

Aspects of Numeral Value of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) Absorber Layer Fabricated in Sol-gel Process by Dip Coating Technique

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Abstract: This paper characterizes the exploration of structural and optical configuration of CZTS films grown by dip-coating and its implementation as an absorber in thin film solar cells. The CZTS thin films were processed in normal glass substrates for a various number of deposal. The optical band gap and absorption coefficient of a CZTS absorber layer linked to the congregation of aqueous precursors containing copper (II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), zinc (II) chloride (ZnCl_2), tin (II) chloride (SnCl_2) and thiourea ($\text{CS}(\text{NH}_2)_2$) were fixated. The solution was organized by shrinking cation ore salts and thiourea in 2-methoxyethanol and monoethanolamine. It is perceived that two times deposited film shows good quality Kesterite structure of CZTS is revealed by the XRD. Optical affinities have been drifting out using UV-Vis spectroscopy techniques. The direct band-gap of 1.48 eV was found in one sample which is very close to the optimal value as an absorber layer and absorption coefficient was found greater than 10^4 cm^{-1} which exhibits CZTS phase in the film.

Keywords: $\text{Cu}_2\text{ZnSnS}_4$, Thin films, Dip-coating formula, Sol-gel, Annealing, Band gap, X-ray diffractometer.

1. Introduction

Dissimilar conglomerate material showed congruity in Thin-film solar cells among which Polycrystalline cadmium telluride (CdTe), copper indium diselenide (CIS), and copper indium (gallium) diselenide (CIGS) are being utilized for materialistic motivation to embellish cost-effectiveness. Due to restrictions on heavy metal usage for Cd and scarcity of In and CdTe have raised concern about limitations on fabrication capacity of the PV devices. To elucidate this issue, it is needed to develop another light absorber materials that are both nontoxic and solely obtainable. In this situation, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) quaternary semiconductor compound has flourished as one of the promising candidate [1]. As a propitious thin-film solar-cell ramification, CZTS has strained high premeditation in the past few years [2-4]. CZTS absorber layer has a fabulous absorption coefficient and a direct band-gap of (1.4-1.6 eV), which is illustrated in previous literature [5]. Furthermore, all the elements in CZTS are non-pestilential and nature - overflowing [6-9].

Sol process is cognate with the sol-gel process since after congregating the solution, a consecutive gel can be formed in one-step. Meaning of the sol-gel is alignment of an oxide network through polycondensation upshot of a molecular precursor in a fluid [10]. Crumb can be amorphous or crystalline and colloidal suspensions of particles are ruled over the Van der Waals constrain or hydrogen bonds. The presumption of sol-gel assimilation is to melt a precursor compound in a fluid and bringing it back as a solid in a coordinated manner [10]-[11]. Multiple-step systems with a preferred stoichiometry by mixing sols of various mixture can be achieved by Sol-gel system [12]; avoiding problems of hastiness and cherished mixture of reagents at the atomic level by fabricating tiny modicum. To measure the conductivity of semiconducting junctions provides the basic diode mechanism, which coupled with the sensitivity to light and heat and variable resistivity is the main property used to build photovoltaic cells [13]-[14]. A traditional dyeing method of speedy deposition of polymer films over a large region is the Dip coating process. Meaning of Dip coating is submerging of a substrate into a tank including coating material, withdrawing the piece from the tank, and entitling it to drain. The process is performed maintaining precise speed fulfilling controlled temperature and atmospheric conditions. The viscosity of the fluid, the dipping rapidity, the thicken content are some of the elements used to measure the film thickness. As a result of simplicity, this method highly depends on arrangement. Many components give to determining the final condition of the dip coating of a thin film [15]. Mixed kinds of dip-coated film structures and thicknesses can be determined by adjusting many elements such as submersion time, the amount of dipping cycles, solution composition, concentration and temperature, and surroundings humidity. The dip coating technique can give uniform, high-quality films even on bulky, complex shapes [16].

2. Experimental Analysis

Preparation of sol-gel solution for CZTS was set by dip coating technique and the mixture containing copper(II) chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (1.69M), zinc (II) chloride (ZnCl_2) (0.90M), tin (II) chloride (SnCl_2) (0.787M) and thiourea ($\text{CS}(\text{NH}_2)_2$) (6.665M), dissolved in 2-methoxyethanol. The mixture was stirred on the hotplate and magnetic stirrer at 45-55 °C for ½ hour. Meanwhile, the mono-ethanolamine were added (a

few drops as a stabilizer). Then, the assortment treated at room temperature at least 24 hours to yield a homogenous and transparent yellow solution. Lastly, the yellowish assortment from the sol-gel process was fabricated on SLG (soda lime glass) substrates. The glass substrates were cleaned through methanol solution and after that DY water. Dip coater, PTL-MM01 was used to deposit the CZTS film on the cleaned soda lime glass substrates for withdrawing speed about 150 mm per minute. Then the soaked films have been exsiccated on an oven at 200 °C for 10 min. Sample is put into the environment for natural cooling after drying. The process was repeated about 1 and 2 times. The sample name is denoted by A-1 for one time dipped and A-2 for two times dipped. Following that, the specimens were tempered at 250°C directed toward 900 seconds. The junctures and crystal coordination analysis were perceived by using X-ray spectrometer with Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) collected from $2\theta = 22^\circ - 60^\circ$. The optical absorption and observable band gap is estimated by transmittance assortments on the wavelength range of 400 – 1200 nm standardized by UV Vis spectrophotometer. The thickness of the specimens was computed through Stylus profiler in view of this experimentation work.

3. Results and Discussion

3.1 Structural properties

Figure 1 exhibits the XRD patterns of sample A-1 and A-2 of CZTS films prepared by dip coating technique. Broad peaks were obtained at the 2 Theta positions 28°, 47.40° and 55.40° for the films which corresponds to the (1 1 2), (2 2 0), (3 1 2) planes of CZTS thin films and they are distinct characteristic of tetragonal type kesterite structure of CZTS (ICDD card no: 26-0575)[17]. In Fig. 2, the films annealed at 250°C were identified by using XRD as a kesterite CZTS compound with Zn₂SnO₃[18] which corresponds to the (2 0 0) and (2 2 0) planes. The films exposed poor stickiness to the under layer because of the stunted temperature of annealing.

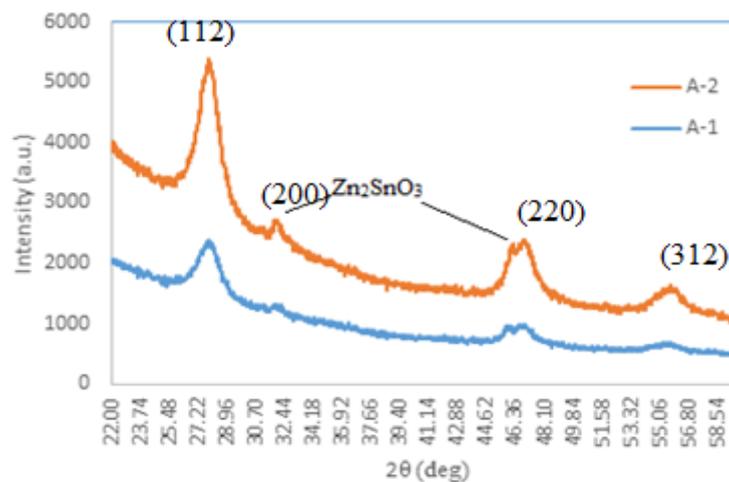


Figure 1: XRD pattern of samples A for 1 and 2 times deposited CZTS film

3.2 Measurement of Thickness

The measurements attained through the surface profilometer shown that the thickness of the film deposited by dip coating were found to 1.92 and 2.85 μm correspondingly for 1 and 2 times deposited films.

3.3 Optical properties

The observable properties were established by easily spread on UV Vis spectrophotometer the transmittance spectra shown in Figure 2 for 1 and 2 times dipped film which is observed for wavelengths of 400 to 1200 nm. It has been checked that the two samples exhibit stunted transmittance in the visible region for not high-temperature annealing.

For CZTS thin film absorber layer, stunted transmittance is required so the samples difference were naturally the same in transmittance vs wavelength curve. The other optical characteristics manifested variation so comparable result can be found.

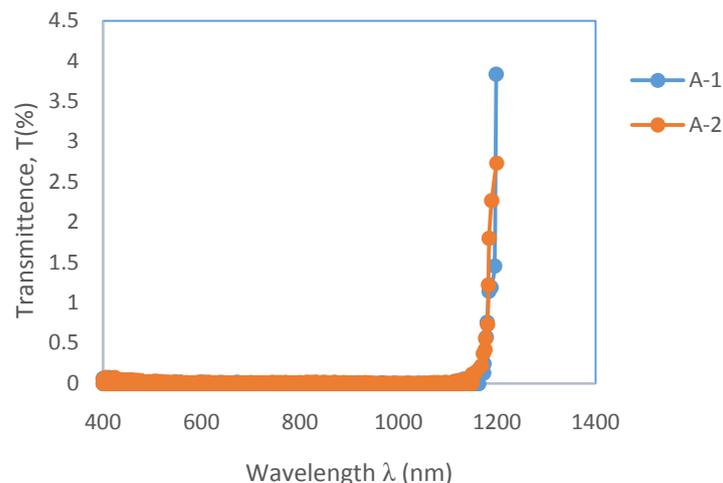


Figure 2: Transmittance Vs Wavelength of 1 and 2 times settled CZTS thin films

We need to establish the absorption coefficient (α), of CZTS films, was settle on the transmittance data as demonstrated in Figure 3 [19].

$$\alpha = (1/d) \ln(1/T) \quad (1)$$

Where d is film thickness and T is transmittance. The absorption coefficient is $10.3 \times 10^4 \text{ cm}^{-1}$ and $6.9 \times 10^4 \text{ cm}^{-1}$ respectively of samples A-1 and A-2. The absorption coefficient for dissimilar layer declines with rising depth.

One of the significant traits, observable band gap of CZTS absorber layer, is as manifested in Figure 4 from the accordance to Tauc's formula [20].

$$(\alpha h\nu) = A(h\nu - E_g)^m \quad (2)$$

Where A is a constant, the power of " m " is $1/2$ for direct allowed, 2 for indirect allowed, $3/2$ for direct forbidden and 3 for indirect forbidden. The band gap energy was endorsed by plotting $(\alpha h\nu)^2$ versus the $h\nu$ in Figure 4, therefore, the direct band gaps (E_g) of CZTS tempered at 250°C during 15 minutes were predicted to be 1.40 eV and 1.48 eV accordingly of samples A-1 and A-2. The band gap energy was calculated to be near 1.5 eV, which is in good compact with previously reported value [21].

The band gap increments with the numeral layer is detected to be higher. It is raised that the band gap of sample A-2 is near to the superlative for photovoltaic implementation.

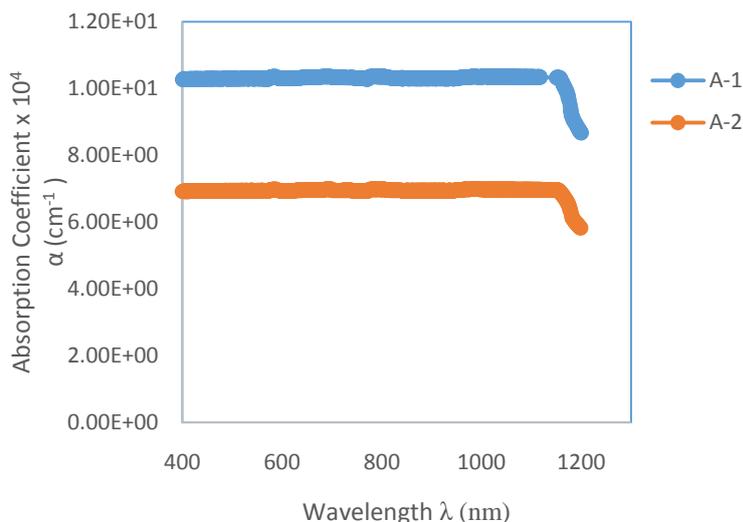


Figure 3: Absorption coefficient of A-1 and A-2 coated CZTS thin films as a constituent of wavelength λ

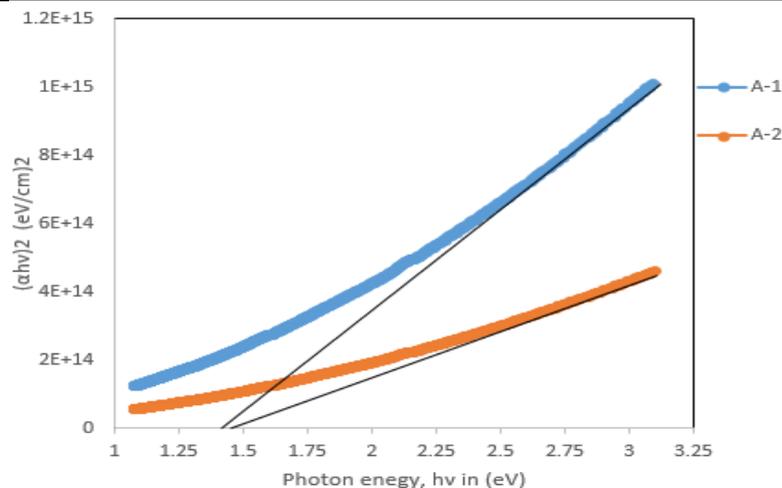


Figure 4: Band gap $(\alpha hv)^2$ in terms of $h\nu$ (eV) of CZTS thin films

Table 1: Optical Properties of CZTS with Various Layer

Sample name	A-1	A-2
Thickness (μm)	1.92	2.85
Optical band gap (eV)	1.40	1.48
Absorption coefficient(cm^{-1})	10.3×10^4	6.9×10^4

The extinction coefficient (k), was immovable from α using the following relation [22]

$$\kappa = \alpha \lambda / 4\pi \quad (3)$$

It is seen from Figure 5 that the extinction coefficient ranges between the extremes of 0.228 and 0.917 for the samples of A-1 and A-2 layer in the wavelength scope of 400- 1200nm. The conduct of curves seems to be associated where the value of "k" rising with increment wavelength. as "k" is straight to the absorption coefficient(eq.3). Also, since the absorption coefficient of the CZTS is very elevated ($>10^4 \text{ cm}^{-1}$), so "k" will be uplifted.

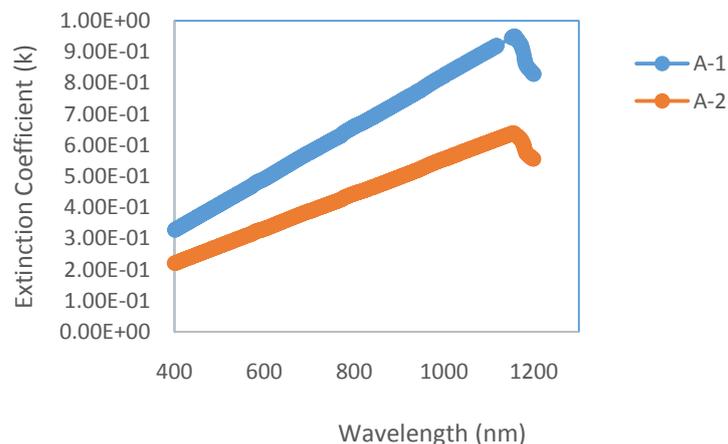


Figure 5:Extinction coefficient of A-1 and A-2 coated CZTS thin films as a constituent of wavelength λ

4. Conclusion

This research was observant to the synthesis and characterization of non-stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layers. Dip coating technique and anneal at air atmosphere had proclaimed to be convenient for kesterite CZTS thin film composition. The films exhibit poor adhesion to the substrates because of low annealing temperature. Several impurities are the cause of the secondary phase in the films. Here, layers were varied and sample A-2 had a band gap energy of 1.48eV which is appropriate for photovoltaic implementation. The X-ray diffraction presents that CZTS has a kesterite structure with anopulent position along the (112) plane. It seems thatthe band gap arising with upscale in thickness and absorption coefficient subsidence at the same time. Thus the extinction coefficient decreases as α has undeviating relation to k .

5. Acknowledgement

This experimentation was upheld by the Solar cell Fabrication Lab of IFRD (Institute of Fuel Research and Development (IFRD), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka.

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