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Synthesis and Optical Properties of Porous CZTS Films Deposited by Dip Coating Technique

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Abstract: The CZTS film was synthesized by dip coating technique for increasing the surface area absorption to optimizing efficiency of thin-film solar cell. We proposed a simple dip coating method to synthesize the CZTS films by using the precursor solution from sol-gel process. This progress augmented the porous surface by petal structure, which is used the metal chloride and thiourea is a precursor to sol-gel process prepared or synthesized the precursor solution for dip coating method. The CZTS film was annealed various temperatures in Argon gas for 1 h without sulfurization. The XRD and Raman result confirmed the CZTS tetragonal type kesterite structure, well-crystallinity depends on annealing increasing temperature. The morphology can be observed that porous petal structure nano size on surface film. The optical properties show high absorption coefficient of 10^4 cm^{-1} and optimum energy bandgap of 1.5 eV. The result can be modified the porous surface to enhance conversion efficiency very suitable for the absorber of solar cells.

Keywords: Kesterite, Sol-gel process, Thin-film solar cells, Absorber layer, Cu_2ZnSnS_4.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is a quaternary semiconductor compound with series of quaternary I_2-II-IV-VI_4 compounds such as Cu (I), Zn (II) Sn (IV) and S (VI). The CZTS materials consists of abundant and cheap elements and very important part of thin-film solar cell (TFSC).In currently, the photovoltaic cellwas development based-on thin film technology because the thin-film solar cellwas used low amount of material, low weight and coating on flexible substrate. The CZTS compound is a one of the most promising absorber layer materials due to it is being both abundant in the earth's crust, non-toxic element and low costthin film solar cells. The CZTS films have been deposited by various techniques such as electrodeposition [1], spray pyrolysis techniques [2], sol-gel processing [3], spin-coating methods [4], chemical bath methods [5], SILAR method [6] and dip coating technique [7, 8]. Among these, the dip coating technique has the advantages of simple deposited film, low cost and suitable for large-scale manufacturing of TFSC. In recently, Pengcheng Dai et al. reported energy bandgap 1.45 eV for good conduction of solar cell application prepared by solvothermal method [9], Om Pal Singh et al. reported energy bandgap 1.5 eV by sputtering method [10], The CZTS has energy bandgap ranged from 1.4 – 1.6 eV and high absorption of light >10^4 cm^{-1}on visible wavelength [11, 12]. Although CZTS thin film by different methods show similarly energy bandgaps but their efficiencies have reached only 10% [13].

In the present work, we developed the surface area of CZTS films for reduced energy bandgap and increasing absorption coefficient synthesized by dip coating technique and annealing various temperatures on the glass slide substrate.

2. Materials and Method

The CZTS films were synthesized by schematic diagram, as shown in Figure 1.CZTS films were synthesized by dip coating a solution containing the metal ion of Cu, Zn, Sn and S from analytical grade (AR) precursor of a copper (II) chloride dihydrate ($CuCl_2$·2H2O, 99%; QRëC, 2 mmole), zinc (II) chloride ($ZnCl_2$, 95%; QRëC, 1.6 mmole), tin chloride (SnCl2·2H2O, 99%; QRëC, 1 mmole) and thiourea (CH_4N_2S, 99%; HiMedia, 4 mmole) dissolved in 50 ml of 2-methoxyethanal (C_3H_8O2, 99.8%, Ajax) to break down into ions. The mixture was stirred on the hotplate and magnetic stirrer (85-2 Magnetic Stirrer) at 60 °C for 1 h. Meanwhile, the mono-ethanolamine (C_2H_7NO, Aldric) were added the few drop about ~3 ml to the stabilizer). Then, the mixture incubated at room temperature least 24 h to yield homogenous a clear yellow solution. At last, the mixture from sol-gel process were deposited on glass slide substrates by dip coating technique for withdraw speed about 30 mm min^{-1}. Then the wet films dried at 80 °C on the hot plate for 5 min in air, the process was repeated about four times. After that, the CZTS films were annealed in the Argon gas for 1 h in a commercial

furnace tube system (Lenton; LTF-1200) at 200 °C, 300 °C, 400 °C and 500 °C, respectively, as shown in Figure 2. The furnace temperature was increased about 10 °C min^{-1} from room temperature to 200 °C and then soaking temperature for 1 h and 5 °C min^{-1} from 200 °C to 300 °C, 400 °C and 500 °C in Argon gas. The samples were left to cool down naturally, as shown in Figure 3. The condition to prepare CZTS films by dip coating technique is porous surface morphology, thickness and composition ratio studied by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS; Hitachi, SU8000). The phases and crystal orientation analysis were identified by using an X-ray diffractometer (Shimadzu, XRD-6100) with $CuK\alpha_1$ radiation (λ = 1.5406 Å) collected from $2\theta = 20° – 80°$. Raman spectra (Renishaw, inVia Raman microscope) observed on a resolution 100× in backscatter used 785 nm laser and power 0.5 W. The optical absorption and optical bandgap calculate by transparent spectra on the wavelength range of 300 – 1100 nm measured by UV-Vis spectrophotometer (Shanghai, UV-6100).

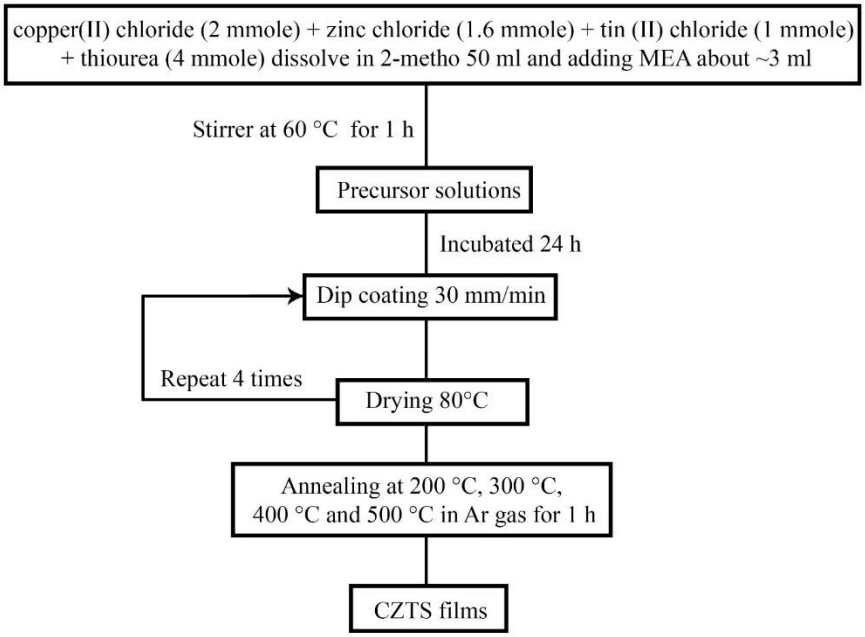

Figure 1: Schematic diagram synthesized of CZTS films.

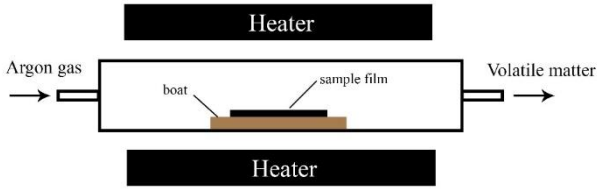

Figure 2: Schematic annealing process of CZTS films.

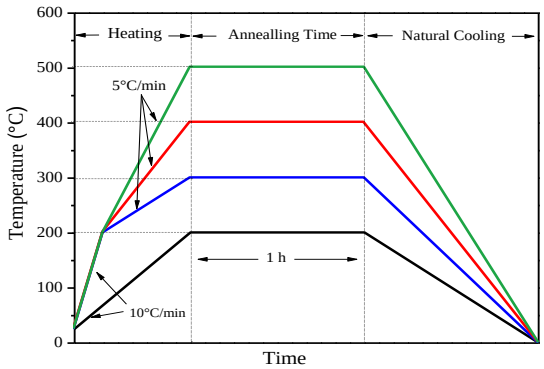

Figure 3: Schematic annealing temperature step of CZTS films

3. Results and Discussion

The XRD patterns of CZTS films deposited by dip coating technique are shown in Figure 4 (a). The maximum peak of all post-annealed samples shows that 2θ about ~28° which is referred to (112) plane. The CZTS films showed shape peaks at 500 °C annealed due to calculate the lattice parameter a = b = 5.07 ± 6.06 Å and c = 11.67 ± 7.5 Å corresponded with the tetragonal type kesterite structure PDF # 26-0575. The tetragonal lattice parameter ($a = b \neq c$) determined by Equation (1) [14].

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

when d_{hkl} is inter planar spacing distance between adjacent planes (h, k, l plane).

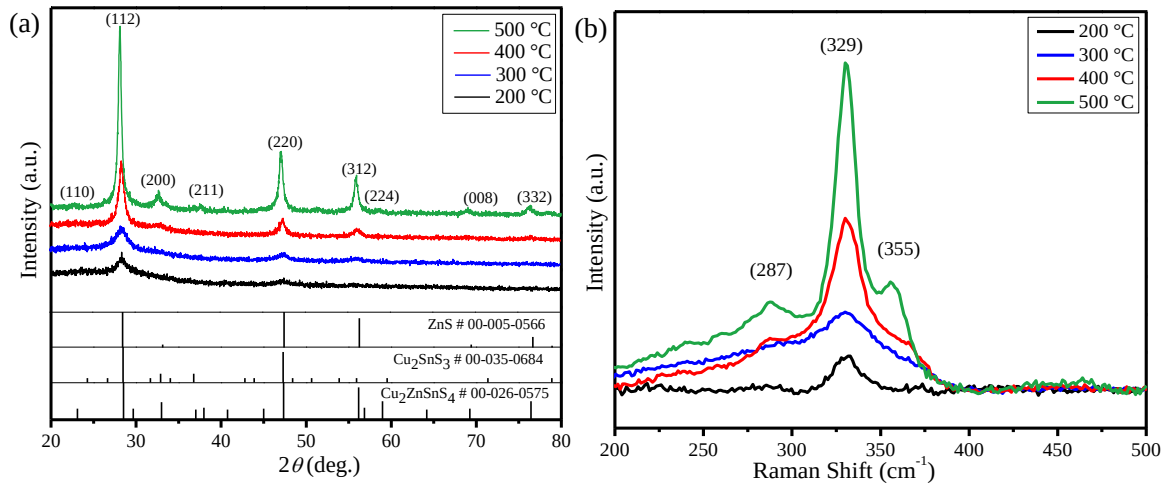

Figure 4: (a) XRD patterns and (b) Raman spectra of CZTS films growth by dip coating.

However, the lattice parameters *a*, *b* and *c* have different value about *a* = 5.42 Å and *c* = 10.848 Å corresponding to Sheleg et al. [15]. Although the results structure of films was mixing the Cu_2ZnSnS_4 phase (PDF # 00-026-0575), ZnS phase (PDF # 00-005-0566) and Cu_2SnS_3 phase (PDF # 00-035-0684) with comparison the standard diffraction pattern, as shown in Fig 4(a). We confirmed lattice parameters by Raman spectra, as shown in Figure 4(b). The CZTS was observed most prominent peaks at 287 cm^{-1} and 329 cm^{-1} corresponding to Ito et al. [16] and Seboui et al. [17]. The impurity phase of ZnS found that the Raman spectra peak at 355 cm^{-1}, which correspond with Ito et al. [16]. The crystallinity is important to explain the crystal formation in the film, which it can be estimated from the average crystallite size (*D*) determined by Scherrer's formula Equation (2).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (2)$$

The stresses or lattice imperfections can be considered that the microstrain (ε) occurs in films was calculated by Equation (3) [6, 18]

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan\theta} \qquad (3)$$

The microstrain (Figure5) was indicated that the lattice imperfections are decreased because of crystallite size increased with increasing higher temperature [6].

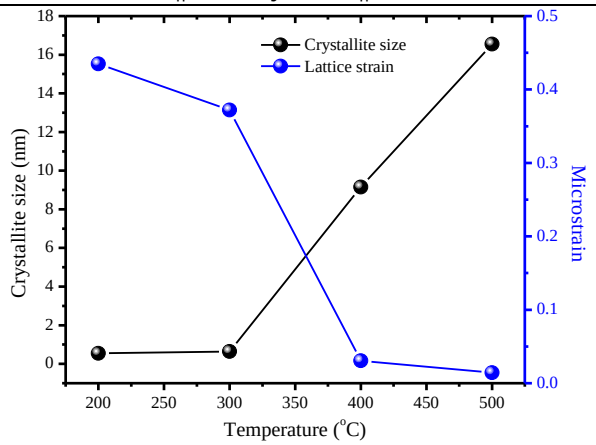

Figure 5: Crystallite size and microstrain of CZTS films growth by dip coating deposition.

The surface morphology of CZTS films at 200 °C to 500 °C observed by scanning electron microscopy (SEM) are shown in Figure 6. The CZTS films show non-uniform surface texture, together with some cavities and voids. In particular, the porous surface of the sample film was promoted a more compact with low density packed grains and high porosity due to volatile matter such as ammonia, chlorine and alcohol, as shown in Figure 7, which the average size of petals about 46.33 nm corresponding to Sarkar et al. [19].

Furthermore, the thickness CZTS films was observed by SEM, which it increased slightly from 3.32±0.02 to 4.50±1.81 µm at temperatures rang 200 °C to 500 °C as shown in Figure8(a - d). The thickness of CZTS films may be caused by the formation of small crystals, which is corresponding to the XRD crystallite size compared to other methods [8, 19].

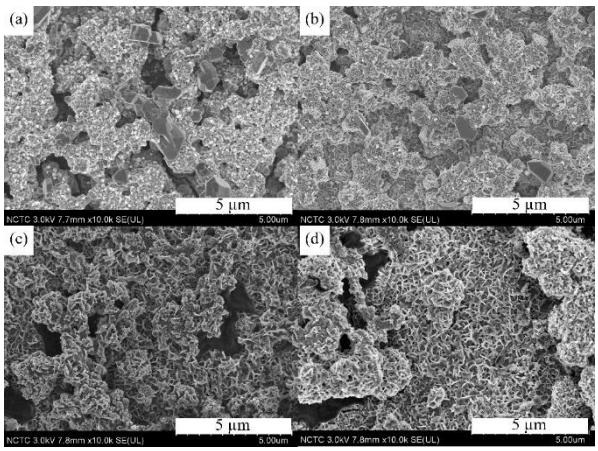

Figure 6: Surface morphologies of CZTS films (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.

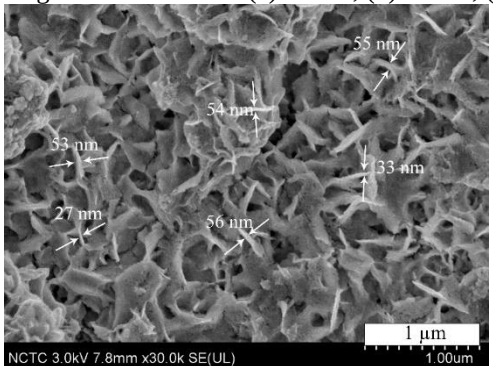

Figure 7: Petal structure of CZTS film at 500°C

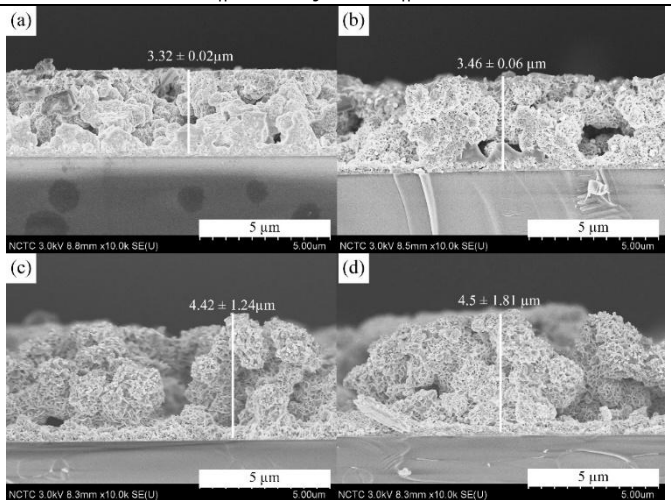

Figure 8: SEM cross-section image of CZTS films (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C

The chemical composition of CZTS films was analyzed by energy-dispersive X-ray spectroscopy (EDS) as shown in Table 1. The ratio of Cu and Zn were slightly decreased with increasing the annealed temperatures indicate that the atomic composition of Cu-rich and Zn-rich. The ratio of S and metal show low values indicate low impurity phase [20, 21]

Table.1 the elemental composition of the CZTS films analysis.

Sample	*Chemical composition (At %)*				*Ratio of composition*	
	Cu	*Zn*	*Sn*	*S*	*Zn/Sn*	*Cu/(Zn + Sn)*
200°C	34.45	19.83	8.731	36.97	2.27	1.20
300°C	25.88	12.52	13.67	47.91	0.91	0.98
400°C	26.42	11.06	17.88	44.63	0.61	0.91
500°C	24.25	14.26	17.05	44.42	0.83	0.77

The transmittance was measured by UV-Visible spectrophotometer, as shown in Figure 9(a). The transmittance shows low transparent (less than 1%) indicate with high absorption in visible light wave length (300 – 700 nm) [6].

Moreover, absorption coefficient (α) can be calculated by the absorbance is followed in Equation (4)

$$\alpha = \frac{2.303 \times A}{t} \qquad (4)$$

where α is the absorption coefficient, t is the thickness film and A is the absorbance spectra.
The optical absorption coefficient as a function of photon energy, $\alpha > 10^4$ cm^{-1}[22] was observed (Figure 9(b)) and indicated that the occurrence of direct transitions. Therefore, the energy bandgap (E_g) can be determined by Tauc's formula [21] plotting a graph between the square of absorption coefficient, Plank constant and frequency relationship photon energy ($h\nu$) as following in Equation (5).

$$(\alpha h\nu)^2 = \beta\left(h\nu - E_g\right) \qquad (5)$$

There β is an energy independent constant depend on photon energy, h is the Planck constant, ν is frequency.

The relation of $(\alpha h\nu) \wedge 2$ versus the ($h\nu$)is shown in Figure 9(c). Our determined the energy bandgap is 1.72 eV for 200 °C, 1.68 eVfor 300 °C, 165 eV for 400 °C, 1.50 eV for 500 °C, respectively, agrees with

literatures [23], [24], [25], [3, 22]. The CZTS film at 500 °C has closed the optimum absorption value of solar cell [26]. The different$E_g$of the CZTS films depended the morphology, crystallite size and annealing temperature.

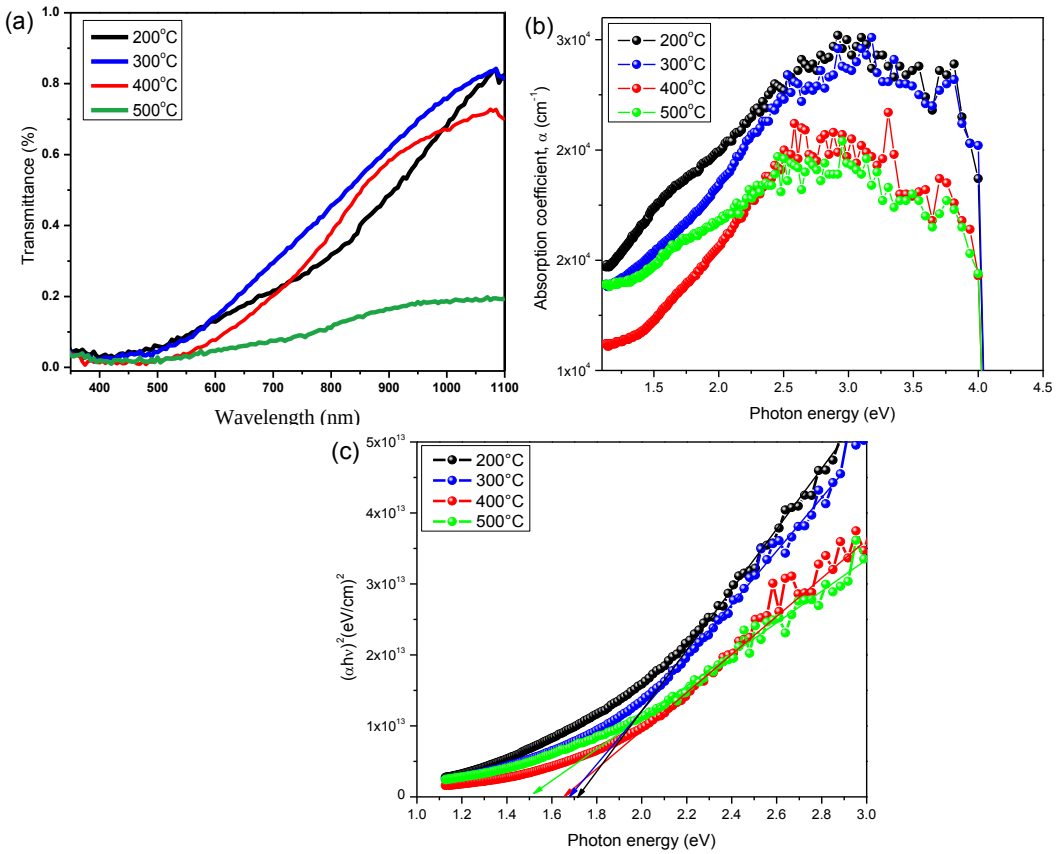

Figure 9: Optical properties of CZTS films annealed different temperature (a) transmittance (%*T*), (b) absorption coefficient (α) and (c) energy bandgap (E_g).

4. Conclusion

We successfully prepared the CZTS films by dip coating technique and annealed without sulfurization process. The CZTS films show the tetragonal type kesterite structure, low impurity phase, high poroussurface area and good absorption. The decreased energy band gap is good for solar cell however depended annealing temperature and thickness.

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