



Structural and optical properties of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films Prepared by varying copper and zinc amounts in sol-gel precursor

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Abstract: The thin films of CZTS ($\text{Cu}_2\text{ZnSnS}_4$) have been successfully deposited on soda lime glass by spin coating technique. In this work, CZTS films were prepared by spin coating technique for different molar concentrations of copper and zinc in the precursor solution. The SEM micrographs showed some change in granules for different concentration of copper and zinc. The X-ray diffraction results showed the formation of kesterite phase with the peaks corresponding to (112), (220) and (312) planes. Optical properties of the CZTS thin film absorbers were studied by UV-vis spectroscopy. The optical band gap was found in the range of 1.48 to 1.6 eV for CZTS thin films of different molar concentrations.

Keywords: CZTS; Absorber layer; Spin coating.

I. Introduction

Though the bulk material is considered as a better light absorber layer compared to thin film semiconductor materials, adoption of thin film solar cells (TFSC) could be a better solution due to low material consumption. As the light absorption becomes weak with decreasing film thickness the TFSC have not beaten the light to power conversion efficiency of bulk Si based solar cell yet. Copper Zinc Tin Sulfide (CZTS) solar cell showed about 10% of the highest cell efficiency in the recent report [1]. Though the optical and electronic properties of CZTS are very much similar to copper indium gallium selenide (CIGS), in recent years CZTS thin films, favorable for the TFSC absorber layer has become quite promising to replace CIGS. Among various important TFSC absorber layers, such as cadmium telluride, copper indium selenide, CIGS, etc., only CZTS is composed of earth abundant, cheap and non-toxic materials.

CZTS has a high absorption coefficient in the order of 10^4 cm^{-1} . CZTS has a direct band gap of around 1.5 eV, close to the optimal band gap for single-junction solar cells [2]. Katagiri et al. reported a promising conversion efficiency of 6.77% in 2008 CZTS TFSC which was fabricated by co-sputtering technique using three targets of Cu, SnS, and ZnS followed by annealing in H_2S [3]. IBM improved the efficiency to 6.81% using a co-evaporation process in 2010 [4].

The first approach to fabricate CZTS TFSC by sol gel method with sulfurizing precursors was taken by Tanaka et al. [5], they prepared films by annealing oxyhydrate precursors deposited by the sol-gel method in an $\text{N}_2+\text{H}_2\text{S}$ atmosphere. The XRD peaks showed desired structure of CZTS with stoichiometric chemical composition and a direct band gap of 1.49 eV. Next year same group tried to improve transmittance in IR region and to eliminate voids in the CZTS films by pre-annealing the precursors in air or in N_2+H_2 (5%) atmosphere before annealing of precursors in H_2S contained atmosphere [6]. In 2009, same group reported fabrication of CZTS TFSC via non-vacuum method. They used CZTS films prepared over 'Mo' coated glass substrates by sulfurizing precursors deposited by sol-gel technique as the absorber layer [7, 8]. The CZTS absorber layer that exhibited the highest efficiency of 1.6% was Cu poor and Zn rich. The problem with sulfurizing spin coating precursors was that there was a deficit of sulfur in the absorber layer even though sulfurization was carried out at a high concentration of hydro sulfur [9].

The low cost fabrication process is as important as the materials and their availability. To manufacture low-cost TFSC it is preferred to imply non-vacuum deposition techniques, as the high vacuum techniques require expensive equipment, complicated operations and significant maintenance. Whereas, for non-vacuum method, it has some advantages such as lower cost and faster process than vacuum method.

To fabricate p-type CZTS absorber layer researchers have applied different non-vacuum processes which involve spin coating [10,11], spray pyrolysis [12], electro-deposition [13] chemical bath deposition [14], dip coating etc. Among various non-vacuum techniques spin coating is a fast and easy method to prepare CZTS. It is a process to achieve a homogeneous thin film onto a flat substrate out of solutions. Seo et al. reported on $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films prepared with different amounts of sulfur and copper, and their effects on film growth, crystal properties and optical properties. All CZTS thin films exhibited kesterite structures with absorption coefficients larger than 10^4 cm^{-1} in the visible region. Band gap energy increased with increasing amounts of sulfur and decreasing amounts of copper [15]. Chung et al. synthesized CZTS thin films by spin coating method using two kinds of mixture solvents of 2-methoxy-ethanol and mono-ethanolamine (2-metho/MEA) and methanol and de-ionized water (methanol/DIW). CZTS films attained from both solutions are oriented to the (112) plane, indicating kesterite structure. Compared to methanol/DIW solvent, reduced void defects and better surface roughness are observed using 2-metho/MEA solvent. An appropriate E_g from both solvents is attained with $1.3 \sim 1.4 \text{ eV}$. Zn-poor and Sn-rich states from both solvents caused additional secondary phases such as Cu_2SnS_3 and SnS_2 , affecting material properties, but film with 2-metho/MEA solution had less secondary phases.

In this work, the CZTS thin films were deposited on soda lime glass by the spin coating method followed by sulfurization [16]. The CZTS sol gel is prepared using 2-metho and MEA as solvent. The aim of this study is to see the changes in optical, structural and compositional properties of CZTS thin films with the change of the molar concentration of Cu and Zn. The films were investigated by studying their compositional, structural and optical properties and thus reveal the feasibility to fabricate a CZTS PV device by an inexpensive sol-gel process.

II. Experimental

A. Preparation of Thin Films

Three sets of CZTS thin films, CZTS-1, CZTS-2 and CZTS-3 were prepared by changing the molar concentration of Cu and Zn. For CZTS-1 the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was taken as 1.937 mol and ZnCl_2 as 1.194 mol. For CZTS-2 the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was taken as 1.566 mol and ZnCl_2 as 1.566 mol. For CZTS-3 the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was taken as 1.194 mol and ZnCl_2 as 1.937 mol. For all the three sets of precursors for CZTS thin film preparation SnCl_2 was taken as 1.244 mol and $\text{SC}(\text{NH}_2)_2$ as 3.996 mol. The three sets of precursors were dissolved in 2-metho and MEA. The solutions were stirred at 50°C for 30 minutes. Clear yellow sol-gel was formed after being stirred for several minutes by a magnetic stirrer. Spin coater (SPIN 150) was used to deposit the CZTS film on properly cleaned soda lime glass substrate ($2.5 \text{ cm} \times 2.5 \text{ cm}$). The glass substrates were cleaned with methanol-acetone-methanol-DI water for about 10 mins successively in an ultrasonic bath. The films were prepared with 3000 rpm for 30 seconds. After spin coating, the postbaking was carried out in an oven (Binder, ED53) at 300°C for 5 minutes to eliminate solvent and unwanted residues from the film layer. The spin coating and drying process were repeated two times to attain the desired thickness. The baked films were then sulfurized in a furnace (Thermconcept, KLS 10/12) at 580°C for 1 hour. The sulfurization was carried out by placing the samples in a sealed container along with a small amount of sulfur to ensure the presence of sulfur in the film.

B. Characterization

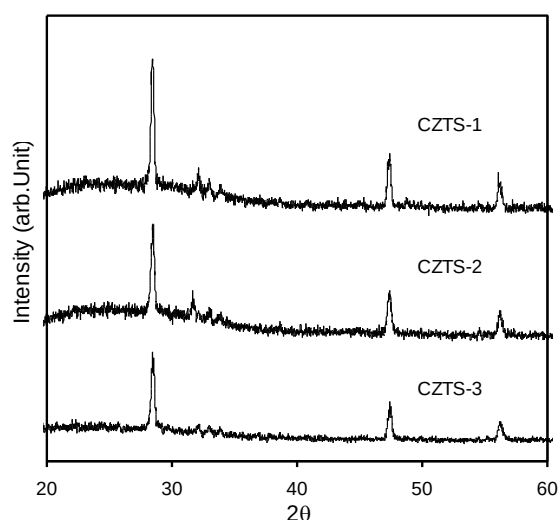
The thickness of the thin films in this research work was measured by using surface profiler (Veeco Dectak-150), the ultraviolet visible (UV-vis) spectroscopy were performed using a dual beam UV-Vis spectrophotometer (Shimadzu, UV-1601V, Japan). This spectrometer was used to measure the relative transmittance and absorbance of CZTS thin films. To investigate the structural properties of the CZTS thin films the X-ray diffraction (XRD) spectroscopy was done using a XRD spectrometer (Bruker, D8). The microstructure and the surface morphology were observed using a scanning electron microscope (JEOL JSM-7600F).

III. Results and Discussion

A. Structural properties

The XRD patterns of CZTS thin films prepared from sol-gel solutions with different molar concentrations of copper and zinc are shown in Figure 1. The sharpness of the major peaks indicates a good crystallinity for all sulfurized CZTS thin films. According to JCPDS collection code: 01-075-4122 the major diffraction peaks were observed at 23.1° , 28.4° , 32.9° , 36.9° , 37.9° , 47.3° and 56.1° corresponding to the phases (110), (112), (200), (202), (211), (220) and (312). The preferred orientation is observed with (112) plane at 28.4° . All the phases indicating the characteristic kesterite CZTS phase [15] except the XRD peaks at 18.2° assigned to (101) crystal planes of wurtzite ZnS nanocrystals in the films. All of the films were kesterite CZTS phase, with a little bit of wurtzite ZnS [17]. The lattice structure is tetragonal body centered. Some Bragg peaks which may be due to the phases of $\text{Cu}_2\text{-xS}$ can be observed in the XRD patterns of CZTS thin films. These phases may arise due to the decomposition of Cu_3SnS_4 precursors during sulfurization process [18].

Figure 1 Superimposed XRD pattern of CZTS thin films



θ_B is a peak position of diffracted X-ray beam. The grain sizes calculated are 580, 435 and 424 nm for CZTS-1, CZTS-2 and CZTS-3 respectively indicating large grain size of the annealed CZTS thin films. It is recognized that the efficiency of TFSC increases with increasing crystal size of the absorber layers [22].

The zincblende-derived kesterite structure of CZTS is recognized to be the most stable [19]. No significant peaks related to secondary phases are observed in XRD spectrum, but there are a few low intensity peaks that do not match with the kesterite phase which may be from the secondary phases such as SnS, SnS₂ and CuS [20]. In Figure 1 the highest peak intensity is observed for CZTS-1 after that for CZTS-2 and the lowest intensity is observed for CZTS-3 indicating that as the amount of zinc decreases and copper increases in the solgel, crystallinity improve in the resulting films.

Grain size is obtained using Debye-Scherrer equation as below [21].

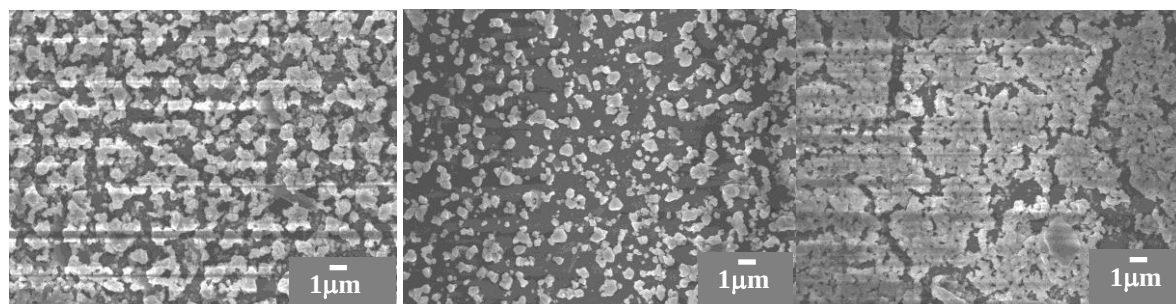
$$d = \frac{\lambda}{\beta \cos \theta_B} \quad (1)$$

where d is the calculated grain size of the film, λ is the wavelength of x-ray radiation ($\lambda=1.54\text{\AA}$ of CuK α radiation). β is full width at half-maximum (FWHM),

B. Surface morphological analysis

Figure 2 shows the surface morphology of CZTS films using different solvents. The surface was non-uniform with some granular agglomerates which are homogeneous in size throughout the thin film. It is seen that as the copper content decreases and that of zinc increases there are some change in the type of granules. Figure. 2(a) shows particle type granules may be due to the copper rich content in CZTS-1 whereas for zinc rich content in CZTS-3 flowery type granules is observed [23].

Figure 2 (a) SEM image of CZTS-1, (b) SEM image of CZTS-2 and (c) SEM image of CZTS-3 thin films.



C. Optical properties

Figure. 3a shows the optical absorption spectrum of CZTS-1, CZTS-2 and CZTS-3. The optical absorption spectra for all the CZTS samples were recorded in the wavelength range of 300 to 700 nm at room temperature. It is also seen that the absorbance decreases in the visible region with increase in wavelength in case of three samples. It is seen that the maximum absorbance in the visible region (380 to 700 nm) of the spectrum is 1.476, 1.4807 and 1.7963 for CZTS-1, CZTS-2, and CZTS-3 thin films respectively. Comparing among these three

Figure 3(a) Absorbance vs. wavelength plots for CZTS thin films of different molar concentrations.

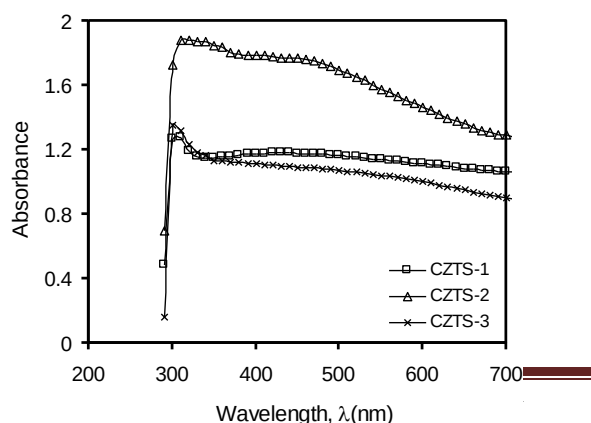
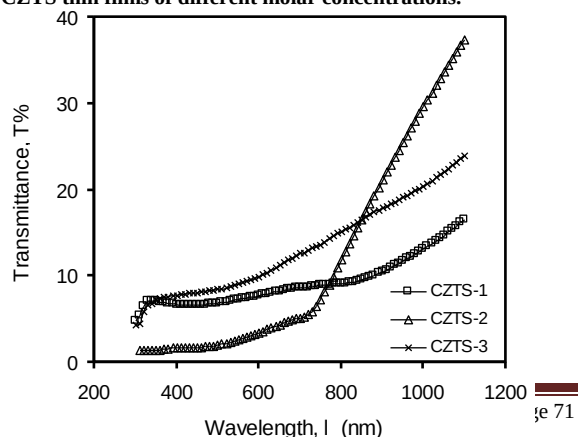


Figure 3(b) Transmittance vs. wavelength plots for CZTS thin films of different molar concentrations.

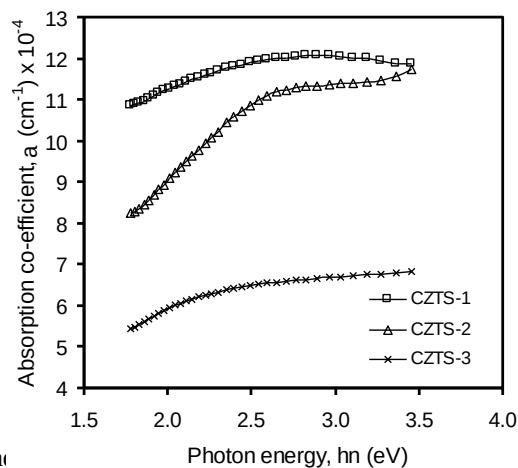


samples it is seen that the absorbance of CZTS-2 sample is higher than the other two samples in the visible, and infrared regions indicating its better suitability than the other two samples for solar cell applications. Figure 3(b) shows the variation of transmittance with wavelength λ (nm) in the wavelength range from 300 to 1100 nm for three types of CZTS thin films. The minimum transmittances within the visible region of the spectrum (380 to 700 nm) were 3.33%, 3.32% and 3.03% for CZTS-1, CZTS-2 and CZTS-3 samples respectively. It is seen that the transmittance decreases with decrease in light wavelength for all samples.

In order to confirm the nature of optical transition in all samples, the optical absorption coefficient is calculated using classical absorption equation: $\alpha = \frac{2.303A}{d}$... (2)

where $A = \log_{10}(\frac{I_0}{I})$ is the absorbance (I_0 is the intensity of photon striking the sample and I is the intensity of photon emerging from the sample) and d is the thickness of the thin film. The absorption coefficient calculated using the absorbance data was higher than 10^4 cm^{-1} in most of the visible region (Figure 3c).

Figure 3(c) Absorption co-efficient vs. photon energy plots for CZTS thin films of different molar concentrations.



The absorption coefficient α can be determined using the Tauc relation [24].

$$\alpha h\nu = B(h\nu - E_g)^n \dots (3)$$

where E_g is the optical energy gap between the bottom of the conduction band and the top of the valance band, the value of B is a constant and n is an index which can assume value of 2 for direct transition. The E_g was estimated from the $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating the linear part of the curve as depicted at Figure 3d. Thus CZTS-1, 2 and 3 has yielded the E_g of around 1.43, 1.75 and 1.9 eV respectively. A slight increase in E_g was observed with increasing zinc and decreasing copper concentrations in the precursor solution. Seo et al. also showed an increase in E_g of CZTS absorber layer from 1.46 to 1.52 eV as, the amount of copper in sol gel solution decreased. These values are quite close to the theoretical optimal value for a single-junction solar cell [25]. The E_g and absorption coefficient are comparable to the results of several other reports on sol-gel derived CZTS thin films [14, 26, 27]. The values of E_g of CZTS thin film prepared by the spin coating method imply the application of CZTS thin films as an absorber layer of TFSC.

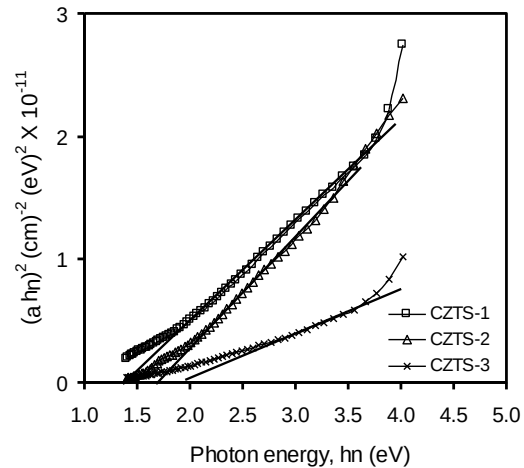
IV. Conclusions

From XRD analysis it is observed that as the amount of zinc decreases and copper increases in solgel the crystallinity improve in the resulting films. The X-ray diffraction results showed the formation of kesterite phase. The SEM shows that as the copper content decreases and that of zinc increases there are some change in the type of granules. The optical properties of the CZTS thin film absorbers were studied by UV-Vis spectroscopy. A slight increase in E_g was observed with increasing zinc and decreasing copper concentrations in the precursor solution.

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Figure 3(d) $(\alpha h\nu)^2$ vs. photon energy plots for CZTS thin films of different molar concentrations.



be determined on the basis of the dependence of α on $h\nu$ by

Engineering and Technology (BUET), Dhaka for SEM. Institute of Electronics, Bangladesh Atomic Energy Commission, Dhaka for thickness measurement.

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