Effect of Annealing Time on Electrodeposited-n-Cu_2O Thin Film

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***Abstract*—This work focuses on the analysis of structural, morphological, topological and optical properties of n-type cuprous oxide (Cu_2O) thin film through the various duration of the annealing process. The n-type Cu_2O thin film used in this research was fabricated on Fluorine-Doped Tin Oxide (FTO) glass substrate by using potentiostat electrodeposition method at optimized parameters. The optimized parameters were fixed at pH 6.3, temperature of 60°C, deposition time of 30 minutes and potential voltage at -0.125 V vs Ag/AgCl. Then, the samples of n-type Cu_2O were subjected to a different annealing time set of 20, 30, 40, 50 and 60 minutes. It was found that the most optimized annealing duration was 60 minutes with a fixed annealing temperature of 200 °C. From the results, the properties of the n-type Cu_2O thin film had enhanced by introduction of the annealing process. All the properties had characterized by using X-Ray Diffraction (XRD), Field Emission-Scanning Electron Microscopy (FE-SEM), Atomic Force Microscopy (AFM), Ultraviolet visible spectrometer (UV-Vis) and Four Point Probe.**

***Index Terms*—Annealing Time; Copper Oxide; Electrodeposition Method; Thin Film; Homojunction.**

I. INTRODUCTION

In photovoltaic development (PV), solar cell device had appeared as an interesting alternative source in harvesting important sustainable energy sources which is solar energy from the sun [1]. It plays an essential role as an effective greenhouse energy source due to the pollution problem by carbon dioxide from fossil fuels and completely safe to the environment [2]. Currently, wafer silicon is the typical material for a solar cell which established the conversion of solar energy to electricity. However, the high-cost material and processing of wafer silicon modules are very expensive which demands another photovoltaic cell which more convenient. Thus, fabrication thin film technology had introduced because it is affordable utilizing and non-toxic materials prepared by energy-efficient processes [3]. In addition, a solar cell based on copper Oxide (Cu_2O) thin film acts as an active layer in this new photovoltaic cell. It is also one of replacement material in a solar cell because this metal-oxide semiconductor offers several characteristics that useful for the production of solar cells such as inexpensive, simple and able to produce high efficiency and long lifetime [4].

Cuprous Oxide is an attractive semiconductor material for photovoltaic devices because of its high absorption coefficient, abundant availability, non-toxicity and low production cost. Moreover, it had known as a p-type semiconductor with 2.1eV direct band gap due to the intrinsic Cu vacancies in the Cu_2O lattice [5,6]. There were many deposition approaches have been explored by researchers to prepare Cu_2O thin film such as thermal oxidation [7], solvothermal method [8], electrodeposition [9], radio-frequency magnetron sputtering [5] and pulsed laser deposition [10]. However, electrodeposition method is more preferred because this method is versatile, low processing temperature, low cost and simple process compared others [6].

The fabrication of Cu_2O thin film p-n heterojunction thin films such as n-ITO/p-Cu_2O and n-ZnO/p-Cu_2O had been broad over past year three decades [11]. However, there was low conversion efficiency for this p-n heterojunction thin film which presented around 2% with Cu_2O as an active layer. It was challenged due to improper band alignment and lattice mismatch between the Cu_2O crystal structures with other different materials [12]. There were also caused by interface defects and loss of performance between the structure layers. Thus, this n-type Cu_2O thin film in p-n homojunction thin film had introduced and received attention as a candidate for next-generation thin film solar cell because it was believed that no interface strain occurs between the same material of the Cu_2O thin film.

In addition, a great work on p-n homojunction which using same material of Cu_2O had been carried out included improving the properties of n-type Cu_2O thin film by annealing treatment. Normally, annealing process had introduced to enhance the properties of the thin films and improve the conversion efficiency of solar cell device [6,13,14]. Kim *et al.* reported that the average grain sizes increased with annealing durations of up to 30 minutes then decreased at 60 minutes. The increment of average grain size was believed due to the growth of small Cu_2O grains by diffusion, which dominated during annealing treatments [9].

In this study, the fabrication of n-type Cu_2O thin film on Fluorine-Doped Tin Oxide (FTO) glass substrate was carried out with optimized parameters by using electrochemical deposition technique. Then, the samples of n-type Cu_2O were annealed at a different time set of 20, 30, 40, 50 and 60 minutes. The improved properties of the Cu_2O thin film before and after annealing were characterized to obtain the optimum annealing time that possible to increase the efficient conversion of solar cell application.

II. Methodology

In this study, an optimized n-type Cu_2O thin film was fabricated by using electrodeposition method. Then, several samples of n-type Cu_2O thin film were annealed with various annealing time in the furnace. The characterizations of each sample were carried out to get the optimization of the annealing time.

A. *Deposition of Cu_2O Thin Film*

Before deposition of n-type Cu_2O thin film, copper acetate based solution was prepared by using 0.4M copper (II) acetate monohydrate ($C_4H_8CuO_5$) and 3M lactic acid ($C_3H_6O_3$). The pH of the solution was adjusted by Potassium Hydroxide (KOH) until reached pH 6.3. Next, Fluorine-Doped Tin Oxide (FTO) glass substrate was prepared by cleaning process and covered with Kapton tape in order to determine 1cm x 1cm deposition opening area. The taped glass substrate undergoes polarization process using 1M of sodium hydroxide (NaOH) at a current density of 10mA/cm^2 for 60 seconds.

Potentiostatic electrodeposition process was carried out by using three electrodes configuration which the glass substrate, platinum electrode and Ag/AgCl serve as working, counter, and a reference electrode, respectively. As deposited on n-type Cu_2O thin film had optimized, the fixed parameters were used to deposit an n-type Cu_2O thin film on FTO glass substrate before annealing process. The optimized parameters are shown in Table 1.

Table 1
The Optimized Parameters of n-type Cu_2O Thin Film on FTO Glass Substrate

pH value	Deposition time (minutes)	Potential (V vs Ag/AgCl)	Solution Temperature (ºC)
6.3	30	-0.125	60

B. *Annealing Treatment*

Annealing treatment was introduced to determine the changes of properties of the fabricated thin film [6]. In this study, the annealing temperature was fixed at 200 ºC. The period of annealing was varied to ascertain the optimum duration of the annealing process. Different characterization of n-type Cu_2O thin films had shown when the thin films were exposed to the various annealing times of 20, 30, 40, 50 and 60 minutes.

C. *Characterization of Annealed n-type Cu_2O Thin Film*

Next, the annealed n-type Cu_2O thin films were characterized by using several characterization tools. The structural characterization was analysed by using X-ray diffraction (XRD) to identify the information of crystalline material structure. Meanwhile, Field Emission Scanning Electron Microscope (FE-SEM) was used to determine the morphological properties of the fabricated thin film. The topological characterization also carried out by using Atomic Force Microscopy (AFM) which to determine the roughness of thin film. Ultraviolet-Visible Spectrometer (UV-Vis) is an instrument used to determine the absorbance of optical properties and Four Point Probe is an equipment used to examine the resistivity of the sample.

III. Results and Analysis

A. *Structural Properties*

For structural properties, X-ray diffraction (XRD) was used to determine the orientations of the fabricated n-type Cu_2O thin film. During the XRD scanning process, the scan rate was set up from 20° to 80°. There were several peak detected at 29.7, 36.5, 43.4, 63.2, 74.3 and 77.4° which correspond to [110], [111], [200], [220], [311] and [222] plane orientation of Cu_2O, respectively. Based on the results obtained, the highest peak was observed at 36.5° compared the others. The results were consistent with Fariza *et al.* which indicated that [111]-Cu_2O thin film was successfully deposited on FTO substrate [15]. In addition, the highest peak also located at sample had been annealed for 60 minutes, while the as-deposited sample was presented the lowest. A similar research by Kim, T.G *et al.* had stated that the [111] and [200] peaks of Cu_2O did not shift although they undergo annealing treatment [9]. The peak patterns of XRD graph are shown in Figure 1.

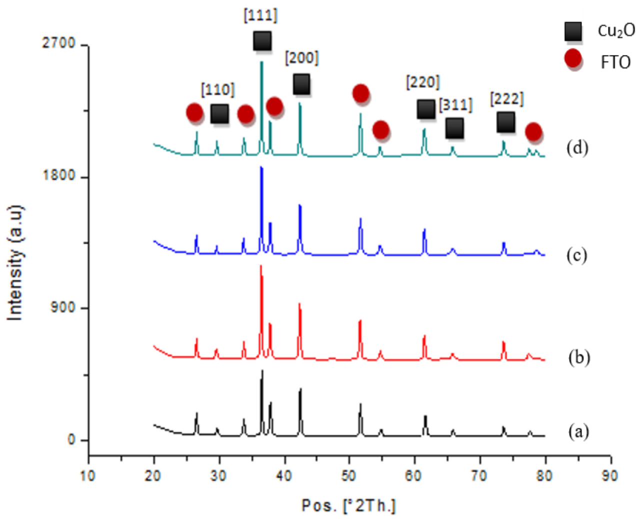

Figure 1: XRD pattern of samples were prepared at (a) 0, (b) 40, (c) 50, and (d) 60 minutes, respectively

B. *Morphological Properties*

In this study, Field Emission-Scanning Electron Microscope (FE-SEM) was used to examine the morphological properties of the sample deposited. According to the results, there were formations of Cu_2O morphology on the FTO substrate before and after annealing. There were triangular and pyramidal shapes of Cu_2O were observed according to their corresponding annealed time [16]. The as-deposited Cu_2O sample was examined to have small grains present. However, all annealed samples exhibited a tremendous decrease in small grain when compared to the as-deposited sample. Based on the previous study, the enhancement of the morphological properties was observed by the decrement of the small grains after annealing treatment [9]. Figure 2 shows the FE-SEM images of the Cu_2O thin film before and after annealed with different period.

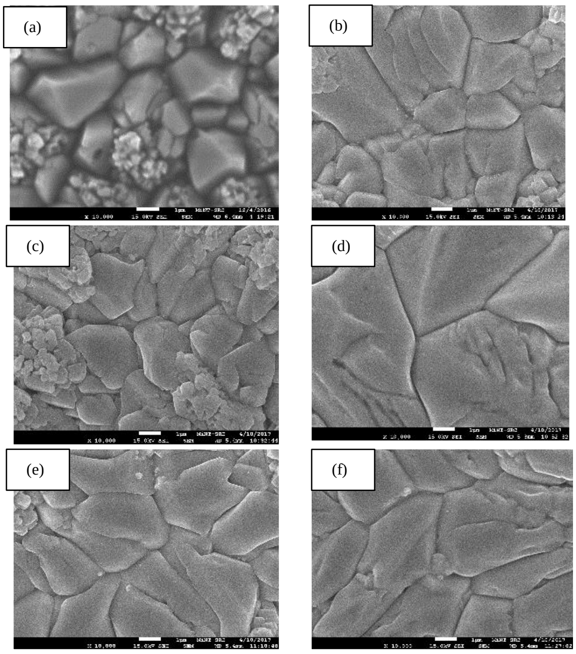

Figure 2: FE-SEM images of Cu_2O prepared (a) As-deposited and annealed at (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60 minutes, respectively

C. Topological Properties

For topological properties, the average surface roughness of the samples was examined by using Atomic Force Microscopy (AFM). From the results, the highest average surface roughness was determined at as-deposited sample [17]. The roughness seems became lower after annealing period was increased. However, the average surface roughness of 60 minutes annealed sample was the smallest compared to others. It was believed that the highest number of small grain was recorded without going through the annealing process. Thus, the annealing process can help to enhance the properties of the Cu_2O thin films. The average roughness of each sample is presented in Table 2.

Table 2
Average Surface Roughness for Cu_2O Thin Film Before and After Annealed

Sample	Average surface roughness (nm)
As-deposited	299.000
Annealed 20 mins	234.000
Annealed 30 mins	238.000
Annealed 40 mins	182.367
Annealed 50 mins	176.000
Annealed 60 mins	142.188

D. Optical Properties

The absorbance of the Cu_2O thin film was obtained by using Ultraviolet-Visible Spectrometer (UV-Vis). The results showed the increment absorbance in the wavelength range from 300 to 800 nm. In order to determine the band gap of the deposited thin films, the absorbance of the sample was taken into account. From Figure 3, it was observed that there was a dramatic increment of wavelength around 600 nm for all samples. The extrapolation graph for a sample that annealed for 60 minutes also represented band gap energy of 1.9 eV. The result was corresponding to the previous study by Fariza *et al.* which Cu_2O has a band gap range between 1.9eV to 2.2eV [3]. The absorbance spectrum and extrapolation band gap of the Cu_2O thin films are shown in Figure 3 and Figure 4, respectively.

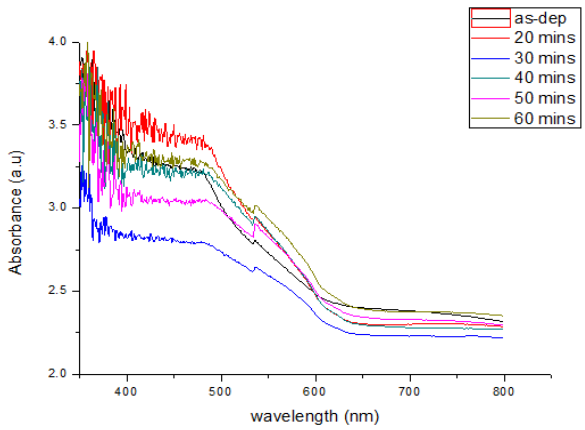

Figure 3: The absorbance spectrum of the Cu_2O thin film before and after annealed

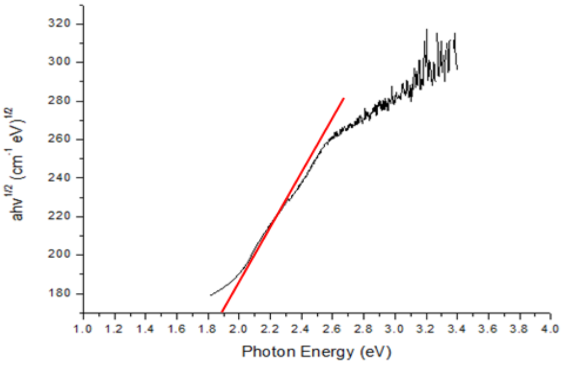

Figure 4: The band gap energy of Cu_2O thin film annealed at 60 minutes was extrapolated from graph

E. Electrical Properties

The sheet resistivity of the Cu_2O thin films can be determined by using Four Point Probe. Figure 5 shows the sheet resistivity of Cu_2O thin films at the various time of annealing. From the results obtained, the sheet resistivity decreased when the samples endured the annealing process. A similar result had been reported by Yonezawa *et al.* by indicating that the resistivity of copper oxide will be decreased after the annealing process [18]. Hence, the introduction of annealing treatment process to reduce the sheet resistivity of the Cu_2O sample has been proven.

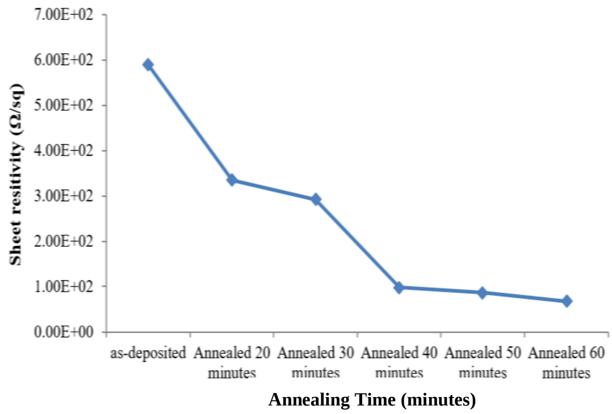

Figure 5: The resistivity of the Cu_2O thin films at various time of annealing

IV. CONCLUSION

In this experiment, n-type Cu_2O thin film has been successfully deposited on fluorine-doped tin oxide glass substrate. The pH value used for the deposition was pH 6.3 and bath temperature was set at 60°C. Meanwhile, deposition time and potential voltage were 30 minutes and -0.125V vs Ag/AgCl, respectively. By manipulating the annealing duration between 20 to 60 minutes at a fixed temperature of 200°C, the annealed samples exhibited different properties compared to as-deposited sample. The optimum annealing treatment duration acquired was 60 minutes. This had proven based on the characterized results that obtained from all samples. In conclusion, n-type Cu_2O was successfully fabricated on the substrate and the effect of annealing time on electrodeposited n-type Cu_2O thin film was determined

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