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The Effect of Annealing Treatment on n-Cu_2O Thin Film for Homostructure Application

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ABSTRACT

This experiment is about fabrication of homojunction (n-type and p-type) based cuprous oxide (Cu_2O) thin film by using electrodeposition method. The Cu_2O thin film were deposited on fluorine doped tin oxide (FTO) substrates by using copper acetate based solution through potentiostatic electrodeposition method. The n-type Cu_2O was fabricated at pH 6.3 with a fixed potential of -0.125V vs. Ag/AgCl and time deposition at 30 minutes. While, for p-type Cu_2O was fabricated at pH 12.5 with fixed potential obtained from cyclic voltammetry measurement of -0.30V vs. Ag/AgCl for 2 hours. Annealing treatment was introduced to enhance the properties of the homostructure thin films. The quality of Cu_2O thin film were studied and varied in term of annealing temperature and duration. Structural, morphological, optical and electrical properties were characterized using X-Ray Diffractometer (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Ultraviolet-visible Spectroscopy (UV-Vis) and Four Point Probe, respectively. Lastly, photoelectrochemical cell (PEC) measurement was studied to confirm the conduction type of each thin film and their photoresponse between as-deposited and annealed sample.

Key words : Electrodeposition, annealing treatment, Cu_2O thin film.

1. INTRODUCTION

Solar cells deviced used to convert sunlight into electricity by the photovoltaive effect. Photovoltaic effect is defined as the creation of voltage or electric current in a material upon exposure of light. This happen because when the light is incident upon a material surface, the electron in the valence band absorbs energy and become excited, making them jump to the conduction band and become free electrons [1].All this while, silicon-based cells have been dominant material for So, consume a lot of electricity [2].researcher were trying to find others material and cuprous oxide (Cu_2O) was one of them. With the material come in abundance, non-toxic and having low cost of production.

In order to fabricate high efficiency of solar cell, the heterojunction is produced this is proven by researches, that solar cells can be fabricated using the heterojunction process [3]. However, the greatest efficiency that manage to obtained by researcher was 5.38% [4] and its still considered as a small value. Thus, homojuction was introduced and has been proven that it was able to perform better than heterojunction in relevant applications [3]. Homojunction can be explain as the interface between two layers of similar semiconductor with equal energy band gap [5]. Which for this studied, the homostructure thin film consist a layer of n- and p-Cu_2O fabricated by electrodeposition method. Many approaches have been explored to prepare Cu_2O thin film. For example, thermal oxidation method [6], magnetron sputtering method [7], sol-gel process [8] and solvothermal method [5]. Among these method, electrodeposition was used since the properties of the thin film can be easily changed by altering the composition of the material. By fabricate homostructure thin film, the efficiency was believed increased. Annealing treatment was introduced to enhance the properties of the thin film. Thus, this research focus on the effects of based homostructure Cu_2O thin film by manipulating the annealing duration and temperature through the annealing treatment on n-Cu_2O thin film. The structural, morphological, optical and electrical characteristic of homostructure based Cu_2O thin film was studied using X-ray Diffraction (XRD), Field emission-scanning electron microscope (FE-SEM), spectrometer (UV-Vis) and four point probe respectively.

2. EXPERIMENTAL PROCEDURES

Practically, the experiment has been carried out in the laboratory which required some apparatus and tools. Fluorine doped thin oxide was used as the base substrate for deposition of Cu_2O thin films in a mixture solution of copper acetate. The mixture contain of 0.4M of copper acetate that act as precusor, 3M of lactic acid act as stabilizer and potassium hydroxide to control the pH of the solution. There are three electrode involved in electrodeposition process which were working, counter and reference electrode. Each electrode possess their own role in deposition process. Homostructure Cu_2O thin film was prepared at pH 6.3 for n-type and 12.5 for p-type, respectively. For n Cu_2O thin film, the bath temperature used was 60°C at 30 minutes duration with deposition potential of -0.125 V vs. Ag/AgCl.

In order to enhance the properties of the fabricated n-Cu_2O thin film, the thin film were annealed with a certain temperature and different duration of annealing treatment. The annealing temperature was in the range of 200, 250 and 300oC. The duration of annealing treatment was varied in 20, 30, 40, 50 and 60 minutes. The preparation of n- Cu_2O thin film which not involved any annealing process called as-deposited was fabricated in order to compare the performance between the samples. Prior to the deposition of p-Cu_2O thin film, cyclic voltammetry measurement was carried out to determine the suitable deposition potential of p-Cu_2O thin film. Then, p- Cu_2O was deposited onto the n-Cu_2O /FTO substrate. Table 1 shown the fixed deposition parameter and Table 2 various annealing process parameter of each samples, respectively.

For characterization, XRD, FE-SEM, UV-Vis and four point probe was used to analyse the structural, morphological, optical and electrical properties of the thin film. Photoelectrochemical cell (PEC) measurement was carried out to confirm the conduction type of the homostructure Cu_2O thin film.

Table 1: Deposition parameter.

Deposition parameter		
	n- Cu_2O	p- Cu_2O
Potential (V vs. Ag/AgCl)	-0.125	-0.30
Bath temperature (oC)	60	40
pH value	6.3	12.5
Deposition Time (min)	30	120

Table 2: Annealing parameter.

Annealing temperature (°C)	Annealing time (min)
200	20, 30, 40, 50 and 60
250	20, 30, 40, 50 and 60
300	20, 30, 40, 50 and 60

3. EXPERIMENTAL RESULT

3.1 The Effect of Annealing Treatment on Annealed N-Cu_2O Thin Film

The n- Cu_2O thin film with the addition of annealing treatment with variety of temperature and duration of annealed were compared. The structural state of the annealed n- Cu_2O thin film on FTO substrate were characterized by using XRD, respectively. From Figure 1, the XRD pattern for all the samples were observed. The peak labelled with grey square is refer to Cu_2O material. The peaks with 2θ values of 29.65, 36.47, 42.37, 61.74 and 73.65 corresponding to (110), (111), (200), (220) and (311) crystal planes of Cu2O, respectively. Hence, the peak list of Cu_2O material are shown in Table 3. The most dominant orientation was (111) plane at position 2θ of 36.47° which could be determined by referring to the highest peak in the XRD pattern. The results can be related with previous research which mentioned that the dominant orientation of (111) at 36.47°of Cu_2O material [9]. The (111) was the preferred orientation because of the molecule absorption has been performed onto this plane and the surface of the plane is non-polarized with the most stable surface when pairing with Lewis acid-basic pairs [10]. For annealed n- Cu_2O thin film, there was a negligible different in the XRD pattern as compared to as-deposited sample. As an example to that, the peak of annealed n- Cu_2O thin film did not shift and stay at their position of 2θ. The similar research has reported by Kim, T.G and his co-worker which proved that annealing treatment do not affect the position peak of 2θ [11]. Among those samples, n- Cu_2O thin film at temperature of 200°C with duration of 60 minutes exhibited higher peak of intensity compared to others. This leads to the increment of the crystallinity of the material. Hence, the sample was differed with n- Cu_2O thin film at an annealed duration of 40 minutes with temperature of 300°C since it exhibit the lowest intensity of the peak. This is due to the peak has a kind of mixed Cu_2O -CuO phase as the samples has been annealed due to heating process in which the Cu_2O will be converted to CuO in the presence of oxygen [12]. Another pattern that can be interpreted from the figure is, the increasing in annealed temperature leads to decreasing in annealed duration in order to improve to the crystallinity of the material. The relationship that can be interpreted from this result is a low temperature of annealing required a longer duration of process and vice versa.

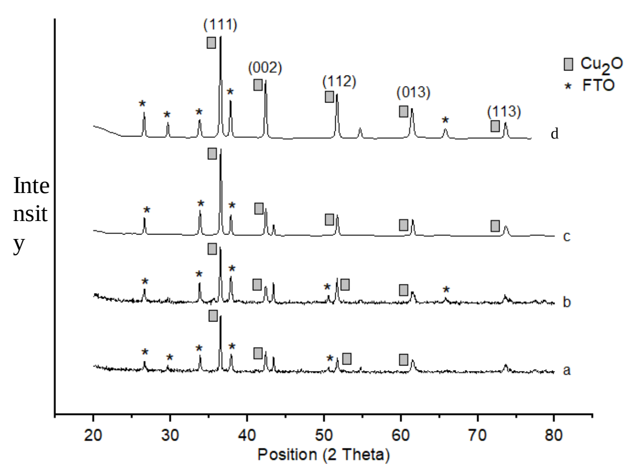

Figure 1: XRD pattern for (a) as-deposited and annealed n-Cu_2O thin at annealed duration of (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60 minutes, respectively

The morphological surface of the annealing n- Cu_2O thin film was studied with FE-SEM instrument. Figure 2 shows theFE-SEM image of (a) as-deposited, and optimize Parameter of annealing duration and temperature,

Table 3: Corresponding plane for Cu_2O reflection peaks

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2 Theta (Degree)	Phase [h k l]
29.65	(110)
36.47	(111)
42.37	(200)
61.74	(220)
73.65	(311)

. The triangular and pyramidal shapes of the Cu_2O were observed according to their corresponding annealed time. The as-deposited n- Cu_2O thin film was examined to have small grain as an additional structure to the material. As annealing treatment was introduced, the samples showed a varying changes in reference to the amount of small grain structure. Based on the previous study, the enhancement of the morphological properties was observed by the decrement of the small grains after annealing treatment [6]. The triangular and pyramidal shapes of the Cu_2O were observed according to their corresponding annealed time. The as-deposited n- Cu_2O thin film was examined to have small grain as an additional structure to the material. As annealing treatment was introduced, the samples showed a varying changes in reference to the amount of small grain structure. Based on the previous study, the enhancement of the morphological properties was observed by the decrement of the small grains after annealing treatment [6]. It was believed that the small grain in the sample agglomerated to form further bunches of larger grain but when the temperature was too high, it induced larger amount of stress in Cu_2O thin film. However, when the annealing temperature reached 300°C and above, the morphology of the material as well as structural properties was obviously change. This change leads to the degradation performance of the material. Thus, by controlling the annealing duration and temperature must be taken into account to produce a better performance of Cu_2O thin film. Hence, 60 minutes of annealed duration with 200°C annealed temperature was the optimal parameter for n- Cu_2O thin film.

3.2 Construction of Cu_2O Based Homostructure

Cyclic Voltammetry measurement (CV) was performed prior to the deposition of p-type Cu_2O (p- Cu_2O) thin film. CV measurement applied to identify the reaction mechanism of n-Cu_2O thin film by obtaining a suitable and optimum potential for deposition of p- Cu_2O onto n- Cu_2O /FTO. During the process of CV measurement, there are two reactions occurred which are oxidation and reduction reaction. However, in this study, only reduction reaction is taken into account. Figure 3 shows the potential range determination of Cu_2O using CV measurement at pH 12.5 with a water bath temperature of 40°C. Since the optimum parameter for annealed n- Cu_2O thin film with annealed temperature of 200°C of 60 minutes duration, a CV measurement was performed on the optimized thin film to obtain the suitable potential deposition for p-Cu_2O thin film. The voltammogram range was set up between 0.5 and -1.0 vs Ag/AgCl at a scan rate of 5mV/s. From the CV measurement of the optimized thin film, two reduction at cathodic regions were observed in the graph of Figure 3. The first regions occurred from -0.2V to -0.35V vs. Ag/AgCl. The first peak was referred to the reduction reaction of Cu2+ to Cu+ and hence to Cu_2O. Then, the second peak belongs to reduction reaction of Cu2+ to Cu which can be said as a metallic copper formation. Then, the deposition potential of -0.30V vs Ag/AgCl was chosen as the optimum potential for this homostructure.

For structural properties, the graph showed peaks detected at 29.65, 36.47, 42.37, 61.74 and 73.65 which corresponding to Cu_2O plane orientation at (110), (111), (200), (220) and (311), respecively. Obviously, the (111) plane orientation presented a highest intensity among other peak which make it as the preferred orientation of Cu_2O material. The result indicated that more crystallize grain was obtained at the

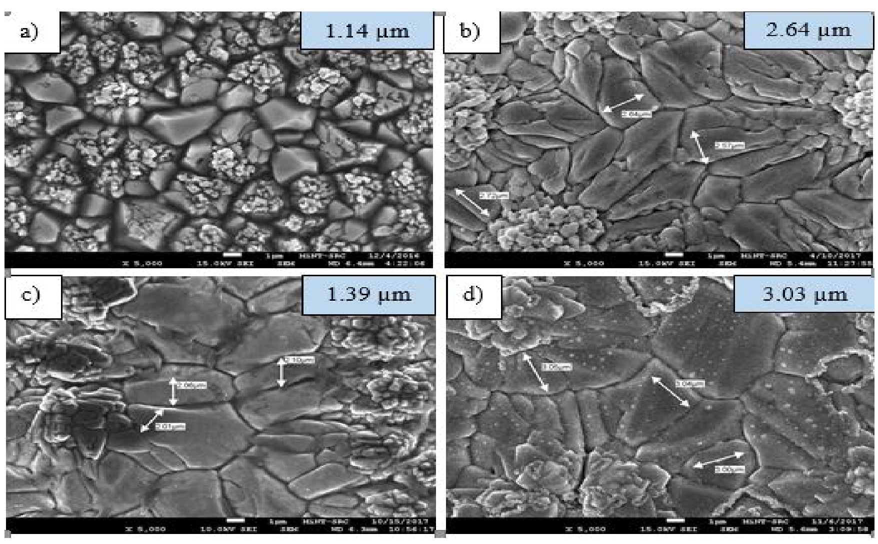

Figure 2: FE-SEM images of surface morphology of n-Cu_2O thin film (a) As-deposited and at annealed duration of (b) 60 mins at temperature of 200°C, (c) 50 mins at temperature of 250°C, (d) 40 mins at temperature of 300°C, respectively

preferred orientation plane. From Figure 4, the increment of Cu_2O peaks was observed indicating the p-Cu_2O was successfully fabricated on n-Cu_2O/FTO substrate. Furthermore, both acidic and basic electrolyte will lead to a

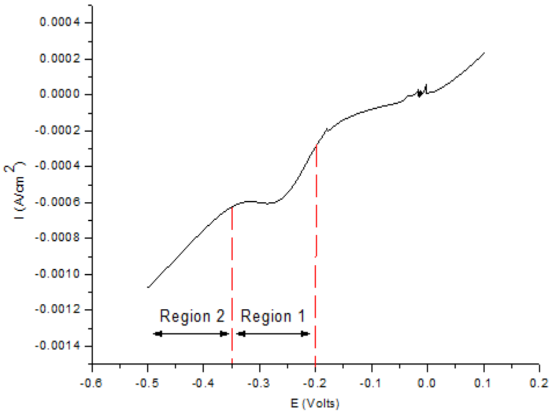

Figure 3: Potential range determination of Cu_2O at pH 12.5 with a fixed temperature of 40°C

stable environment for growth of Cu_2O thin film during electrodeposition process [13].

These statement can answered the possibility of obtaining the fully grown Cu_2O material onto FTO glass substrate which directly help the process of molecule absorption at the preferred orientation of (111).

For morphological properties, there are slightly different in term of their morphology structure before and after fabricating the p- Cu_2O thin film. The size structure of n-Cu_2O material that was produced in a bigger and larger surface is compared to p- Cu_2O. However, even the pyramidal triangular shape of p- Cu_2O are considered as small in size, but it is more compact and the surface is more covered. In addition, an identical condition which can be related to previous researcher which stated that the acidic electrolyte with pH 6.5 is used to grow an n- Cu_2O did not disrupt the layer of p- Cu_2O or degrade the quality of the thin film [13]. Not only that, the morphology of the homostructure sample seems to grow with better and well defined pyramidal triangular shape. By implementing annealing treatment on n-Cu_2O thin film with addition of p- Cu_2O deposited, more uneven shaped grain agglomerate to form crystallite grains

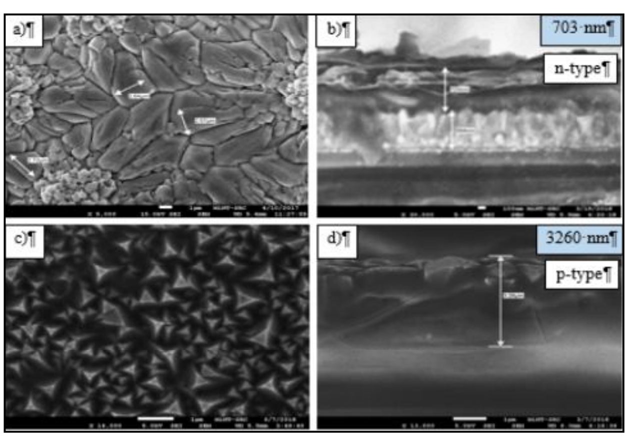

Figure 5: FE-SEM images of (a) surface (b) cross sectioned of optimize annealed n-Cu_2O and (c) surface (d) cross sectioned of p-Cu_2O onto optimize annealed n-Cu_2O/FTO thin film

and the surface mobility enhanced indirectly [14].

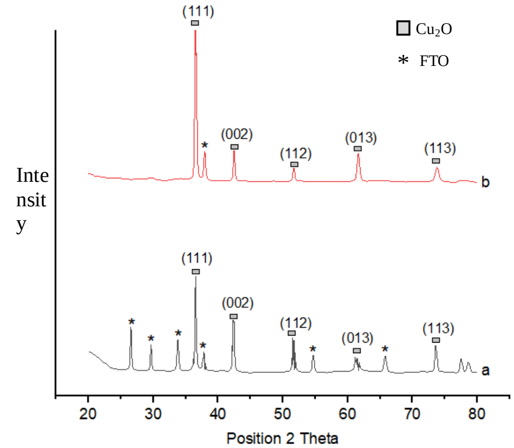

Figure 4: XRD pattern of electrodeposited (a) annealed n- Cu_2O (b) p-Cu_2O on n- Cu_2O /FTO thin films

The PEC measurement was carried out to verify the conduction type of Cu_2O material whether it is successful deposition of p- Cu_2O or n- Cu_2O. The mechanism of PEC measurement can be explained by, when the thin film was illuminated with light, the electron-hole pairs were generated in the space charge region of the surface Cu_2O thin film which were then being separated by the built-in electric field. This mechanism leads to the formation of photocurrents. The two conduction of Cu_2O material which are n-type and p-type have an opposite photocurrents where the former is anodic and the latter is cathodic [15]. Based on Figure 6, the optimum annealed n- Cu_2O thin film which at temperature of 200°C with annealed duration of 60 minutes was tested to examine the conduction type of Cu_2O material. The result shows that the sample with a pH value of 6.3 was confirmed as n- Cu_2O thin film. This finding can be explained as when light illuminates an n-type semiconductor, the absorbed light generates carriers that cause a negative shift of Fermi level potential vs Ag/AgCl [13]. However, Cu_2O thin film in a basic electrolyte at pH 12.5 displays a positive shift under illumination, which reflects the p-type character of the Cu_2O thin film. These photocurrent results consistent with CV measurement and demonstrated that the pH of electrolyte can control the conduction type in electrodeposited Cu_2O thin film [16].

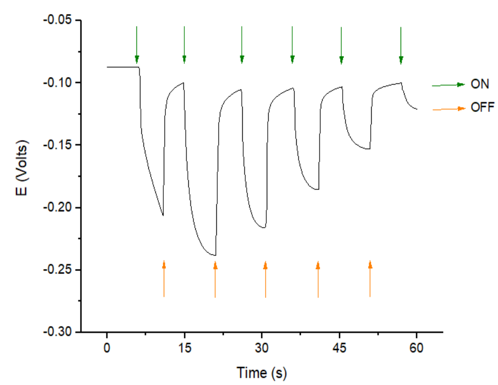

Figure 6: Open circuit photovoltage measured as a function of time under pulse irradiation for As-deposited n-Cu_2O thin film

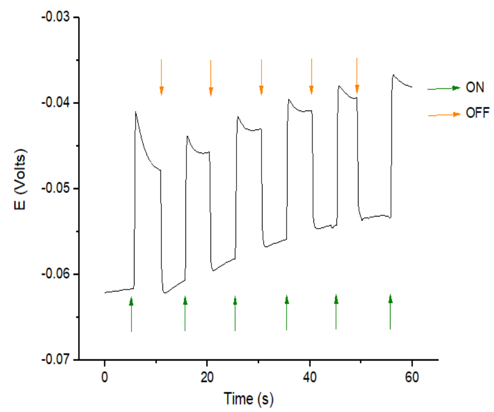

Figure 7: Open circuit photovoltage measured as a function of time under pulse irradiation for p-Cu_2O thin

4. CONCLUSION

This project is conducted to study the effect of annealing treatment parameter on n- Cu_2O thin film for homostructure application by using electrodeposition method. The homostructure thin film was formed by fabricating two types of Cu_2O layers. Firstly, the n- Cu_2O was deposited onto FTO substrate. Then, the sample undergoes annealing treatment for different temperature and certain duration of annealed. Characterization process was carried out to determine the optimum annealing parameter for annealed n- Cu_2O thin film. Next, deposition of p- Cu_2O occurred onto the optimized annealed n- Cu_2O /FTO substrate. The properties of the thin film was improved after annealing with certain optimum parameter with addition of p- Cu_2O deposited (based homostructure). The structural properties of n- Cu_2O were analysed and all sample possessed (111) preferred orientation. Among these samples, annealed n- Cu_2O thin film at temperature of 200°C with duration of 60 minutes shows a highest intensity of the peak at preferred orientation of (111). For morphological characterization, the properties of the samples Cu_2O thin exhibited pyramid triangular shapes. In addition, the morphology of the material was change as the annealed parameter was varied. However, annealed n- Cu_2O thin film at temperature of 200°C with duration of 60 minutes shows an better morphology among all due to the minimize present of the small grain in the FE-SEM image. From CV measurement, the optimum deposition potential chosen was -0.30 V vs Ag/AgCl. Next, the p- Cu_2O thin film was fabricated on an optimized annealed n- Cu_2O thin film. Characterization process occurred to determine the properties of the material. For XRD analysis, 36.45° shows the highest peak of the intensity at orientation plane of (111) which indicates a higher crystallinity of the p- Cu_2O thin film. The morphological properties exhibited pyramidal triangular shape which are considered to be Cu_2O structure. Besides, the negative and positive shift of PEC measurement also indicated that the pH value 6.3 and 12.5 were n- Cu_2O and p- Cu_2O thin film.

As for the conclusion, the Cu_2O based homostructure thin film was successfully fabricated from the acid-based copper acetate based solution by electrodeposition method. The optimum parameters of n-Cu_2O and p- Cu_2O thin film were obtained by characterizing each sample which all the results were supported by previous research findings. However, further investigation and research need to be carried out to obtain a more successful fabrication on Cu_2O homostructure thin film.

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