



Synthesis of Copper Zinc Tin Sulfide ($\text{Cu}_2\text{ZnSnS}_4$) Thin Film Using Thermal Evaporation

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Abstract - In an effort to develop a thin film solar cell free from environmental contaminants, a new absorber layer of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) was synthesized. Three CZTS thin films were fabricated using two stage sequential evaporation method, deposition of metallic precursors at the substrate temperature of 200°C and then sulfurization of the stacked Cu-Zn-Sn metallic layers for 30, 60 and 90 minutes at 500°C . The film sulfurized for 90 minutes was found to be grown well with good crystalline structure, X-ray diffraction pattern shows highly visible (002), (101), (110), (112), (220), (211) and (220)-plane of CZTS observing only small amount of impurity phases at $\theta = 54^\circ$. The energy bandgap was found to be between 1.5eV and 1.64eV. The results clearly show that new thin film solar cell absorber layer can be synthesized using materials free from environmental contaminants.

Keywords - absorber, substrate, precursors, bandgap, sulfurization

1. INTRODUCTION

Copper Zinc Tin Sulfide, $\text{Cu}_2\text{ZnSnS}_4$ is a quaternary compound derived from CuInS_2 (CIS) by replacing In(III) with Zn(II) and Sn (IV) in the ratio 50:50. It is a direct bandgap semiconductor material, moreover it is a non-toxic and its elements are abundant in the earth crust.

Silicon is the most commonly used material for the manufacturing of solar cells. Due to its indirect bandgap and low absorption coefficient, Si-based cells are typically very thick leading to significant increase in the module cost. Therefore it is highly desirable to develop low-cost photovoltaic materials with high absorption efficiency (Chan, 2010).

Thin-film solar cells offer the promise of both low-cost and scalability features that are vital for any approach towards providing large amount of carbon free power (Shannon et al., 2009).

The most successful thin film solar cell belong to the following material families: (i) CIGS (Copper indium gallium selenide) family, where the absorbing semiconductor consist of CuInSe_2 , or related material or alloy, such as CuInS_2 , Cu(In,Ga)Se_2 or even Cu(In,Ga)(Se,S) ; (ii) the CdTe family; and (iii) the silicon family, consisting of an amorphous or micromorphous silicon-hydrogen alloy (a-Si:H or $\mu\text{-Si:H}$) or related alloy such as a-SiGe:H or a-SiC:H (Burgelman, 2005)

Chalcopyrite-type semiconductors like Cu(In,Ga)S_2 or Cu(In,Ga)Se_2 have very beneficial properties for photovoltaic applications, which led to a strong scientific interest in thin film solar cells based on

these materials, however, gallium and indium used for the preparation of the active layer are very rare and expensive elements. This could lead to a shortage in the supply of these elements and would inhibit a cost-effective large-scale production (Achim, 2010). To overcome these imitations, alternative materials are heavily researched in order to substitute the expensive elements In and Ga.

In an effort to develop the solar cells absorber layer free from the environmental contaminants, promising solar cell of a thin-film type could be produced by Copper Zinc Tin Sulfide ($\text{Cu}_2\text{ZnSnS}_4$, CZTS) film as the absorber layer. This is obtained by substituting the selenium with sulfur, the rare metal indium with zinc and tin in CIS ternary compound. Each component of CZTS are abundant in the earth's crust (Cu: 50ppm, Zn: 75ppm, Sn: 2.2ppm, S: 260ppm) and they possess extremely low toxicity, on the other side, in the case of CIS compound, the content of indium and selenium in the earth crust are 0.005ppm or less (Hironori et al., 2009). The CZTS film possesses promising optical properties, a bandgap energy of about 1.5 eV and large absorption coefficient in the order of 10^4 cm^{-1} , which means that large possibility of commercial production of the most suitable absorber by using the CZTS film and in addition CZTS film contains neither rare metal nor toxic material (Hironori, 2005). The aim of this study is fabricate a CZTS-based absorber layer using sulfurization time of 30 minutes, 60 minutes and 90 minutes.

2. EXPERIMENTAL

Zinc (99.99%), Tin (99.99%) and Copper (99.99%) metallic precursors were deposited on glass substrate by sequential thermal evaporation technique using

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EDWARD FL 400 Thermal evaporator equipped with SQC-310C deposition controller.

The following steps were taken to achieve the deposition of the alloy (Hironori et al., 2009). The thermal evaporator chamber was opened and four substrates were mounted on the substrate holders directly above the molybdenum boats at 11.5cm as the source to substrate distance, the crystal monitor was switched on to control the thickness of the film. Zn, Sn and Cu of sufficient quantity were placed on their respective boats. The chamber was then closed and the air inside the chamber was flushed by N₂ gas and then vacuum was created until a pressure of 9.0×10^{-9} torr. was achieved, the substrates were heated to temperature of 200°C and then Zn, Sn and Cu were deposited at the rate of 14Å /s was maintained until 150nm Zn, 150nm of Sn and 150nm of Cu film thickness respectively was achieved.

Then one precursor was sulfurized for 30 minute, another one was sulfurized for 60 minute and then the last one was sulfurized for 90 minutes at the sulfurization

temperature of 500°C each and named CZTS-1, CZTS-2 and CZTS-3 respectively.

2.1 Characterization

The structural characterization of the CZTS thin films was carried out by X-ray diffraction using X-ray diffractometer type XPERT-PRO equipped with a copper source (wavelength $\lambda=1.54056$ Å). The current and the acceleration voltage are 30 mA and 40 kV, respectively. The SEM was carried out using AVO|MA 10 Scanning Electron Microscope. The Energy High Tension (EHT) was set at 20.0 kV and working distance was set at 9.0 mm and the accelerated voltage was set to 20kV. For the optical transmittance and reflectance measurements of the films a UV-Visible spectrophotometer AVASPEC 2048 (wavelength=200nm to 900nm) was used.

3. RESULTS AND DISCUSSION

3.1 Chemical Composition

Table 1: Chemical Composition of CZTS Films

CZTS Name	Sulfurization time (min)	Chemical Composition (%)				Composition ratio		
		Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn	S/Metal
CZTS1	30	16	12	14	58	0.62	0.85	1.38
CZTS2	60	18	12	13	52	0.72	0.92	1.20
CZTS3	90	19	12	11	46	0.83	1.09	1.10

Table 1 shows the chemical composition of the deposited films with varying sulfurization time. It is evident that with the increase in sulfurization time the ratio of Zn/Sn increases from 0.85 to 1.09 which is near the stoichiometric value while the ratio of Cu/(Zn+Sn) also increases approaching unity which is the theoretical stoichiometric value (Hironori, 2009). It can be seen from the S/metal ratio that as the sulfurization time decreases the sulfur to metal ratio is reaching near optimal value of 1.00 at 90 minutes.

3.2 Optical properties

Using the optical transmittance and reflectance data, the absorption coefficient has been calculated using the following equation (Buba, 2010)

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (1)$$

Where

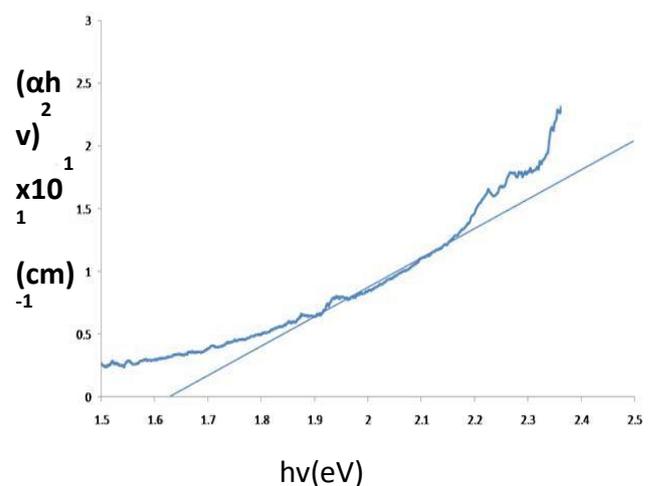
d = film thickness

T = transmittance of the film.

In order to evaluate the band-gap energy (E_g), the transmittance and reflectance of the CZTS films were measured over the wave length 300–1800 nm. In the case of allowed direct transitions, the absorption coefficient has the following spectral dependence (Hironori, 2005).

$$\alpha h\nu \approx (h\nu - E_g)^{1/2} \quad (2)$$

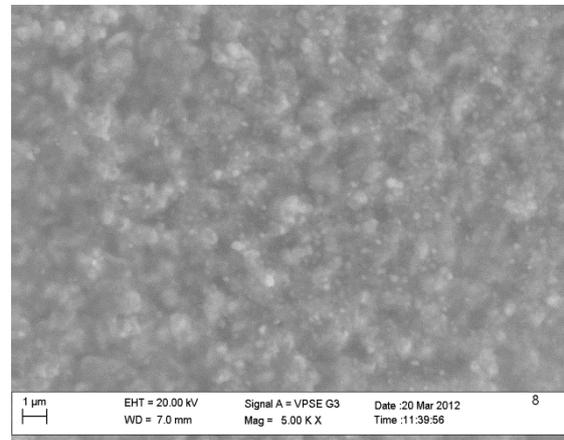
Where h is the Planck's constant and ν is the frequency of radiation. E_g is estimated by plotting $(\alpha h\nu)^2$ against $h\nu$ and extrapolating the linear portion of the curve and the intercept on the horizontal axis gives the Energy bandgap of the film.



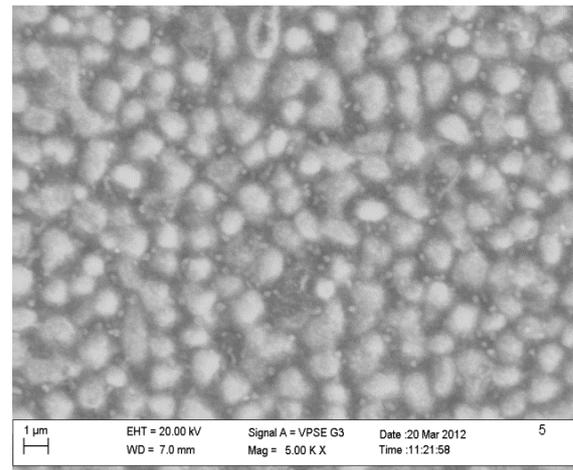
(a)



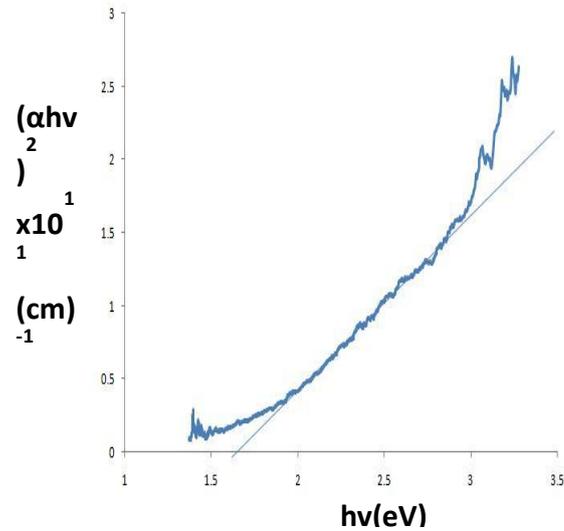
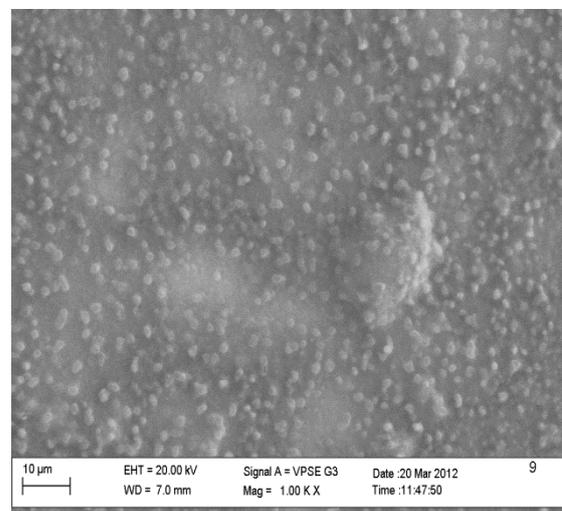
will be reduced (Chan, 2010). The roughness increases as the sulfurization time increases this could be explained by the agglomeration of micro crystallites. The grain sizes are between 1 and 1.5 μm meaning that the Scherer's formula gives the crystallite size normal to the X-Ray beam direction and does not give lateral dimension (Kishore, 2009).



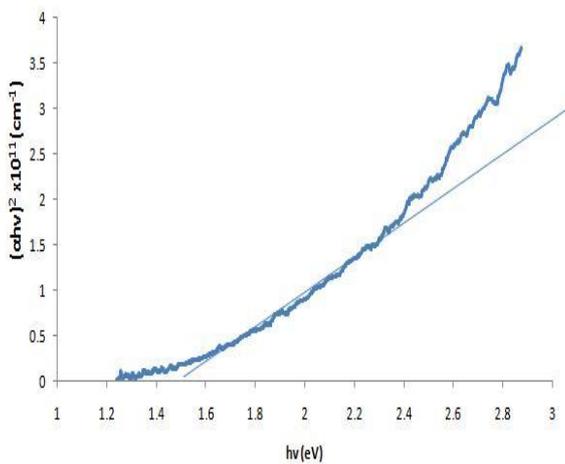
(a)



(b)



(b)



(c)

Fig.1: Relation between $(\alpha h\nu)^2$ and photon energy $h\nu$ of CZTS film deposited at 200°C and sulfurized for (a) 30 minutes (b) 60 minutes (c) 90 minutes

3.3 Scanning Electron Micrograph

The CZTS films were polycrystalline with uniform and comparable surface morphology they are also densely packed as there are no visible voids this confirmed that the surface morphology is considerably affected by that of precursor as seen in Fig 2. The films thickness obtained using the micro maker of SmartTiff, ranging 1 μm to 1.5 μm are found to be generally firmly adhered to the glass substrate, this is attributable to the substantial volumetric expansion of CZTS films during sulfurization process and thicker films would suffer much higher strain than their thinner counterpart. Also large grain size are observed on all the sulfurized films which will be beneficial in photovoltaic application as the recombination rate of the photo generated electrons



(C) Fig. 2: Scanning Electron Micrograph of films deposited at 200°C (a) Sulfurized at 500°C for 30mins (b)

Sulfurized at 500°C for 60mins (c) Sulfurized at 500°C for 90mins.

3.4 X-Ray Diffraction Pattern

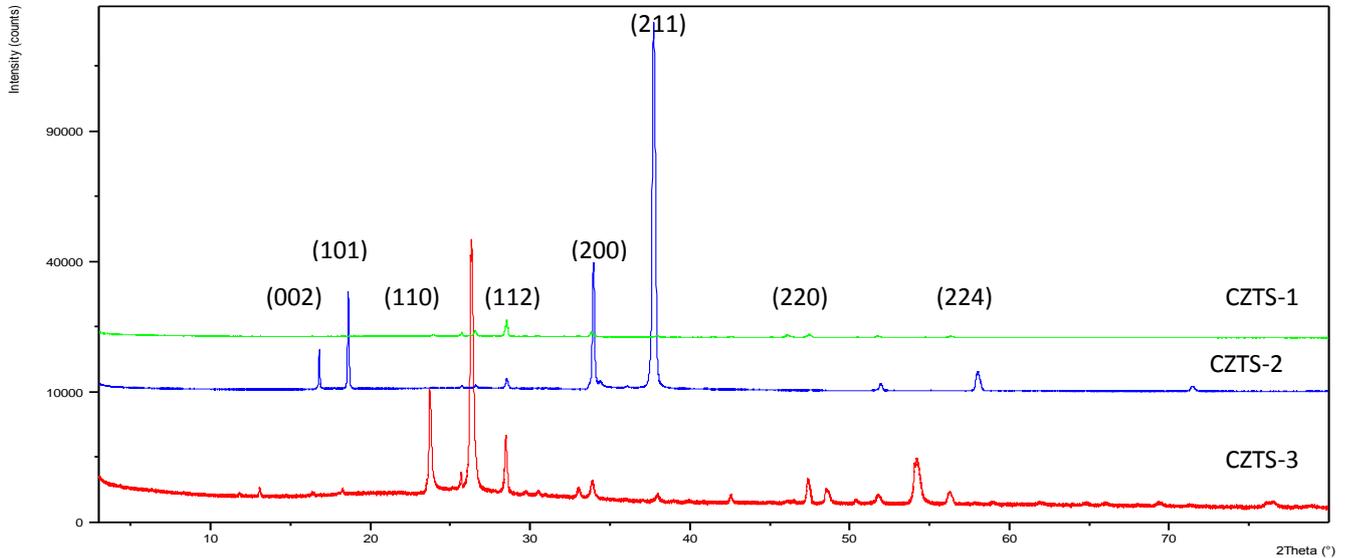


Fig. 3: X-ray diffraction pattern of the CZTS Films

Fig. 3 Shows the X-ray diffraction pattern for films deposited at 200°C showing highly visible (002), (101), (110), (112), (200), (211) and (220)- planes of CZTS, only small amount of impurity phases are observed suggesting that the films are close to stoichiometry (Chan, 2010), it also shows that the (112) diffraction peak observed in CZTS-1 decreased and the (211) diffraction peak relatively increased with increase in sulfurization time, this indicate that polycrystalline growth was suppressed and the oriental growth were induced in the films grown at high sulfurization time temperature.

3.5 Energy Bandgap

Fig.1 shows the plot of the squared of absorption coefficient and energy $(\alpha h\nu)^2$ versus the photon energy $h\nu$ for films sulfurized for 30 minutes, 60 minutes and 90 minutes respectively. The energy bandgap which is the intercept at x-axis is found to be 1.64eV, 1.6eV and 1.5eV. it can be seen that the bandgap energy of films deposited at 200°C and sulfurized for 90 minutes is in agreement with the reported theoretical values for solar cell which is between 1.4eV to 1.5eV (Hironori *et al.*, 2001). In their research work, Hironori *et al.*, (2001) estimated the bandgap energy from the optical properties of the films as between 1.45eV and 1.6eV. The bandgap energy of 1.64eV and 1.6eV is attributable to secondary phases of Cu_2SnS_3 , CuS (Kishore *et al.*, 2009). This observation that the films contain the secondary phases is in agreement with the conclusion from XRD pattern of the films sulfurized for 30 minutes.

4. CONCLUSION

For the development of the thin film solar cell without environmental contaminants, a new type of thin film absorber layer using CZTS was fabricated. In order to investigate the influence of the Cu/ (Zn+ Sn) ratio on the physical properties, CZTS thin film with the ratio of nearly 0.6- 0.8 was fabricated. From SEM observation, it was confirmed that the binary compound of Sn and S coexist. In order to fabricate the solar cell with high conversion efficiency, the optimum sulfurization time was studied and the best was obtained at 60 minutes. In this study, it can be seen that a new type of thin film solar cell absorber layer without any environmental contaminants can be synthesized.

REFERENCES

- Achim, F., Thomas, R., Wernfried, H., Heinz, A., Albering, J., Dorith, M., Sonja, L., Micheal, E., Robert, S., Ferdinand, H. and Gregor, T. (2010). Investigation of $\text{Cu}_2\text{ZnSnS}_4$ Formation from Metal Salts and Thioacetamide. *Chemistry of Material Article*, 30:2.
- Buba, A. D. A. and Adelabu, J.S.A. (2010). Optical and Electrical Properties of Chemically Deposited ZnO Thin Films. *The Pacific Journal of Science and Technology*, 11: 429-434.
- Burgelman, M. and Nollet, P. (2005). Admittance spectroscopy of thin film solar cells. *Solid State Ionic*, 176:2171-2172.



Chan, C.P., Lam, H. and Surya, C. (2010). Preparation of $\text{Cu}_2\text{ZnSnS}_4$ Films by Electrodeposition using ionic liquids. *Solar Energy Materials and Solar Cells*, 94:207-211.

Hironori, K., Kotoe, S., Tsukasa, W., Hiroyiko, S., Tomomi, K. and Shisuke, M. (2001). Development of thin film solar cell based on $\text{Cu}_2\text{ZnSnS}_4$ thin films. *Energy Materials and solar cell*, 68:141-148.

Hironori, K. (2005). $\text{Cu}_2\text{ZnSnS}_4$ Thin Film Solar Cell. *Thin Solid Films*, 481: 426-432.

Hironori, K., Kazuo, J., Win, S.M., Koichiro, O., Makoto, Y., Hideaki, A. and Akiko, T. (2009). Development of CZTS-based thin film solar cells. *Thin Solid Films*. 517:1.

Kishore, Y.B., Suresh, G.B., Uday, P. B., Sundra, V.R. (2009). Preparation and characterization of spray-deposited CuZnSnS_4 thin films. *Solar. Energy Materials and Solar Cells*, 93:1230-1237.

Shannon, C. R., Bruce, A. P. and Amy, L.P. (2009). Solution based synthesis and characterization of $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals. *JACS Communication*, 131:12054-12055.