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Synthesis of Cu$_2$ZnSnS$_4$ Thin Film Using Electrodeposition Method:
Its Potential Use as Light Absorber Layer in Solar Cells

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Abstract.
Thin film Cu$_2$ZnSnS$_4$ (CZTS) is an alternative semiconductor used as a light absorber layer in solar cells. CZTS can replace silicon that is commonly used as a commercial semiconductor. The advantage of using CZTS as an absorber layer is due to the abundance of its elemental components, and the high value of its absorption coefficient. The absorber layer was electrodeposited on ITO glass substrates. The films were deposited at room temperature using potentiometer at a potential of -1.05 V for 30, 45, and 60 minutes. After that, the films were annealed at 500 °C, for 45 minutes in N$_2$/H$_2$S atmosphere. Based on X-ray diffraction analysis, the polycrystalline thin film obtained fell into the kesterite crystal phase. The value of the optical band gap energy for the CZTS thin film varied from 1.50 to 2.2 eV with a film thickness of 1.039 to 3.352 μm, depending on the length of time of electrodeposition. The sample of CZTS from the electrodeposition time of 45 minutes showed the best result and met the requirements of an absorber layer for solar cells.

1. Introduction
The first generation of solar cells is based on single crystal, multy crystal, and thin layer silicon, with high efficiency [1]. However, commercially, mass production of this type of solar cell is still expensive due to the low availability of pure silicon. Thus, economically, it is expensive to mass produce the solar cell panels. Silicon is an element in group IV, therefore, it can be substituted with a combination of elements from group II and VI such as cadmium tellurium (CdTe), group III and V such as GaAs and InP, and group I, III, and VI such as CuInS$_2$, and group I, II, IV and VI such as Cu$_2$ZnSnSe. The second generation of solar cells that is based on thin layers of cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) still poses a drawback because the semiconductors used are toxic and potentially pollute the environment [2]. Moreover, in nature, indium and gallium are scarce and therefore expensive, this could limit the production of the thin layers for solar cells. Studies on third and fourth generations of semiconductors which are not or less toxic are still ongoing.

The fourth generation semiconductor can be made from copper, zinc, tin, and sulphur which are abundantly available, and relatively environmentally friendly. Pawar [3] and Todorov [4] reported that Cu$_2$ZnSnX$_4$ (S or Se) made by thermal evaporation method has a band gap energy of around 1.5 – 2.7 eV and adsorptivity coefficient of 10$^4$ cm$^{-1}$, an ideal value for converting sun rays into electricity with a power conversion efficiency of 9.7 %. The major challenges to producing Cu$_2$ZnSnS$_4$ (CZTS) are the difficulty in controlling the volatile species within the film, and to minimize the formation of impurities by secondary
phases [5]. One way to solve this problem is by low temperature deposition of metal salt followed by a high temperature annealing [6]. Synthesis of CZTS by electrochemical deposition can be carried out at low temperature as reported by Scragg [7]. The problem with this method is finding the suitable electrochemical potential to reduce each metal in the synthesis of CZTS. Furthermore, the reduced metals are stack on top of each other, not blended to form a single crystal CZTS. Here we report the synthesis of thin film CZTS by electrodeposition method on ITO glass. The electrochemical deposition is done on one potential value - 1.05 V. In this system, complexing materials were added to cause all the metals to have a new similar reduction potential. Therefore, the deposition can be done using just one potential value.

2. Materials

Materials used in this study were CuSO$_4$.5H$_2$O, ZnSO$_4$.7H$_2$O, SnSO$_4$, Na$_2$S$_2$O$_3$.5H$_2$O, C$_6$H$_5$Na$_3$O$_7$. 2H$_2$O, C$_4$H$_6$O$_6$, acetone (Merck), isopropanol (Merck), deionized water, N$_2$, FeS (Merck), concentrated HCl (Merck), HNO$_3$ 65% (Merck), indium tin oxide (ITO) 10 and 500 Ω 25.0x25.0x1.1 mm glass, Ag/AgCl electrode, and Pt electrode.

Synthesis of CZTS was done using potentiostat EDaQ 410. Analysis of the thin layer was done using X-ray diffractometer (XRD) Shimadzu XRD-7000 Maxima, scanning electron microscope (SEM) Zeiss EVO 50, energy dispersive x-ray (EDX) Bruker AXS XFlash Detektor 4010, UV-Vis spectrophotometer Ganesys 10, and atomic absorption spectrometer (AAS) for Cu, Zn AA-7000, and Sn AA-6300 metals.

3. Methods

Before use, all ITO glass was rinsed and dried. Stock solutions of CuSO$_4$.5H$_2$O, ZnSO$_4$.7H$_2$O, SnSO$_4$, Na$_2$S$_2$O$_3$.5H$_2$O, C$_6$H$_5$Na$_3$O$_7$. 2H$_2$O, and C$_4$H$_6$O$_6$ were made to a concentration of 0.500 M.

Electrochemical Bath Deposition was done based on a modified procedure previously reported [8]. An electrolyte solution was made by adding 20 mL CuSO$_4$.0.02 M, 10 mL ZnSO$_4$.0.02 M, 20 mL SnSO$_4$.0.01 M, 40 mL Na$_2$S$_2$O$_3$.0.02 M, 15 mL C$_6$H$_5$Na$_3$O$_7$.0.1 M and 1 mL C$_4$H$_6$O$_6$.0.1 M into a glass beaker. The solution was maintained at pH 4.5. This synthesis used 3 types of electrodes, the working electrode of ITO 10 and 500 Ω glass, the reference electrode of Ag/AgCl, and the auxiliary electrode of Pt. All the electrodes were soaked in the electrolyte solution, then the electrodeposition was done by linear sweep stripping voltammetry mode with beginning potential of -950 mV, and ending potential at – 110 mV, frequency of 10 kHz, and scanning rate of 25 mV/s. Deposition potential was kept at -1.05 V at room temperature of 28 °C, and varied deposition time of 30, 45, and 60 minutes. After deposition, a black colored thin layer was formed on the surface of the ITO glass. This CZTS film was then rinsed with deionized water and flushed with nitrogen gas before being annealed. The CZTS was annealed at 500 °C under flow of H$_2$S and N$_2$ gas for 45 minutes. The phase of the film was analyzed with XRD, its morphology and composition was analyzed with SEM-EDX and AAS, and the band gap energy was determined by UV-Vis spectrophotometer. Band gap energy (Eg) was analyzed at wavelength between 250 and 800 nm. Eg was determine from Tuoc plot by plotting ($\frac{1}{\lambda}$) with photon energy (hv). Where $\alpha$ is calculated from equation $\alpha = \frac{2.303 \times A}{d}$, where $d$ is the thickness of the sample.

4. Results and Discussion

Electrochemical bath deposition technique was used to synthesis CZTS because its low cost, environmentally friendly properties, wide deposition area, and use of simple equipment. Referring to the Faraday law, as time of deposition extended more metal will be deposited. Figure 1 shows the black colored thin layer of CZTS, which visually became darker with longer deposition times.
Figure 1. the CZTS thin film on ITO glass after electrodeposition for (a) 30 minutes, (b) 45 minutes, and (c) 60 minutes

The ability of the thin layer to attach to its substrate is dependent on the adhesive property of the coating. A coating with low adhesivity will allow air to slip between the coating and substrate and cause contamination. The annealing process is needed to overcome this problem, and also to form the crystallite phase of the CZTS [9]. After annealing, the thin layer becomes more transparent and is not easy to peel off as seen on Figure 2. The ITO glass must be cut in order to be put in a specific container for the annealing process while allowing the flow of H2S and N2 gas, the reason for their unsymmetrical shapes.

Figure 2. the CZTS thin layer after annealing with varied time of deposition (a) 30 minutes, (b) 45 minutes, and (c) 60 minutes

The X-ray diffractogram of CZTS crystal phase before and after annealing is given on Figure 3. Before annealing, the CZTS film is in an amorphous phase. After annealing crystallization process is completed as shown by the appearance of sharp peaks on the diffractogram. The crystallinity of the thin film after annealing was 71%. Based on this data, it was very clear that the thin film contains large amounts of impurities. These impurities could be caused by the oxidation of reduced metal before it was flushed with N2 and H2S gas.

Figure 3. Diffractogram of thin layer CZTS before (a) and after (b) annealing
Table 1. Observed phase of thin film analyzed with Match 2 program

| Duration of sample deposition | Observed Phases      | Name          | Amount (%) |
|------------------------------|----------------------|---------------|------------|
| 30 minutes                   | \( \text{Cu}_2\text{ZnSnS}_4 \) | Kesterite     | 3.7        |
|                              | \( \text{Cu}_2\text{S} \)       | Chalcocite    | 65.9       |
|                              | \( \text{ZnS} \)             | Wurtzite-2H   | 12.2       |
|                              | \( \text{SnS} \)             | Herzenbergite | 18.1       |
| 45 minutes                   | \( \text{Cu}_2\text{ZnSnS}_4 \) | Kesterite     | 6.7        |
|                              | \( \text{Cu}_2\text{S} \)       | Chalcocite    | 66.5       |
|                              | \( \text{ZnS} \)             | Wurtzite-2H   | 10.7       |
|                              | \( \text{SnS} \)             | Herzenbergite | 16.1       |
| 60 minutes                   | \( \text{Cu}_2\text{ZnSnS}_4 \) | Kesterite     | 7.3        |
|                              | \( \text{Cu}_2\text{S} \)       | Chalcocite    | 68.9       |
|                              | \( \text{ZnS} \)             | Wurtzite-2H   | 7.2        |
|                              | \( \text{SnS} \)             | Herzenbergite | 16.6       |

Analysing the diffractogram using Match 2 program with ICDD database as reference, it was found that the amount of CZTS formed was very small. The CZTS has kesterite crystal structure with the highest intensity obtained at a crystal plane of (112). The majority of the thin layer consisted of secondary phases such as Cu₂S, ZnS, and SnS, and their percentage is given on Table 1. This showed that the formation of CZTS was not yet complete. According to Moreno [10], the formation of perfect crystal needs an annealing at a high temperature around 500 °C for a period of 1.5 hours. However, the Match 2 program also showed peaks that belong to the elemental components of the ITO glass and aluminum metal of sample holder.

Figure 4. SEM image of the CZTS thin film top view (a) and cross-section (b)
Figure 4 shows the morphology of the thin film from the deposition time of 45 minutes with thickest part measured to be 1.950 μm. The top view image shows that the size of granules of the thin film was not uniform, as shown by the presence of big chunks with width more than 20 μm. These big chunks may be composed of secondary phases. As the time of deposition is longer, the thickness of the thin layer increased with greatest thickness of 1.039 at 30 minutes deposition time to 3.352 μm after 60 minutes deposition time.

| Element         | Atom. C (at. %) | Element         | Atom. C (at. %) |
|-----------------|-----------------|-----------------|-----------------|
| Copper          | 0.45            | Silicon (ITO)   | 20.08           |
| Zink            | 0.14            | Oxygen          | 64.79           |
| Tin             | 1.86            | Indium (ITO)    | 0.19            |
| Sulfur          | 0.34            | Sodium          | 8.35            |

The elemental analysis of the thin film with EDX showed that tin is the major element. Table 2 shows the major elements present in the film. Since the film was transparent, the EDX also identified the elemental components of the ITO glass. The highest value is given by silicon and oxygen, from the silicate components of the ITO glass. The sodium metal presence might be from the complexing materials, sodium thiosulfate and trisodium citrate, which were still attached to the metal. The metals content is closely related to the composition of CZTS.

The EDX results was supported by the elemental analysis using AAS. Similar to the results obtained from elemental analysis by EDX, results by AAS also showed that Sn is the highest element in the film. However, some of this may have been from the Sn in the ITO glass destructed using a strong oxidator solution of HNO3 acid during preparation for AAS analysis.

| Sample deposition time (min) | Mass (mg) | [Cu] (ppm) | [Zn] (ppm) | [Sn] (ppm) |
|------------------------------|-----------|------------|------------|------------|
| 30                           | 1.5000    | 0.5730     | 0.6693     | 4.7667     |
| 45                           | 1.3000    | 1.6927     | 0.1485     | 6.8462     |
| 60                           | 1.4000    | 1.5992     | 0.2261     | 8.7143     |

The optical characteristic of the thin film was tested based on its response toward a high intensity light, which caused the material to transfer electrons. Knowing its ability to transfer electrons, gives information on its photocatalytic activity. Band gap energy is defined as the amount of energy needed to eject electrons from the valence band to create a flow of electricity. The smaller the value of the band gap, the easier to transfer electrons from the valence band to the conductive band. The absorptivity coefficient value of an ideal film to be used as a sunlight absorber is more than 10^4 cm^{-1}, with the band gap energy around 1.4 to 1.6 eV [3]. The band gap value of the thin film in this experiment was obtained using UV-Vis spectrophotometer, from which the data was then plotted as shown by Figure 5. The band gap value of the film varied depending on the deposition time, with the lowest value of 1.5 to 2.2 eV. The high value of band gap is due to the formation of secondary phases. The band gap of Cu2S is 1.21 eV [11], while that of ZnS is 3.58 eV [12].
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