Synthesis and Deposition of High Crystallinity Cu₂ZnSnS₄ (CZTS) Using Dip Coating Method

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Abstract. Kesterite Cu₂ZnSnS₄ (CZTS) thin film was successfully obtained using simple dip coating method. Synthesis of CZTS consist of mixing copper chloride, zinc chloride, tin chloride, and thiourea into a mixture of ethanol and ethanolamine to make CZTS suspension. Soda lime glass was used as a different substrate for dip coating method. Dip coating method uses 3 cycles of dip and drying at 170°C to remove ethanol and ethanolamine and then the sample was annealed at 550°C in argon atmosphere. X-ray diffraction was used to check the formation of kesterite before and after annealing. After annealing the diffraction pattern shown high crystallinity of kesterite with little secondary phase. Using Scherrer equation we can predict the crystallite size of CZTS before and after annealing. The scanning electron microscope was used to show the morphology of the CZTS before and after annealing. It is shown that although the grain was distributed homogenously a void can be seen throughout the surface. Optical properties of samples were checked before and after annealing using UV-vis Spectrometer. The result shows that dip coating method could create a good properties CZTS.

Keywords: Annealing Effect, CZTS, Dip-coating, Ethanolamine, High Crystallinity.

1. Introduction

With the recent increasing use of sustainable energy as main source of the energy, the study around photovoltaic material has significantly increased. One of the commonly researched photovoltaic material was Cu₂ZnSnS₄ (CZTS) [1]. CZTS was selected because it has a relatively good band gap of 1.4-1.5 eV, cheap production, non-toxic and the material source is abundant [2].

In the solar cell application device, CZTS was used as the absorber layer because CZTS have the absorber coefficient of 10⁴ cm⁻¹ in visible spectrum range [2]. And as n-type semiconductor like silicone but because the absorber coefficient is a lot higher than silicone the film did not require high thickness. So it reduces the cost of raw materials [3].

Many processes have been conducted to create CZTS including solid-state method [4]. But the chemical method is often selected because it creates CZTS with high purity, low cost and simple [5]. Many papers synthesized CZTS using successive ion layer adsorption reaction (SILAR) method but the complex method...
and require a lot of time are slowing the production of CZTS [6]. Another method that has been used was spin coating method of Cu-Zn-Sn precursor then annealed with sulfur atmosphere [7]. Spin coating method creating relatively good homogeneity of CZTS because of centrifugal energy can create evenly distributed precursor of CZT. But comes the problem of the film not sticking in the spin coater if the contact angle was too high, the film would just slip off the glass and did not create good evenly distributed CZTS [8]. In addition, although many researchers have successfully created a perfect variable for sulphurization, it is still relatively hard to control the environment of sulphurization if we did not use trial and error method.

Dip coating method offers the benefits of SILAR method with already CZTS precursor formed. Almost every precursor will stick to the substrate using dip coating method [9]. This paper will discuss the performance of CZTS using dip coating method and compared the use of annealing CZTS at 540 °C with the performance characterized by X-ray diffraction (XRD), ultraviolet-visible (UV-vis), Energy dispersive spectroscopy (EDS) and field emission scanning electron microscope (FE-SEM).

2. Method and material

The dip-coating method to create CZTS also shown in the Fig. 1. The synthesis of precursors was done by dissolving each one chloride elemental constituents in solvent and stabilizer [10]. Whereas ethanol was used as solvents and ethanolamine as a stabilizer. The volume fraction of ethanol compared to ethanolamine was 70% and 30% of the total volume respectively. The molar value of the constituent elements are and the volume of the solvent is adjusted with theoretical calculations of 0.075 M, 0.050 M, 0.050M and 0.23 M for Cu²⁺, Sn²⁺, Zn²⁺, and S²⁻ concentration respectively. The optical and morphological properties of CZTS which are found in conditions of Cu poor (Cu / (Sn + Zn) <1) and Zn rich (Zn / Sn> 1) [11,12].

![Figure 1. Dip coating process.](image)

After the precursor was made the deposition technique that been used is dip-coating with 3 cycles dipping and drying at 150 C for 10 minutes each cycle continued with final drying at 200°C for 10 minutes for removing all ethanolamine. For each dipping, the surface was homogenized by introducing airflow vertically. Lastly, the sample was annealed at 540°C in Argon atmosphere for 15 minutes to make crystalline structure of CZTS.

The samples then characterized before and after annealing by PANanalytical X-ray diffraction with an inert atmosphere to check the diffraction pattern of samples. AMETEK scanning electron microscope and
EDS are used to check the morphology and the chemical composition of the samples. Shimadzu UV-vis under atmospheric pressure to check the optical properties of the samples.

3. Result and Discussion

3.1. Visual result

It is shown in Fig. 2 That comparison of the visual result of CZTS before and after being annealed. Fig 2a. Shown that before annealing the color of presumably CZTS is mostly black, this phenomenon happens because there is still no formation of crystalline CZTS and only form a paint-like layer. In other hand Figure 2b. Shown the CZTS after being annealed, and shown to have a slightly different tone of black almost like grey [3]. The different gradations of color possibly change the outcome properties of CZTS.

![Figure 2. CZTS (a) before annealing and (b) after annealing.](image)

3.2. Diffraction Result

Diffraction result of the CZTS was carried out using X-ray diffraction shown in Fig. 3 and Fig. 4. With comparison with 00-026-0575 reference in UCDD PDF2. Fig. 3 shown the diffraction patterns of CZTS before annealing was being used, it is shown that although the crystallinity was still very low the peak with the highest intensity already formed. This means the CZTS was there but not yet formed to be crystal kesterite structure.

![Figure 3. The diffraction pattern of non-annealed CZTS compared to reference 00-026-0575 (Kesterite).](image)

On the other hand, the diffraction pattern of CZTS after annealing is shown in Fig. 4. It is clearly shown that crystallinity was higher compare to CZTS that did not go through the annealing process. The CZTS sample shown to have matched with the diffraction pattern of kesterite reference. This proves that CZTS samples were almost made entirely by kesterite CZTS crystal structure.
These diffraction patterns hinted that the synthesis was successfully carried out and resulting in high crystallinity that almost identical to the reference [13].

3.3. Crystallite Size

Using X’pert highscore we can calculate the FWHM (full width at half maximum). This need to be done in order to calculate crystallite size using Scherrer equation with FWHM. Scherer equation is shown in equation 1. With K is the shape factor and the value are 0.89, \( \lambda \) is 1.54 Å, B is FWHM and D is the crystallite size [14].

\[
D = \frac{K \lambda}{B \frac{1}{2} \cos \theta}
\]  

All peaks of CZTS with and without annealing were labeled and calculated. The crystallite size is the average of crystallite size from each peak. Table 1 shows that the crystallite size of the annealed sample was a lot higher with almost 3-time multiplier compared to CZTS without annealing process. This concludes the successful process of CZTS synthesis.

| Process              | D(nm) |
|----------------------|-------|
| CZTS Non-annealing   | 8.01  |
| CZTS annealing       | 24.81 |

3.4. Morphology Result

The morphology of CZTS was then checked using scanning electron microscope to check not only the grain but also the distribution of the surface of CZTS. Distribution result will show if this process is applicable to making CZTS thin film [15]. Fig. 5 show the CZTS before and after it was annealed. Fig. 5a shows a blurry image over the substrate, this means that there is still a lot of impurities considering this process may still be left some Cl⁻ and some ethanolamine since it is not fully evaporated [16]. Using ImageJ we are able to obtain the average size of the particle was around 400 nm which was acceptable considering the CZTS has not yet gone through the annealed process. The homogeneity of the non-annealed sample shows that although the image was blurry we can safely assume that it is not fully distributed because there are still a lot of color tones in it means the voids can still be made.

Fig. 5b show CZTS after being annealed, the blurry part was completely removed. This means the
impurities that habit in CZTS without annealing was completely removed. From imageJ we can calculate the average ratio size of particle CZTS, it was shown that CZTS annealed have a particle size of around 700 nm which is higher from CZTS that has not yet been annealed. This phenomenon can be caused by grain growth during annealing effect which normally happens around the annealing sample [17]. The distribution of the particle was spread homogenously but we can see a hole in every bit of the surface. This means that although the dip coating method created the homogenous result it still needs to improve to eliminate the void.

Figure 5. Morphology result of CZTS (a) without annealing and (b) with annealing.

3.5. Chemical Result
The chemical result of CZTS with annealing process and without annealing process was carried out using electron dispersive spectroscopy (EDS). EDS was tested to see the confirmation on the chemical result in impurities from CZTS without annealing process and also to see the loss of impurities in CZTS after being annealed. Fig. 6 shown EDS result of CZTS before going through an annealing process and it is confirmed that CZTS before annealing have high impurities such as Chlorine, Oxygen, and Nitrogen because the hydrocarbon material from ethanolamine is not fully evaporated yet and the chlorine from the salt used to make CZTS was not yet to be removed.

Figure 6. The chemical result of CZTS with annealing.  
Figure 7. The chemical result of CZTS without Annealing.
CZTS without annealing was not the perfect candidate for CZTS and not yet be ready to be a semiconductor. In other hands, the chemical result of CZTS after annealing are shown in Fig. 7 are not showing the chlorine impurities at all which mean that the impurities were completely removed. This proves that the crystalline structure of CZTS was almost pure made of CZTS and that is a good indication of a good absorber CZTS.

3.6. Optical Result

The optical result of CZTS was carried out using UV-vis spectroscopy. CZTS with annealing process and without annealing process was placed in the holder and the optical properties (absorbance, transmittance, and reflectance) was calculated in the specific wavelength [18].

Fig. 8 show the comparison absorbance optical properties between CZTS with annealing and without annealing process. CZTS without annealing process shown to have almost linear absorbance from all the wavelength. This means the crystalline structure that responded to specific optical properties has yet to be formed. CZTS without annealing process was acting more like black paint compared to an absorber layer. In contrary CZTS with annealing process create specific optical properties when in contact with a specific wavelength. This phenomenon proves that the crystalline structure/semiconductor layer was already formed because it acts in a specific order.

![Figure 8. Absorbance optical result of CZTS.](image)

If we calculate the average of absorbance in CZTS after annealing process we can calculate the average transmittance using beer’s law in equation 2. With $\%T$ is a transmittance in percentage and $A$ is absorbance value [19].

$$\%T = 10^{(2-A)}$$  \hspace{1cm} (2)

Since the average absorbance in all wavelength is $\sim$1 A it can easily be calculated that transmittance of the absorber layer was 10%. The value of this transmittance was good since we want the transmittance of the absorber layer was as low as possible. This concludes this CZTS can deliver for being absorber layer.
The other properties we can calculate for semiconductor was the band gap of the absorber layer. The band gap was used to indicate how many energy it takes to turn the semiconductor material from isolator to conductor. Fig. 9 shown the band gap of CZTS using tauc’s plot. The value of band gap of this CZTS was around 1.36 eV which is still acceptable range for CZTS absorber layer in theory [20]. This proves that the CZTS semiconductor absorber layer was formed perfectly with this process.

![Figure 9. Tauc plot of CZTS after annealing.](image)

Overall the characterization leading towards to the formation of CZTS was confirmed by optical, diffraction pattern, morphological and chemical.

4. Conclusion

The characterization of CZTS synthesized by using metal-ETA complex is resulted in good properties of CZTS with crystallinity kesterite structure after the annealing with almost identical peaks with reference. The dip coating method is shown to have created a homogenous structure across the surface with a little void which can be improved by perfecting the deposition method. Optical measurement resulted in proving that CZTS are present in the structure with low transmittance optical properties that indicating a good absorber layer. The band gap that has been found for CZTS using this method was 1.36 eV which later prove that this method creates a good properties CZTS. And annealing process will highly improve all properties that require to make a good CZTS.

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