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Effect of different copper precursor layer thickness on properties of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films prepared by sulfurization of thermally deposited stacked metallic layers

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Abstract: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were fabricated by sulfurization of thermally evaporated metallic precursors on glass substrates. While the Zinc and Tin thicknesses were kept constant at 300 and 200nm respectively, three Copper layer thicknesses of 100, 150 and 200 nm were used to obtain the metallic precursors. The precursor films were sulfurized for 3 hours at 550 °C with an initial ramping rate of 10 °C/min. X-ray diffraction studies reveal polycrystalline films exhibiting Kesterite structures with preferential orientation along [112] direction. The films with lowest Cu layer thickness exhibited binary metal alloy contents, which disappears with higher Cu precursor layer thickness. The surface morphology and elemental composition of CZTS thin films was determined from scanning electron microscopy and energy dispersive spectroscopy analysis respectively. The grain size become large with increasing Cu/(Zn + Sn) ratio, exhibiting an enhancement of the grain growth under Cu – rich condition. There is a nominal increase in the optical band gap from 1.49 to 1.51 eV with increase in Cu content. The samples resistivities are in the range of 0.8 to 1.5Ωcm

Keyword - CZTS, Sulfurization, Thermal evaporation. XRD, SEM.

I. Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising, and suitable material for low-cost thin film solar cells owing to the suitable optical band-gap energy of 1.4 to 1.5eV coupled with its large absorption coefficient in the order of 10^4cm^{-1} , it is also non toxic [1]. CZTS is a p-type semiconductor with a direct band gap [2]. It consists of abundant material and is a new type of absorber for thin film solar cells. This semiconductor material is obtained by replacing half of the indium atoms in chalcopyrite CuInS_2 with Zinc, and substituting the other half with Tin. All constituents of this material are abundant in the earth's crust with Zinc and Tin having an abundance of 75 and 2.2 ppm respectively [3].

CZTS thin films have been grown using various methods such as co-evaporation [4], RF sputtering and vapour phase sulfurization [5], electrodeposition [6], RF sputtering [7], hybrid sputtering [8], reactive sputtering [9], nano crystal ink deposition [10], and spray pyrolysis [1]. The stacked precursor deposition with subsequent sulfurization has two different approaches: (i) simultaneous deposition of precursors and (ii) sequential stacked deposition of precursor thin films [11]. The sequential stacked precursor has some advantages over simultaneous deposited precursors as the compositional ratio of CZTS thin film is more easily controlled by adjusting the thickness of each stacking layer. Also the stacked precursor is cost-effective and viable for large area production in the industrial field which can be easily adapted to non vacuum condition methods [6]. In this work, CZTS thin films were prepared by sulfurizing sequential stacked Zn_Sn_Cu precursors deposited by vacuum thermal evaporation of the metallic precursors. Three different Cu thicknesses were used, while the Sn and Zn thicknesses were kept constant. The metallic precursor films were sulfurized using elemental sulphur vapour.

II. Experimental

CZTS films were prepared by a two-stage process consisting of vacuum thermal Vapor deposition of metallic precursors followed by the sulfurization of the deposited precursors. The deposition of Zn, Sn and Cu metallic precursors was carried out on a corning 7059 glass substrate using an EDWARD Auto 306 thermal evaporator with the FL 400 deposition chamber, pumped down to 10^{-5} torr. The substrate temperature was 150 °C and the substrate to source separation distance was 10 cm. The precursors were deposited in the sequence Zn/Sn/Cu from Zn, Sn and Cu evaporation pellets. All the evaporants were 99.99% pure. The film thickness was monitored in-situ using a Sigma thin film deposition controller and subsequently confirmed by Dektak 150 surface profiler. The Zn and Sn thicknesses were kept constant at 300nm and 200nm respectively, while the Cu

thicknesses were 100, 150 and 200 nm. The ratio of the thickness of the metal precursors layer in the stacking order Zn:Sn:Cu, were thus 3:2:1; 3:2:1.5 and 3:2:2. Prior to deposition, the glass substrate was ultrasonically cleaned in detergent at 100 °C for 10 minutes, rinsed in deionizer water, immersed in boiling H₂O₂ for another 16 minutes and then rinsed in deionized water, then blown dry in high purity N₂.

The sulfurization process of ZnSnCu precursor thin films was carried out using a carbolite tubular oven attached to a 3-zone SVG SYTEM 2610 diffusion furnace. The whole sulfurization system was purged with argon for one hour prior to sulfurization. The elemental sulfur was vaporized in the oven at a temperature of 140 °C. The sulfur vapor was subsequently transported to the diffusion furnace where the samples were placed using high purity (99.99%) argon as a carrier gas, at a flow rate of 50 sccm. The films were sulfurized in the diffusion chamber for two hours at 550 °C. The initial temperature ramping rate of the diffusion furnace was 10 °C/minute. The samples were labeled Zn_Sn_Cu_100, Zn_Sn_Cu_150 and Zn_Sn_Cu_200 for the Cu thicknesses of 100, 150 and 200 nm respectively.

The phase analysis of the CZTS thin film was carried out at room temperature with a PANalytical XPERT-PRO MPD X-ray diffractometer at 40 mA and 42 kV, with monochromatic CuK_α radiation of wavelength $\lambda = 1.54060\text{\AA}$. The (2 θ) scanning range used was 10°-70° with a step size of 0.008°. The films morphology was analyzed with a CARL ZEISS MA 10 scanning electron microscope (SEM), while the elemental composition was determined by energy dispersive spectroscopy (EDS), using an ISIS 300 OXFORD EDS attached to the SEM. The optical transmittance of CZTS films were measured using an Avantes UV-VIS spectrophotometer (AVASPEC 2048), in the wavelength range 250-900nm. To examine the electrical properties, the four-point probe and hot-probe technique were used for resistivity and determination of conductivity-type respectively.

III. Results And Discussion

3.1 X-Ray Diffraction Studies

The XRD patterns of CZTS films having different thickness of Cu layers are shown in Fig. 1. It can be seen that the samples are essentially polycrystalline. They exhibit kesterite structures with diffraction peaks at $2\theta = 16.34^\circ, 18.24^\circ, 26.67^\circ, 28.44^\circ, 33.02^\circ, 33.92^\circ, 47.34^\circ, 56.26^\circ, \text{ and } 58.88^\circ$. These peaks are attributed to the diffracting planes of (002), (101), (110), (112), (200), (212), (220), (116) and (224) respectively, which is confirmed by the powder diffraction file ICSD 01-075-412. The diffraction peaks of (002) and (101), indicates the presence of Copper Tin Sulfide. These can be attributed to the CZTS formation process thought to involve the formation of Cu-Sn Sulfide followed by the reaction of Cu-Sn Sulfide with ZnS to form CZTS [12]. The observed peaks at $2\theta = 26.67^\circ$ and 33.92° in Zn_Sn_Cu_100 sample, indicates the presence of copper sulfide phase often observed in CZTS thin films during the sulfurization process. The Copper Sulfide phase can be effectively removed by immersing the sample in KCN solution [13]. The weak diffraction peaks at 38° and 51.86° in sample Zn_Sn_Cu_100 are attributable to (321) and (310) reflection planes of Cu₅Zn₈ and Cu₆Sn₅ respectively. These are from the reaction path of CZTS which starts with the elements in the precursor, via formation of binary compounds (Cu₆Sn₅, SnS₂, ZnS, Cu₂S, Cu₅Zn₈, etc.) to more complex compounds like CTS and CZTS [14]. The film with low Cu content thus tends to show binary metal phases, which disappear with increasing Cu content.

The Full Width at Half Maximum (FWHM) of (112) plane gets narrower and the diffraction peak very stronger with increasing Cu/(Zn+Sn) ratio indicating improvement in crystallinity with increase Cu content. The lattice parameters for CZTS films determined from the observed d_{112} and d_{220} spacing are $a = 5.43\text{\AA}$ and $c = 10.87\text{\AA}$. These results are in good agreement with the published work of Kishore *et al.*, $a = 5.42\text{\AA}$ and $c = 10.85\text{\AA}$ [15].

The average grain size D of the films is calculated using Debye Scherrer's formula [16]:

$$D = K\lambda/\beta\cos\theta$$

where K is the Scherer constant, β is the full width at half maximum (FWHM), θ is the diffraction angle, and λ is wavelength of the X-rays. The calculated grain size for the films is 16.3, 22.3 and 22.5nm for Zn_Sn_Cu_100, Zn_Sn_Cu_150 and Zn_Sn_Cu_200 respectively. The grain size is found to increase with increase in Cu content of the films. This is advantageous in photovoltaic application as photo-generated electron recombination rate will be reduced with large agglomerated grains [17].

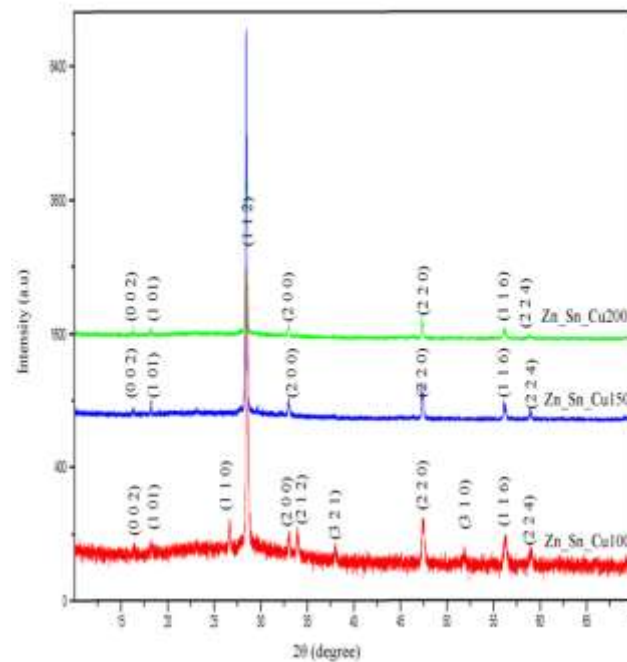
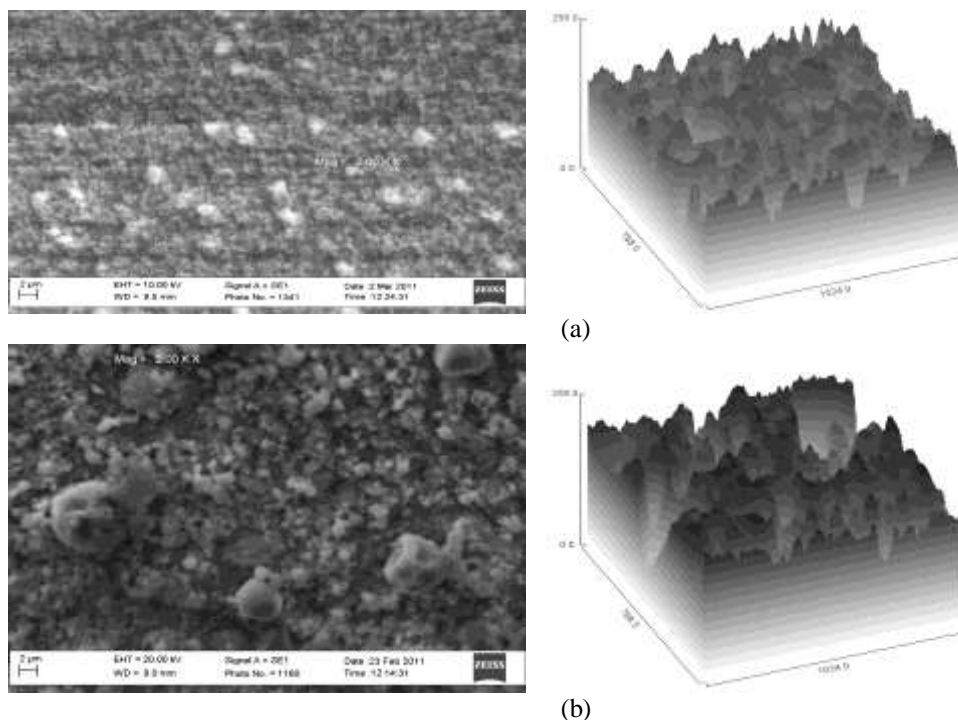


Figure 1. XRD Pattern for Sulfurized Samples

3.2. Surface Morphology

The SEM micrographs and the corresponding 3D topographical maps are presented in Fig. 2 (a-c). The grain sizes are spherical in shape and the distribution is closely packed giving rise to little porosity and voids. Few prominent protuberances are noticed in the Zn_Sn_Cu_150 film. The 3D surface topography shows a columnar microstructure of the film perpendicular to the surface. Shadowing is prominent and the columns are elongated along the preferential growth direction.

The averaged crystallite sizes visualized by SEM are 1.2, 1.4 and 1.6 μ m for Zn_Sn_Cu_100, Zn_Sn_Cu_150 and Zn_Sn_Cu_200 films respectively. The values obtained are three orders of magnitude higher than the grain sizes determined from FWHM of powder diffraction patterns using the Debye-Scherrer equation. Thus, in the former case, agglomerates have been visualized.



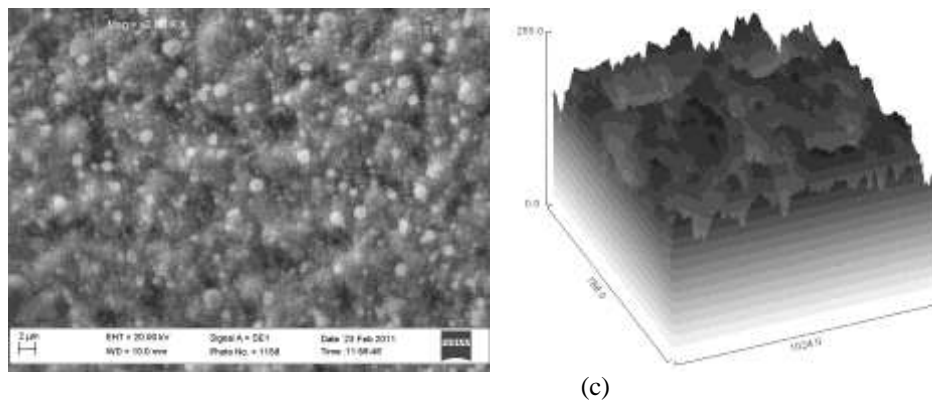


Figure 2. SEM micrograph and corresponding 3D topographical maps of sample (a) Zn_Sn_Cu_100, (b) Zn_Sn_Cu_150 and (c) sample Zn_Sn_Cu_200

3.3. Composition

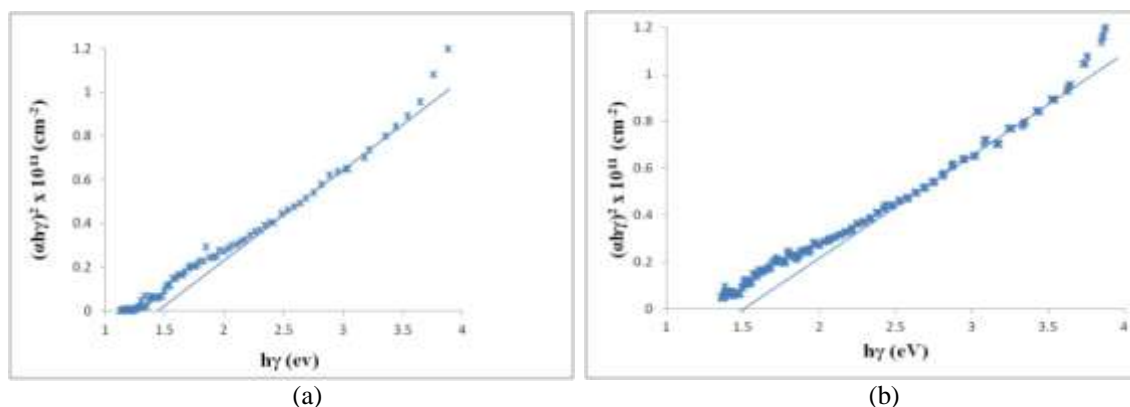
The elemental composition of CZTS thin films determined from EDS analysis for films deposited with different film thicknesses for Cu layer is shown in Table 1. The Zn/Sn and Cu/Sn compositional ratios (> 1) indicate that the films are Zn and Cu rich compared to Sn. It is also observed that Zn_Sn_Cu_150 and Zn_Sn_Cu_200 films are slightly Cu poor compared to Zn+Sn, however Zn_Sn_Cu_100 film is characterized by a significant deficiency of Cu compared to Zn and Zn+Sn. The S/metal compositional ratio is the same for Zn_Sn_Cu_100 and Zn_Sn_Cu_150 samples indicating similar sulfur diffusion during sulfurization for these samples. All the samples are S poor (S/metal < 1). The grain size increases with increase in Cu/(Zn+Sn) ratio; this is an indication of a growth enhancement under Cu rich condition and the influence of Cu/(Zn+Sn) ratio on structural and morphological properties of the film. A similar observation has been reported in growth under Cu rich condition [18].

TABLE 1 Chemical Composition and grain size D of CZTS thin films with various copper thicknesses.

Sample	Cu (%)	Zn (%)	Sn (%)	S (%)	Cu/Sn	Cu/Zn	Cu/(Zn+Sn)	S/metal	D(nm)
Zn_Sn_Cu_100	16.6	24.4	13.6	45.4	1.22	0.68	0.44	0.83	16.2
Zn_Sn_Cu_150	25.5	17.8	9.8	46.9	2.60	1.43	0.92	0.83	22.3
Zn_Sn_Cu_200	25.8	17.9	8.5	47.8	3.04	1.44	0.98	0.91	25.5

3.4. Optical Properties

Fig. 3 shows the $(\alpha h\nu)^2$ versus $h\nu$ plots of the films. The optical band-gap energies are determined by extrapolating the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ curve, to $(\alpha h\nu)^2 = 0$. The band-gaps of Zn_Sn_Cu_100, Zn_Sn_Cu_150 and Zn_Sn_Cu_200 CZTS films are estimated to be 1.49, 1.50 and 1.51eV respectively, showing a nominal increase in band gap with increasing Cu content. These values are appropriate band gap energy of solar cell absorber for high conversion efficiency as they can absorb the photon energy consisting of the visible and infrared rays [7].



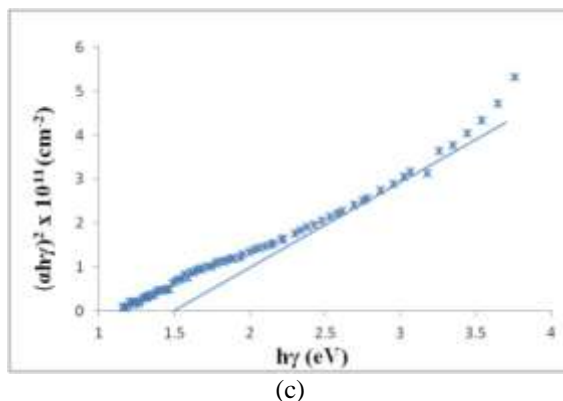


Figure. 3. Optical absorption coefficient of CZTS thin film for Samples (a) Zn_Sn_Cu_100, (b) Zn_Sn_Cu_150 and (c) Zn_Sn_Cu_200

3.5. Electrical Resistivity

The room-temperature electrical properties of CZTS films deposited with different Cu thicknesses as determined using the four-point probe and the hot-probe techniques reveal that all the films are p-type. Their resistivities are found to be 0.94, 1.5 and 0.80 Ωcm for Zn_Sn_Cu_100, Zn_Sn_Cu_150 and Zn_Sn_Cu_200 films respectively.

IV. Conclusions

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films have been fabricated by sequential vacuum thermal evaporation of Cu, Zn, and Sn at 150 °C substrate temperature, and subsequent sulfurization for 3 hours at 550 °C of the resulting CuZnSn thin films. The composition ratios, the structural, morphological, optical and electrical properties of CZTS thin films have been investigated. Analysis of the X-ray diffraction films reveals the presence of tetragonal and cubic phases exhibiting a kesterite structure. The films also show an increase in grain size with increase in $\text{Cu}/(\text{Zn} + \text{Sn})$ ratio, which indicates an enhancement of the grain growth under Cu – rich conditions. All the films show the presence of Copper Tin Sulfide and the film with lowest Cu layer thickness also exhibited binary metal alloy contents. The optical band-gap of the CZTS samples has been estimated to be between 1.49 and 1.51 eV, appropriate for high conversion efficiency for solar-cell absorber. The films have also been found to be p-type, and with the electrical resistivities in the range of 0.8 to 1.5 Ωcm

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