Effects Of Ionic Immersion Time On Optical Properties Of Cu$_2$ZnSnS$_4$ (CZTS) Deposited by Successive Ionic Layer Adsorption And Reaction (SILAR)

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Abstract. Cu$_2$ZnSnS$_4$ (CZTS) thin films fabricated by successive ionic layer adsorption and reaction (SILAR) method is a promising combination to actualize a low cost thin films Solar Cell (TFSC). Ionic exchange and rinsing time are critical point for ionic layer formation in SILAR method. The purpose of this study is to investigate the influence of cationic and anionic immersing time on the band gap energy of CZTS. Immersing time was varied into 10, 20, 30 and 40 seconds for both deposited and annealed samples, which annealing was conducted on 300$^\circ$C for two hours. Deposited results showed a linear increase on band gap energy as cationic immersing time extended. Whereas, nonlinear increment with optimum band gap 1.35 eV at 30 seconds immersion happened for anionic time variation samples. Annealed CZTS with cationic time variation also showed a linear increasing band gap. Meanwhile, annealed with anionic time variation showed a backward tendency of the deposited samples which the band gap decrease nonlinearly as anionic immersing time lengthened.

Keywords: Semiconductor, band gap energy, CZTS, SILAR

1. Introduction

Theoretically, solar energy provide 7000 times amounts of whole world electrical energy needs, yet in real utilization solar cell only supplies 0.1% of world’s demands [1]. Earlier development solar cell requires high production cost. To produce 1 watt electricity during 12 hours sun rays expose with intensity about 18% still costs more compare to gas or coal to convert its calorie into 1 watt of electrical energy. Although the newest production cost has been reduced through various modifications of process [2][3], the relatively low efficiency of energy conversion compare to calorie conversion of coal into electrical energy is still a major problem. In addition, high cost of raw materials and expensive technology contribute to the high initial cost of solar panel. Therefore, researchers focus on developing high efficiency solar cell with low-cost method and affordable raw material.

Cu$_2$ZnSnS$_4$ or CZTS is a potentially low cost quaternary thin films which each element of CZTS is earth abundant. Cu, Zn, Sn, and S are relatively non-toxic and cheaper than the rare earth such Ga and In. Katagiri reported that the band gap energy of CZTS is 1.4-1.5 eV with
absorption coefficient greater than 10 cm⁻¹ which suits to be applied as semiconductor on solar cell [4][5]. CZTS thin films have been developed via various method either physical or chemical route, yet wet chemical is the most suitable on low cost thin films solar cell concept. Successive ionic layer adsorption and reaction or known as SILAR is a modified version of chemical bath deposition (CBD) method which is considered as one of promising method to produce thin films in the industrial-scale [6] due to its simple procedures and inexpensive equipment. With numbers advantages SILAR does not need high quality substrate and a set of expensive vacuum system [6][7]. The combination of simple method and cheap based semiconductor assumed to be relatively reduce the production costs.

The key of SILAR process is ionic exchange time, where the length of the ionic immersing and rinsing time process is a critical point in the formation of ionic layers. Unnecessary precipitation growth need to be avoided in SILAR in order to keep bulk less condition for thin film [6]. The present study intends to explore the effect rinsing time and ionic soaking time on CZTS semiconductor optical properties. By controlling immersion variable, the study expected to gain information on optimal treatment to achieve band gap energy of CZTS near to 1.4-1.5 eV.

2. Materials and Methods

The composition of the precursors refers to the experiment conducted by Patill and Mali et al. [7][8]. Concentration of the cationic precursors was 0.2 M of CuSO₄, 0.01 M of ZnSO₄, 0.02 M of SnSO₄ and for anionic precursor was 0.16 M of Na₂S. Those precursors deposited on SS304 substrate with immersion area are 4cm x 4cm. Variable immersion time for each sample can be seen in Table 1 and repeated in 40 cycles as shown in Fig 1. Deposited samples with cationic soaking variable addressed as K1, K12, K3 and K4 while the annealed one marked with K1a, K2a, K3a, and K4a which same rules on anionic variable. Annealed was conducted in atmosphere an oven at a temperature of 300°C for 180 minutes or 2 hours.

Chemical compound on the surface of the samples was examined by X-Ray Diffractometer Shimadzu 700 (Cu Ka, λ = 1.5418 Å) scanned form 20° to 90° (20). Study of optical absorbtion of CZTS was carried out by Shimadzu UV-2410 instrument within wavelength range of visible light 350 – 800 nm. While surface morphology was characterized using field emission type scanning electron microscope (FE-SEM) S-4800, Hitachi Co., Japan.

![Fig. 1. Schematic of repeated immersion](image-url)
3. Results and Discussion

Visual examination

Visual examination on deposited K samples went darker from brown to black as the cationic immersion time increase (Fig. 2). While surface of anionic sample are going darker from dark brown to black until 30 seconds immersion, yet after 40 seconds soaked the surface color turn lighter to brown again. Anionic samples show the same tendency with previous studies lead by Shinde [9][10]. This tendency can be attributed to slight decrease in film thickness where it is due to the formation of outer porous layer or the film may have developed stress which tends to cause delamination that resulting in peeling off the film after the film reaches at maximum thickness [8]

![Fig. 2. As deposited sample’s surface cationic samples (top) and anionic samples (bottom)](image)

Optical absorption studies

Variation of absorbance values ($\alpha_0$) versus wavelength ($\lambda$) of deposited and annealed samples can be observed in Fig 3. The optical band gap energy is estimated by using equation 1. Where $\alpha_0$ is absorption coefficient and $E_g$ is band gap energy. Since CZTS is a semiconductor with a direct transition, therefore the values $n = \frac{1}{2}$. With both sides with the rank constituent quadratic equation then obtained equation 2. By extrapolating the curve to zero ($\alpha = 0$) energy gap values obtained from each sample.

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu}$$  \hspace{1cm} (1)

$$(ah\nu)^2 = \alpha_0^2(h\nu - E_g)$$  \hspace{1cm} (2)

Fig. 3a and 3b show band gap energy of cationic samples. Deposited K samples show an increasing band gap energy as the cationic immersion time increase from 1.37eV to 1.41eV after 40s. K samples with anneal treatment show the same tendency, the band gap energy increases as the cationic immersion time increase. These band energy level of annealed samples surpasses the range of CZTS band energy due to the formation of ZnS structure as it shown in XRD study. The band gap energy is expected to be decrease after anneal treatment, therefore the band gap increment was the contributiton of ZnS which has energy band gap above 3eV.

As for anionic samples in Fig 3c and 3d, the band gap energy of deposited A samples showed nonlinear increasing band gap as the anionic immersion time increase. After soaked for 30s the energy band gap A samples reached optimum value at 1.35eV and decrease to 1.25eV after 40s.
Deposited A samples showed such low energy band gap likelihood due to formation of other substance which have lower band gap energy such as Cu₂SnS₃ (0.9 eV) or Cu₃S (1.2 eV). In the other hand, anionic samples with anneal treatment showed nonlinear decreasing band gap as the immersion time increase which A3a samples hit the lowest band gap energy at 1.3eV. Otherwise A2a and A4a showed such nearly ideal band gap energy, 1.4eV and 1.55eV respectively.
Fig. 3 Band gap energy of a) cationic as deposited sample b) cationic annealed sample c) anionic as deposited sample d) anionic annealed sample with each immersion time 10 seconds, 20 seconds, 30 seconds, and 40 seconds.

**Structural and Morphological Studies**

XRD analysis and SEM observation were carried on the sample with the lowest, highest and optimum band gap energy. Which for deposited cationic samples K1 and K4 and for anionic samples A2 and A3 were selected. As for annealed treated samples K1a, K4a, A2 and A3a were also observed. XRD result for K1, K1a, K4 and K4a are shown in Fig. 4 which the deposited sample K1 show no indication of CZTS peak due to amorphous phase and K4 showed that Zns phase were precipitated on the sample after soaked for 40s. Samples K1a and K4a apparently show (1 1 2) plane in 25 degree 2θ after anneal treatment. Elemental study for A2, A2a, A3 and A3a can be observed in Fig. 3b where the peak of deposited CZTS films are still quite amorphou, thus the diffraction peak of (1 1 2) plane is insignificant and another compound that were expected to be observed such as Cu₂SnS₃ or Cu₄S could not be seen. While Fig. 4 shows
a peak of (1 1 2) plane. The other significant peaks that are observed are SS304 peaks. Fig. 5 shows scanning electron micrographs of as deposited CZTS at 3000 times magnification and Fig. 4b shows annealed CZTS surface with same magnification. It is observed from both surface that CZTS films are not densely packed on substrate surface. Round grains are observed from as deposited CZTS and flakes grains from annealed CZTS. Anneal treatment changes the grain shape of CZTS from round shape into flakes due to the evaporation of hydrate and water content loss.

**Fig. 4.** XRD pattern of as deposited and annealed CZTS on SS304 substrate
**Fig. 5.** SEM images of a) as deposited (left to right K1, K4, A2, A3) b) annealed CZTS (left to right K1a, K4a, A2a, A3a at 3000x magnification

4. Conclusions

Increasing of cationic immersion time for deposited and annealed K sample increase the band gap energy of CZTS, yet this linear increasing tendency is not essentially noteworthy since by keep increasing the variable the band gap will be wider. In the other hand as deposited sample show non-linear increment of band gap energy with optimum band energy achieve at 1.35 eV for deposited anionic sample. While annealed anionic sample also show non-linear decreasing of band gap energy with the opposite trend of deposited samples which A3a sample being the lowest (1.3 eV) and A2a reach ideal value (1.4eV). In other word, the optimum condition anionic samples hold key role in SILAR process.

5. References

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