_2ZnSnS_4 films have nanocrystalline structure with (112) preferential orientation and a crystalline size, ranged from 30 to 50 nm with increasing substrate temperature. The obtained films are composed of SnS, ZnO, ZnS and Cu_2ZnSnS_4 phases. The optical films characterization was carried by the measurement of UV-visible transmission. The optical gap was deduced from the absorption spectra. Broad emissions at around 1.27 eV was observed in the photoluminescence spectrum measured at 77 K.

Keywords: *CZTS, photoluminescence, thin films, Transmission, spray technique, XRD.*

1. Introduction

Quaternary Cu_2ZnSnS_4 (CZTS), which consists of abundant materials, is one of the promising materials for absorber in thin films solar cell, due to its excellent properties, such as suitable band-gap energy of 1.4–1.5 eV, and large over $10^4 cm^{-1}$absorption coefficient [1]. Therefore, these properties make Cu_2ZnSnS_4 a potential material for photovoltaic applications. It is known that the electrical, optical, morphological and structural properties of this material are strongly influenced by the used deposition technique and by the related experimental parameters. Several techniques have been employed for preparing CZTS thin films: sputtering [1, 2], thermal evaporation [3], photo-chemical deposition [4].... Among these techniques, spray ultrasonic appears as an interesting technique for preparing Cu_2ZnSnS_4 thin films [5]. This technique is very attractive because it is inexpensive, easy and allows obtaining optically smooth, uniform and homogeneous layers. In this work, the effect of substrate temperature on both of the structure, chemical composition, optical and electrical properties of Cu_2ZnSnS_4 thin films, deposited by ultrasonic spray, has been investigated.

2. Experimental procedure

CZTS Thin films were deposited by spray ultrasonic in air. The initial solution is prepared from Copper chloride $CuCl_2$ (0.01M), zinc acetate (0.005M), tin chloride $SnCl_2$ (0.005M) and thiourea SC $(NH_2)_2$ (0.04M). These salts used as sources of different elements (Cu, Zn, Sn and S) are diluted in methanol. In order to optimize the temperature deposition, the substrate temperature was changed from T=280°C to 360°C with a step of 20°C and the spraying duration was fixed at 45min. The structural properties were determined by XRD using a Philips X' Pert system with CuK_α radiation (CuK_α =1.5418Å). The films morphology and composition were analyzed using a microscopic scanning SEM equipped with an EDX analysis system. The Optical transmissions in the UV-Visible range (300-2400nm) measurements were used with a Shimadzu UV-3101 PC spectrophotometer.

Finally, for photoluminescence the samples were excited by a 60 mW laser diode emitting at 488 nm. The PL signal was analyzed by a monochromator equipped with a 600 grooves/mm grating and by a photomultiplier tube cooled at 190 K. The spectral response of the detection system was precisely calibrated with a tungsten wire calibration source. For measurements at low temperature, the samples were inserted in a cryostat equipped with fused silica windows.

3. Results and discussion

3.1 Structural properties

The X-ray diffraction patterns of the CZTS thin films synthesized at various substrate temperatures are shown in figure 1. The diffraction angles vary from 20° to 60°. For all of the as-deposited films, peaks assigned to the (112), (200), (204) and (312) planes of CZTS are presents in the whole diffraction patterns. However, preferential (112) orientation was observed for all deposited films. Moreover, for higher substrate temperatures, one can clearly see the apparition of CZTS new peaks assigned by the (114) and (031) orientations [6].In addition, peaks of ZnS, ZnO and SnS related to the secondary phases are seen in figure 1.The individual crystalline size (D) in the films has been determined from (112) peak by using the Scherrer's formula [7].

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

Where K is the Scherrer constant value corresponding to the quality factor of the apparatus measured with a reference single crystal, λ is the wavelength of the X-ray used; β is the full width at half maximum of the peak and θ is the Bragg angle. The crystalline size in films of different thicknesses is of the order 30-50 Å and is in good agreement with the reported values [8].

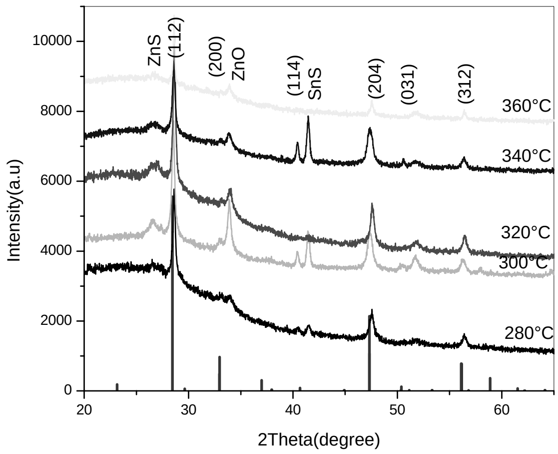

Figure 1: XRD patterns of CZTS films deposited by the spray ultrasonic at different substrate temperature.

3.2 Optical properties

Optical properties of the deposited Cu_2ZnSnS_4 films are studied by the analysis of the spectroscopic optical transmittance in the visible range. In figure 2 is reported the transmittance spectra of films deposited with various substrate temperatures. From the solid band theory, the relation between the absorption coefficient α and the energy of the incident light (hν) is given by:

$$(\alpha h\nu)^n = B\,(h\nu - E_g)$$

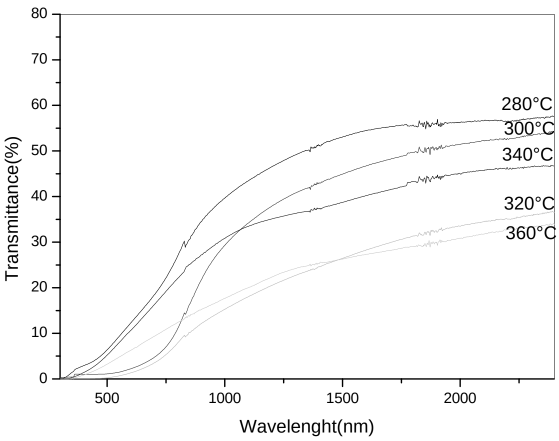

Figure 2: Optical transmission spectra of CZTS thin films prepared at various substrate temperatures.

Where B is a constant, E_g the band gap energy and n=2 or 1/2 for crystalline (direct transition) or amorphous CZTS, respectively.

The variation of the deduced optical gap of films with substrate temperature is reported in figure 3, as seen, at substrate temperature of 280°C, 300°C and 320°C the values of optical gap are 1.6 eV, 1.5eV and 1.45 eV respectively. These values are in good agreement with Cu_2ZnSnS_4 band gap values reported by other authors [9, 10]. Higher substrate temperatures 340°C and 360°C yielded to 1.8 eV and 1.76 eV optical gaps.

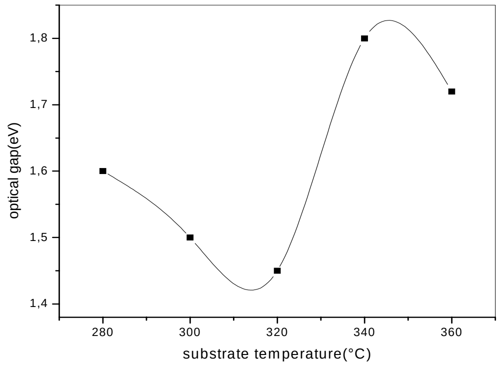

Figure 3: Variation of the optical gap as a function of the substrate temperature

The increase in optical gap with increasing substrate temperature can be due to improvement in the films crystallinity as shown in figure 1. Such a band gap shift can be related to the formation of different Zn-content according to the DRX diffractograms and EDX (Zn-riche, Cu-poor) analysis. The incorporation of ZnS (with gap above 3.5 eV) has resulted in a large shift of the band gap of other materials such as $CuInS_2$ [11]. In another work, Torodov and al [12] fabricated CZTS thin films by soft-chemistry method and they reported that the optical gap vary from 1.33 to 1.86 eV where the films are Zn-riche and Cu-poor.

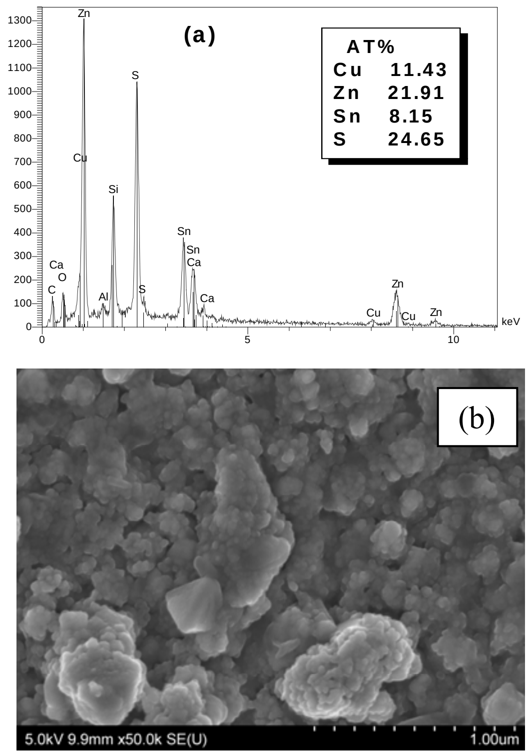

Figure 4: (a), EDX characterizations of as-synthesized CZTS thin films.
(b), Surface morphology images by SEM observation.

3.3 Morphological and composition

As shown in figure 4(a) the elemental composition of Cu_2ZnSnS_4 of thin films deposited at 360°C of substrate temperatures is determined from EDS analysis. From this analysis we conclude that CZTS films are Zn-rich, Cu-poor and sulphur deficient. Sulphur deficiency is significantly higher with increasing substrate temperatures; this is due to the sulphur volatility. Sundra et al [8] have also noticed the sulfur deficiency in CZTS thin films prepared by RF magnetron sputtering. Spray-deposited CZTS films obtained from pure aqueous solution by Nakayama et al [13] in the substrate temperature range 553–633K are also sulphur-deficient (28–38 at %). Previous works suggests that a slightly Zn-rich and Cu-poor composition gives good optoelectronic properties [14, 15, 9].
Figure 4(b) presents the surface morphology images by SEM observation at substrate temperature 360°C. It can be seen from the figure that the films consist of compact structure grains with sub-micron size. Our film had larger and more densely packed grains than that reported in Ref. [16]. It is well known that the efficiency of polycrystalline solar cells increases with increasing grain size in the absorber layer, hence larger grains are required for the fabrication of high efficiency solar cells [16, 17].

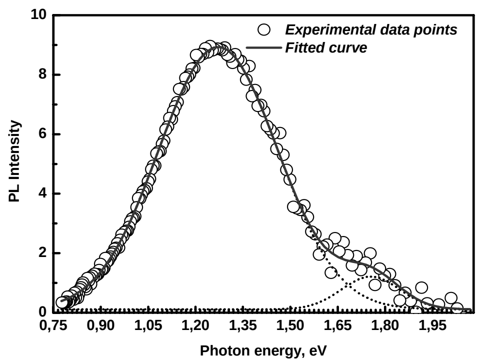

Figure 5: PL spectra of the CZTS thin films grown at substrate temperatures of 320°C.

3.4 Photoluminescence

Figure 5 shows the photoluminescence spectrum of the CZTS film at 320 °C measured at 77 K. As seen, a large peak of emission localized at 1.27 eV was observed. This later peak was observed by several authors [17. 18.19] which is intense and perfectly symmetrical. However, the same authors have noted also the dissymmetry in this peak of emission.

4. Conclusion

Cu_2ZnSnS_4 thin films have been successfully deposited by spray ultrasonic technique. The effect of substrate temperature on the growth of spray-deposited Cu_2ZnSnS_4 thin films was investigated. In conclusion, kesterite structured CZTS with satisfactory nearly stoichiometry and the crystalline sizes in the range 30–50 nm were obtained. The band gap of the obtained CZTS films was ranged from 1.45 to 1.8 eV indicating that the deposited film at 320°C has suitable optical properties for efficient solar energy conversion.

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