Crystal structure and optical properties of non-vacuum solution-based processed Cu$_2$ZnSnS$_4$ (CZTS) thin-film

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Abstract. Cu$_2$ZnSnS$_4$ (CZTS) material has emerged as an attractive material for the absorber layer in solar cells application. CZTS has similar properties with its successful predecessor CIGS, but CZTS offers the advantage of low-cost constituents, material abundance, and non-toxicity. We fabricated CZTS thin-film using non-vacuum solution-based process and then the deposition process using the spin-coating technique in the present work. Afterward, we observed that the CZTS thin-film was successfully fabricated with kesterite structure crystal with an optical bandgap of 1.56 eV. We also confirmed that the CZTS thin-film exhibit a high light-harvesting efficiency at a low wavelength suitable for the solar cells application's absorber layer.

Keywords: CZTS thin-film, non-vacuum solution-based process, crystal structure, absorbance, bandgap energy, light-harvesting efficiency

1. Introduction

Technological and industrial advances that have developed rapidly in the last few decades have led to an increase in energy demand. However, the majority of energy sources used today come from fossil fuels that are not renewable and can negatively impact the environment [1]. Therefore, solar cells have been developed as an alternative solution to meet environmentally friendly energy needs. Among different solar cells, the third-generation solar cells have emerged as one of the most promising candidates [2]. The reason being its possibility of generating high-efficiency (31 – 41% Shockley-Queisser limit), low-cost manufacturing process, non-toxicity, and high elemental abundance [3].

The Cu$_2$ZnSnS$_4$ (CZTS) kesterite compound has been widely studied as an alternative material for absorber layer in thin-film solar cells [1, 4]. As a prospective absorber layer, CZTS offers similar properties with its excellent predecessor CIGS such as high absorbance of $10^4 – 10^5$ cm$^{-1}$, optical bandgap near 1.5 eV, and tetragonal crystal structure [5, 6]. However, CZTS offers more advantages...
than CIGS, including material abundant, cheaper, and non-toxic [7]. Therefore, CZTS solar cells are categorized as third-generation emerging solar cells.

Several techniques for CZTS thin-film fabrication process have been studied including vacuum deposition [8], magnetron sputtering [9], pulsed laser deposition [10], electron beam evaporation [11], spray pyrolysis [6], electrochemical deposition [12], and sol-gel [13]. Basically, there are two categories of the fabrication process which are vacuum and non-vacuum [14]. In vacuum deposition, the layer of materials was deposited in the manner of atom-by-atom or molecule-by-molecule in a solid surface that operates at a pressure below the atmospheric pressure. Meanwhile, non-vacuum deposition usually is carried out by dissolving the material constituent in a solvent and then coated onto a substrate.

It has been widely known that CZTS material has low chemical stability [15]. Therefore, the nominal composition of the CZTS molar ratio is an important matter to be considered. Empirically, the nominal atomic composition of the CZTS material is generally arranged into a non-stoichiometric Cu-poor and Zn-Rich condition to produce high efficiency [16, 17]. In this composition, the secondary phase density of the CuZn profound defect is reduced without reducing the p-type conductivity of the CZTS absorber [7]. This is because the presence of shallow defects VCu is still in high density. Finally, a lower density of deep defects leads to a lower recombination mechanism that improves performance.

In this work, we fabricate CZTS thin-film using a non-vacuum solution-based process. The precursor was prepared using the sol-gel method and the deposition process was carried out via spin-coating process. The CZTS precursor film was then sulfurized for the crystal growth. Afterward, the crystal structure and optical properties characterization were carried out to observe the CZTS thin-film characteristics to apply it as an absorber layer in solar cell application.

2. Experimental procedure

2.1. Substrate cleaning and synthesis of CZTS precursor
The Soda Lime Glass (SLG) with an area of 3 cm x 3 cm was used as the substrate. The substrate cleaning was done utilizing sonication procedure in acetone and IPA for 10 minutes each. The cleaned substrate was then dried fast using a dryer.

The CZTS precursor was prepared using the solution process by dissolving 1.02 gr copper acetate hydrate, 0.724 gr zinc acetate hydrate, 0.596 gr tin chloride dihydrate, and 1.568 gr thiourea into 10 mL Ethylene glycol monomethyl ether. The solution was then stirred at 50℃ for 2 h using a stirring rate of 250 rpm. The Cu-poor and Zn-rich non-stoichiometric condition was obtained by arrange the Zn/Sn and Cu/(Zn + Sn) molar ratio to 1.25 and 0.86, respectively.

2.2. CZTS deposition and sulfurization
A few drops of triethanolamine and monoethanolamine were applied to the precursor solution prior to the deposition process. The CZTS deposition was then done using a repeated process of spin-coating and preheating. For 20 s, the spin-coating process was set at 3000 rpm, and then the coated precursor was heated for 5 min at 280℃. To obtain the appropriate thicknesses, this method was repeated several times. This process was repeated several times to obtain the desired thicknesses. Subsequently, the precursor film was then sulfurized using an RTP furnace at 600℃ for 40 min in the N₂+S atmosphere to obtain CZTS thin-film.

2.3. Characterization
The Bruker Advanced D8 instrument with Cu radiation of 0.154439 nm was used for the crystal structure investigation. Meanwhile, the Thermoscientific evolution 201 UV-Visible Spectrophotometer was used for the optical properties investigation.
3. Results and discussions
The presence of kesterite crystal structure can be observed through the XRD pattern in figure 1. It showed the marked peaks that appear at 2θ of 28.4°, 47.26°, and 56.18°, similar to the kesterite peaks reference at JCPDS No. 26-0575. We also noticed that the absence of Cu2S, SnS2, and SnS secondary phases can be confirmed from the XRD pattern. Meanwhile, the ZnS secondary phase could not be confirmed because of its mutual interference peaks [18]. In this case, the formation of the ZnS secondary phase is possible [19], given that the composition taken is Cu-poor and Zn-Rich which suppresses the formation of a secondary Cu2SnS3 phase instead forms a ZnS phase [17].

![Figure 1. XRD pattern of CZTS thin-film](image)

Using the Scherrer equation (1), the average grain size of kesterite crystals was determined [20]. K is a dimensionless constant, λ is the x-ray wavelength, β is the Full width at half-maximum (FWHM), and D is the average grain size produced in the absorber layer. In this work, the average grain size measured using Scherrer’s equation for the CZTS thin-film absorber is ~53.7 nm.

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D = \frac{k\lambda}{\beta \cos\theta}
\] (1)

The absorbance level from the spectroscopy measurement of UV-Vis is shown in Figure 2. The outcome shows that, at a low wavelength range of 320–498 nm, the CZTS thin-film has excellent optical sensitivity. Meanwhile, the absorbance level tends to be constant at low values at the higher wavelength of 843 – 1080 nm. The optical bandgap of CZTS thin-film was confirmed to be 1.56 eV using the Tauc Plot method from the absorbance level, as shown in Figure 3.
Figure 2. The absorbance level of CZTS thin-film

The absorbance level of CZTS thin-film is shown in Figure 2. The absorbance decreases with increasing wavelength, indicating the absorption of light by the film.

Figure 3. The optical bandgap of CZTS thin-film

The optical bandgap of CZTS thin-film is shown in Figure 3. The bandgap is 1.56 eV, indicating the energy difference between the valence and conduction bands.

The high-efficiency of light absorption at low wavelength can be confirmed using the Light-Harvesting Efficiency (LHE) calculation. LHE is the fraction of the light photon that was absorbed at a certain wavelength by CZTS thin-film. The LHE was calculated using equation (2), where $\alpha$ is absorbance [21].

$$\text{LHE} (\lambda) = \left(1 - 10^{-\alpha}\right) \times 100\%$$  \hspace{1cm} (2)

The LHE data in Figure 4 confirmed the high efficiency of light absorption at a low wavelength for the fabricated CZTS thin-film in this work. It starts to decline gradually at a wavelength of 498 nm and decreases rapidly, starting at 748 nm. Overall, the CZTS thin-film absorber has a high light absorption efficiency. Therefore, it can be concluded that the CZTS thin-film in this work has the potential to produce high Incident Photon to Current Efficiency (IPCE) in its application since IPCE is directly proportional to LHE [22].

Figure 4. The LHE of CZTS thin-film

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4. Conclusions
In summary, CZTS thin-film was successfully fabricated using a solution-based process. The results show that the CZTS thin-film has the kesterite crystal structure with an average grain size of ~53.7 nm. Furthermore, the optical characterization shows that the CZTS thin-film has an optical bandgap of 1.56 eV with excellent light-harvesting efficiency at a low wavelength between 320 and 498 nm. These results indicated that the CZTS thin-film fabricated in this work is suitable for the absorber layer in solar cell application.

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