



Research Article

Investigation on the Fabrication Process of Copper, Zinc, Tin and Sulphur on Molybdenum as Back Contact for Microwire Solar Cell

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Abstract

Background and Objective: There are many types of solar cells that had been designed and fabricated in the past decades to increase the efficiency and productivity of the solar cell. Some examples of fabrication techniques will be sputtering, pulsed laser and also evaporation techniques. All these techniques will be fabricated by using vacuum system. These thin film based solar cell were frequently being used and more research still ongoing to improvise the efficiency of it. However, as for change this research were carried based on investigating the flexible microwire solar cell by using silicon based fiber as substrates. Very less reports were stated regarding solar cell by using molybdenum coated fiber. The objective of this research study is to investigate the interface between molybdenum (back contact) coated silicone fiber and CZTS. **Materials and Methods:** The materials that are suggested to be the coating is Copper, Zinc, Tin and Sulphur (CZTS) solution. The precursors of CZTS was synthesized by using sol gel technique. The layers were coated on top of fiber by using dip coating technique. The CZTS layer were investigated by varying the dipping speed, heating temperature and duration of dipping. **Results:** The samples were send to SEM, AFM, UV-Vis for characterization. The CZTS thin film has the thickness of 0.85 μm . Synthesis CZTS has the bandgap of 1.57 eV and can absorb the visible light in the range of 400-800 nm. **Conclusion:** In this study, it is found that the silicone fiber can be act as substrates for solar cells and more research can be carried on by using it as substrate.

Key words: Sol gel, CZTS, dip coating, solar cell, silicon fibre, dipping speed

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Solar energy has been one of the main research that had been investigated for years. There are many types of solar cells that had been designed and fabricated in the past decades to increase the efficiency and productivity of the solar cell. The solar cells were categorized by three generations. First generation solar cell was made based on wafer, whole second generation solar cells were made by thin films¹ and third generation is the currently under research². Some of third generation solar cell examples are dye sensitized solar cells, organic solar cells and also perovskite solar cells³. Among all this, thin film based solar cell were frequently being used and more research still ongoing to improve the efficiency.

Second generation solar cells have different absorber layers such as CdTe^{4,5}, CZTS⁶ and CIGS⁷. As for this research paper, CZTS will be used as absorber layer. The CZTS has a direct bandgap of 1.5 eV and absorption coefficient of more than 10^4 cm^{-1} . Furthermore, all the elements in CZTS are earth abundant and easily can be obtained low in cost and non-toxic⁸. Micro wire based solar cells are in cylindrical shape, they can be flexible and partially transparent and absorb light efficiently over a wide range of incident angles⁹. There was many previous research has been done to fabricate micro wire based solar cells by using different approaches and fabrication techniques such as 99.98% pure silicon via the molten core fiber drawing method⁹, vapor-solid-liquid (VLS) process¹⁰ and plasma enhanced chemical vapor deposition¹¹. All the research before was conducted on a flat surface. As a change, this study was conducted to investigate the thin film deposition on a cylindrical surface.

In this research work, reported the CZTS micro wire solar cell preparation by using different approach which is dip coat the absorber layer on Mo coated silicon based fiber. By this, the cost of deposition CZTS layer can be reduced and instead of by using circular surface substrate, it may be useful for flexible solar cell application in future. In this research, the speed of dip coating, drying method and heating temperature has been investigated.

MATERIALS AND METHODS

This study was carried on for two years as part of a fundamental research. This study is mainly regarding the active layer of microwire solar cells. Therefore, silicone based fiber was used as the substrates for this experiment. The experimental setup will be discussed further under experimental procedures.

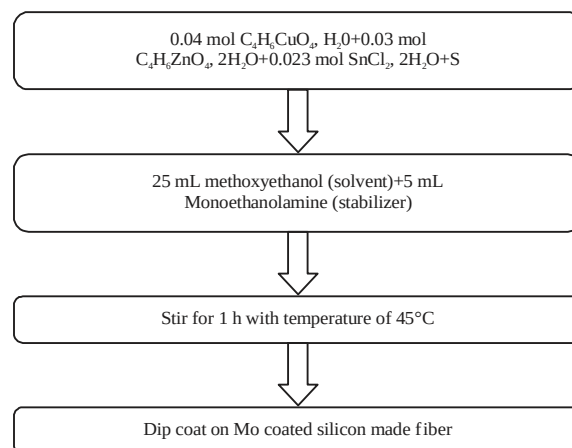


Fig. 1: Flowchart of CZTS synthesis

Experimental procedures: The $\text{Cu}_2\text{ZnSnS}_4$ has been prepared by sol gel method by dissolving CZTS precursors. The mixed solution was stirred for 1 h with 45°C on a hot plate. The silicon made fiber substrates were pre cleaned and coated with molybdenum as back contact by RF sputtering. The summary of CZTS synthezization process and dip coating technique of substrates has been shown in Fig. 1.

The CZTS was deposited on Mo coated fiber by using dip coat technique with the speed of 10 and 100 cm sec^{-1} to obtain the suitable speed of dip coating. Then followed with different samples prepared by manipulating the heating intervals after each and every coated layer. First sample was prepared by heating it after a total of 6 layer of CZTS has been coated, followed by next sample was heating in every two-layer coating intervals and final sample was heated after each and every layer of coating. All the samples have total of 6 coating layer before sent for characterizations.

The next experiment was conducted to study the effect of heating temperature of CZTS layer on fiber substrates. The samples were heated with different temperature from room temperature up to 200°C. Then the duration of heating and dipping also has been studied in this experiment. The microwire samples were investigated by studying their composition, structural and optical properties. Optical microscope and atomic force microscopy (AFM) was used to characterize the samples to obtain the surface morphology and the surface roughness of the coated CZTS layer. Scanning electron microscopy (SEM) and elemental dispersive spectrometer (EDS) was used to reveal more about the morphology of coated layer, the orientation of materials, chemical materials and also the crystalline structure of coated layer. The synthesized CZTS solution was characterized to obtain the absorbance wavelength and to calculate the bandgap of the synthesized solution.

RESULTS AND DISCUSSION

Optical microscopy analysis of CZTS layer: Following are the optical microscope results with $\approx 65\times$ magnification of heating technique of CZTS layer of substrates by varying the heating after coated layer. From Fig. 2, the optical shows the clear view of the coated CZTS layer on substrates. The sample that heated after done with all 6 coating layer shows few blank spaces where the CZTS particles did not deposited. There were many pin holes on the samples where clearly shows the CZTS layer were peeled off during the dip coating process. Therefore, this technique is not suitable for the dip coating.

As for sample that heated in 2 dipping interval has better coating compare to the previous Sample A. However, the CZTS was not coated consistently throughout the substrates. There were some gaps between the coated layer and it was not coated evenly. For sample C, the morphology of surface was totally different from other two samples. The CZTS was distributed evenly and the surface of substrate was coated without any gaps. The particles of CZTS was closely packed as shown in the Fig. 2c.

Atomic force microscopy of CZTS coated layer: After optical microscope results obtained, all three samples were characterized by AFM to measure the average surface roughness of coated layer on substrate. The magnification was carried on ($5\times 5\ \mu\text{m}$) region.

From Fig. 3, the topology scan of each sample obtained were differ from each other. For Sample A, the coated layer average surface roughness was 8.9974 nm which indicates low roughness and less particles have been coated on it. From the 3D view of AFM, the coated layer shows uneven coating and has few peaks at different place of the substrates. It also has thickness of $\approx 0.20\ \mu\text{m}$. Sample B has almost same result as Sample A. The peak of the coating was not in same range and not consistent. The structure more looks like "hills" in between the coated layer. However, the average surface roughness of the coated layer was 10.0814 nm and has thickness of $\approx 0.32\ \mu\text{m}$. For Sample C, the CZTS layer has been coated smoothly and consistently throughout the glass substrate and has average surface roughness of 15.2174 nm. But from this AFM 3D view, there were high peaks at end of the substrate. It due to the excess CZTS solution was flow from the top of

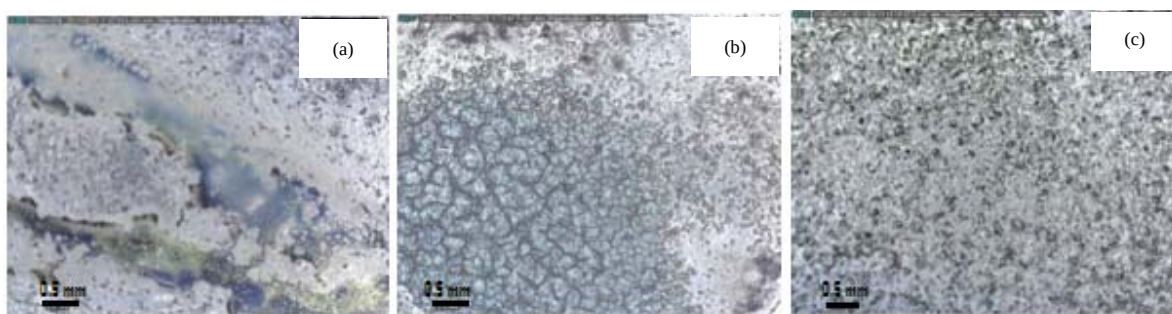


Fig. 2(a-c): Optical microscope results (a) Sample heated after 6 dips, (b) Sample heated in interval of 2 dips and (c) Sample heated after every dips

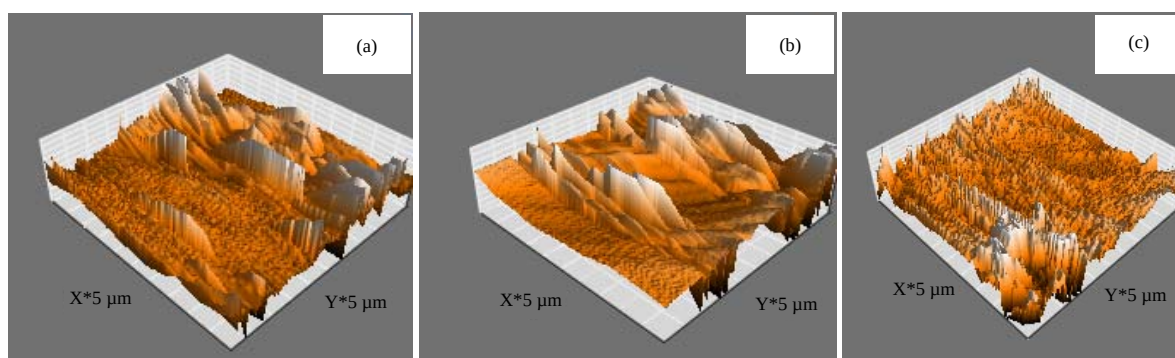


Fig. 3(a-c): AFM 3D topography of samples (a) Sample heated after 6 dips, (b) Sample heated in interval of 2 dips and (c) Sample heated after every dips

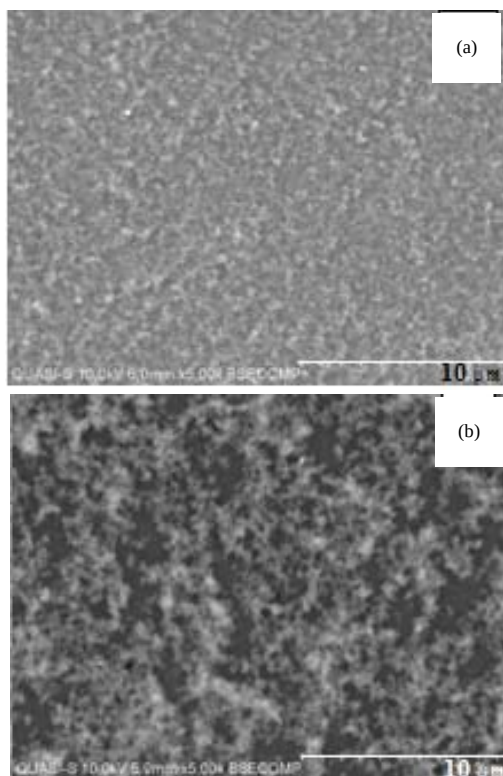


Fig. 4(a-b): SEM image of CZTS layer coated with different speed (a) 100 cm sec^{-1} and (b) 10 cm sec^{-1}

Table 1: Recorded roughness and thickness for 3 different samples

Samples	S_A (Roughness) area ($25.2 \text{ } \mu\text{m}^2$)	Layer thickness (μm)
A	8.9974	≈ 0.20
B	10.0814	≈ 0.32
C	15.2174	≈ 0.85

the substrates while heating. It can prevent by adjusting the speed of dipping which the results will be discussed later on. The obtained thickness for Sample C was larger than other two samples which was $\approx 0.85 \mu\text{m}$. From AFM characterization, the conclusion can be made as the sample prepared by heating every layer of coating can give a better result. The summary of average surface roughness and the thickness of coated layer has been shown in Table 1. Although all three sample has same 6 layers of CZTS been coated, the thickness of each sample were vary.

After AFM characterizations, the samples were tested with scotch tape to test the adhesion of the CZTS particle with Mo coated silicone based fiber. Almost all the particles of CZTS was peeled off from Sample A and Sample B. It indicated that the CZTS particles did not have strong bonds. It can be easily broken by small force. On the other hand, no CZTS particles

were peeled from Sample C when tested with scotch tape. The adhesion of particles in Sample C has stronger bond compare to other samples which the sample still in good shape after 6 months.

Scanning electron microscopy and energy dispersive spectroscopy analysis for CZTS coated with different speed and varying temperature:

The next experiment was conducted to obtain the effect of dipping speed on the coating layer. As stated previously two samples was prepared by varying the speed of dip coating. The samples were characterized by SEM (scale bar = $10 \mu\text{m}$) with 15.0 kV electron acceleration voltage and the image obtained was shown in Fig. 4.

The CZTS layer coated on substrates with the lowest speed has the more compact and well distributed particles on the layer as shown in Fig. 4b. While the samples prepared with the highest speed shows less nanoparticles of CZTS that has been deposited on fiber substrates as in Fig. 4a. The difference of two different coated layer has been shown in Fig. 4. The slow the substrate has been pulled out from the solution the more particles of CZTS can be absorbed and deposit on fiber substrates. Therefore, more particles can be seen in Sample B although both of sample were prepared by using similar CZTS sol gel solution and dipped six times. It was concluded that speed of dip can affect the deposition of particles on surface of substrates.

To obtain more about the effect of speed to coating layer, EDS characterization was carried on. The Sample II which dipped with slowest speed has higher CZTS particles compare to Sample I which prepared by speed of 100 cm sec^{-1} . Sample A has weight percentage (%) of 2.66 Cu, 3.10 Zn and 3.79 Sn while Sample B has 3.29 Cu, 3.35 Zn and 3.27 Sn particles in the coated layer.

Both of the sample were achieved the copper poor and Zinc rich distribution as one of the requirement of efficient solar cell. Sample that prepared by drying at room temperature (R.T) and 50°C has less particles on the coating layer. From Fig. 5, there are few bright spots in SEM characterization like some pin holes where indicates the layer of CZTS did not fully cover the substrates. Due to less heat has been used, the first layer of CZTS was not dried well. When kept coat on top of it, the layer of CZTS has been peeled off during pulled out from the CZTS solution. This might cause the pin holes in the coated layer.

Furthermore, the particle size of coated layer was small and not coated consistently throughout the whole substrates. As for sample heated by 100°C , the CZTS layer

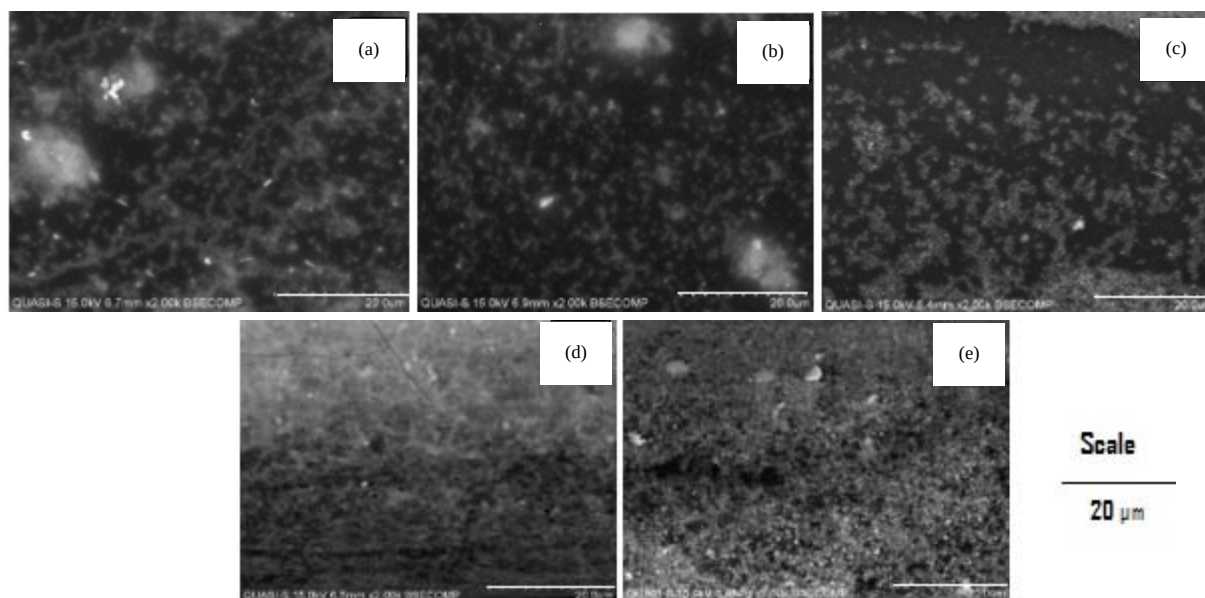


Fig. 5(a-e): SEM images of samples prepared by varying the heating temperature, (a) Room temperature, (b) 50°C, (c) 100°C, (d) 150°C and (e) 200°C

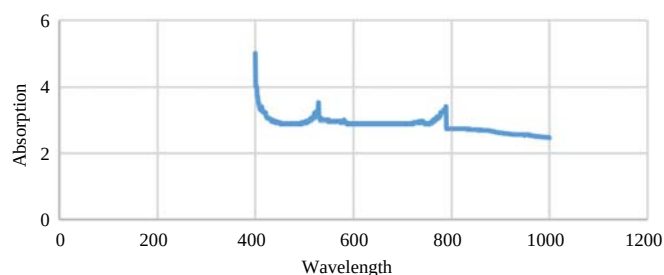


Fig. 6: Absorption graph for CZTS solution

was coated all over the entire substrates. However, the particles size was still small and far from each other. It shows the heated temperature is still not suitable for this CZTS solution. Next sample heated with 150°C has a consistent layer and compact CZTS particles on it. The particles size was increase in size compare to first three samples. To explore more, the next sample was heated by 200°C. When the sample was characterized by SEM, it has more compact and large CZTS particles on the coated layer. The particles were arranged closely and has denser texture compared to all other previous samples. The CZTS particles was also shows large grain in size when heated and dried by 200°C. All the sample as same 6 layers of CZTS coating and the speed and distance during dipping process were kept constant. All the SEM images of the samples were shown in Fig. 5 for comparison. The changes of the coating layer can be observed noticeably from the obtained SEM images.

UV-Vis analysis of the CZTS prepared by sol gel technique:

The prepared CZTS solution was characterized further to obtain the UV-Vis absorption graph as shown in Fig. 6. From the Fig. 6, the prepared CZTS can absorb the visible light from range of 400-800 nm which in range that reported by Rao and Basha¹². The bandgap of the solution was calculated by using the cutoff frequency and can obtain 1.57 eV which indicates the solution prepared by sol gel technique has the characteristic similar as obtained by Xia *et al.*¹³. The CZTS layer deposited on substrate with low cost non-vacuum process which will reduce the dependency on high vacuum process. From this research it was found that cylindrical shaped materials are can be used as substrates for solar cell.

CONCLUSION

The CZTS solution was synthesized by sol gel method and the prepared solution was characterized by UV-Vis and has a

band gap of 1.57 eV. The solution can absorb visible lights from 400-800 nm. The dipping and heating time was varied to obtain the effect of heating of the layer after coating. The sample which was heated after every layer has highest average surface roughness of 15.2174 nm obtained by AFM and $\approx 0.85 \mu\text{m}$ of layer thickness. The heating temperature shows a drastic change in the CZTS particles where the grain size of coated CZTS particles increases with temperature. As conclusion from this research work, silicon fiber can be considered to use as substrate for flexible micro wire solar cell. By using non vacuum deposition technique, the cost of fabrication of solar cell able to reduced.

SIGNIFICANCE STATEMENT

This study discovers the possibility of depositing thin film solar layer on a cylindrical substrate that can be beneficial for new invention by fabricating flexible fiber cloth embedded with solar cell with low cost by using non-vacuum technique. This study will help the researcher to uncover the critical areas of depositing thin film layer on cylindrical surface substrate that many researchers were not able to explore. Thus a new theory on flexible thin film solar cells on fiber may be arrived.

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