



Properties Enhancement of Electrodeposit-n-Cu₂O Thin Film by Annealing Treatment

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ABSTRACT

The report is on analysis of the n-type cuprous oxide (n-Cu₂O) thin film toward the effect of annealing duration. The n-Cu₂O material is firstly accumulated on the glass substrate of fluorine-doped tin oxide (FTO) by approach of electrodeposition with deposition time of 30 minutes, with a 60°C of solution temperature and pH 6.5. The n-Cu₂O sample is then undergoes an annealing treatment with duration ranged from 40 till 70 minutes with an 200°C of annealing temperature. Next, effective properties of structural, morphology, topology, optical, electrical and photoelectrochemical of annealed n-Cu₂O thin film were evaluate against the related instrument. From the characterization finding, 50 minutes possess to be the most suitable annealing time. With the implementation treatment of annealing, the n-Cu₂O thin films properties were significantly enhanced.

Key words : Annealing; Electrodeposition; Solar cell; Homojunction; n-Cu₂O thin film.

1. INTRODUCTION

Effective evolution of photovoltaic application is anticipated to reinstate the undermine source of energy. Among the several semiconducting materials acts as photovoltaic cell application because of the poor dimensions, cuprous oxide (Cu₂O) is the agreeable metal oxide material that received the concern between researcher because of its boundless availability and immense absorption coefficient [1]. Greatly acceptable electrical and optical properties have been invented considering, entry-level of 1920 make Cu₂O alternate in photovoltaic applications as an absorber layer [2]. Furthermore, Cu₂O come up with a characteristic of direct band gap range which good enough for conversion of solar energy about 2.1 eV followed by the theoretical solar efficiency of 18% [3].

Cu₂O operate as p-type semiconductor and used in the making of heterostructure thin film solar. This issue to the

existence of Cu vacancies [4]. Heterostructure in solar cell can be defined as a combination between two different layer of semiconductor material in one [5]. There are various approach suggest for the Cu₂O thin films deposition on conductive substrates such as electrodeposition [6], atomic layer deposition, chemical vapour deposition, , thermal oxidation [7], and radio-frequency magnetron sputtering [8]. Commonly, construction by electrodeposition is broadly carried out since the advantage of charge effective followed by the ability for deposition either on metal substrates or on conductive and transparent glass slides with excessively conducting semiconductor layer [9]. Next, the electrodeposition approach is most convenient because its provide the opportunity of depositing n-type photoresponse of solar cell devices Cu₂O thin film [10].

The progression of heterostructure by two types of different semiconductors material can lead to the restrain the separation of electrons and holes and lattice mismatch [11]. While for homostructure, there is no problem of interface strain and plus, highly efficient compared to the heterostructure solar cell [12]. Nonetheless, the efficiency of Cu₂O thin film for homostructure solar cell has disclosed that the value is differ from its efficiency of theoretical [13]. Accordingly, the annealing treatment was conducted to enhance the Cu₂O thin film properties [9]. Therefore, the parameters of annealing treatment have compelling consequences on the improvement characteristic of Cu₂O thin film followed by its properties of structural, morphology, photoelectrochemical, topology, optical and electrical, respectively.

The study focused about consequence of duration of annealed toward the deposited-n-Cu₂O thin film for homostructure solar cell by electrodeposition method. The approach was mediated for the manufacture of n-Cu₂O by method of electrodeposition. The study will also cover the behaviour in term of it properties of the thin film which may indicate any improvement or degradation performance of the solar cell. To conclude, the optimized annealing parameter will be based on experimental results that will be determined.

2. PROCEDURE

In this work, there are several steps needed to construct the

n-Cu₂O thin film, namely solution preparation, substrate preparation, electrodeposition, treatment of annealing and ending with a process of characterization. Firstly, a solution consists a mixture of lactic acid followed by copper (II) sulfate pentahydrate. The pH value of the desired solution is fixed to 6.5 which can be classified as a solution to produce n-type semiconductor material. Sodium Hydroxide chemical were used as the agent to restraint the pH value of the Cu₂O solution. Next, the substrate were covered with kapton tape and left with window area of 1 cm x 1 cm for deposition plan. Then, polarization process of FTO substrate was occurred with 1.0 M NaOH solution accompanied with 10mA/cm² value of current density and 60 seconds duration. Two electrode system were used in polarization process which counter and working electrode were replace with the platinum sheet and FTO glass substrate, respectively.

Afterward, the electrodeposition technique was carried out followed by suitable deposition parameter. The deposition potential was set up to -0.1V vs. Ag/AgCl. In electrodeposition process, there are three electrode involved which is counter, working and reference electrode, respectively. Each electrode in the system possesses their own role in the process to deposit the Cu₂O material to the FTO glass. Then, the sample were undergoes an annealing treatment with air-closed furnace. This treatment was conducted since it may improve or enhance the capability of the solar cell in term of it efficiency. The annealing parameter that was choosing to varied is annealing duration. Four different data of time were collected and studied which is 40, 50, 60 and 70 minutes, respectively with fixed 200°C of annealing temperature. The annealed sample was then being varied with the sample that does not undergo any annealing treatment which in this study called as as-deposited sample.

Finally, the crucial part of this study can be express within the characterization result. X-ray diffractometer, Field emission-scanning electron microscope, Atomic force microscope, Ultraviolet visible spectroscopy, Four-point probe and Photoelectrochemical instrument were used as a tool to interpret the finding of the sample which can be observed and compared is either the aid of annealing treatment did improve the properties of the Cu₂O thin film.

3. RESULT

The behaviour of the n-type cuprous oxide thin film in term of its properties of structural, morphology, topology, optical, electrical and photoelectrochemical were evaluate by distinct characterization instrument.

3.1. Structural properties

Effective structural properties of sample can be evaluated through the X-ray diffractometer (XRD) instrument. Followed to the Joint Committee of Powder Diffraction Standards (JCPDS) index, Cu₂O formation of phase will be distinguish at a range value of 20 to 80° of 2θ scanning angles. Fig. 1 portrayed the result for 5 different samples of the XRD patterns. The blue box labelled in the peak of XRD pattern can

be associate to the Cu₂O crystal orientation. Various peak of Cu₂O were detected in the Fig. 1 which at position of 36.5, 42.4, 61.5 and 73.6° with orientation plane of [111], [200], [220] and [311], respectively. Another input than can be seen from the Fig. 1 is that there is an absence of metallic copper peak of any other impurities except the peak of FTO material. Based on the result obtained, the highest peak of the XRD pattern which also can be refer as preferred Cu₂O peak is at position of 36.5°. These results were very persistent with previous finding which at orientation plane of [111] [14].

Other than that, the pattern that can be seen from the graph is that, the pattern of Cu₂O peak does not shifted even when the thin film sample were undergo annealing treatment at different annealed duration. This statement may be related with previous finding that mentioned the crystal orientation will not be disrupting by the annealing treatment [2]. Another observation is that the intensity of the preferred peak increased with the increased of annealing time but only up to 50 minutes. Beyond this time, the intensity starts to drop. Thus, 50 minutes was the optimum condition for the annealing parameter of 200°C.

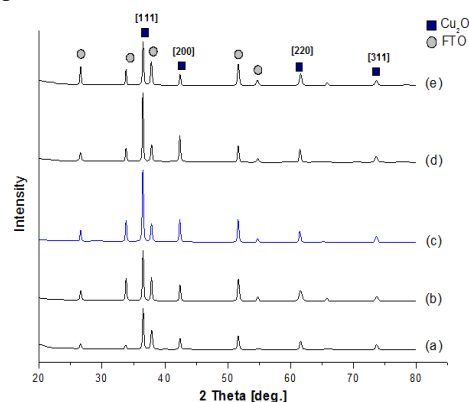


Figure 1: XRD pattern of n-Cu₂O thin films prepared by distinct annealed duration of (a) as-deposited, (b) 40, (c) 50, (d) 60 and (e) 70 minutes, respectively

3.2 Morphological properties

To determine the properties morphology of thin film, FE-SEM was used. Fig. 2 portrays five different morphological images according to different annealing duration.

From Fig. 2, it can be seen that the pyramidal and triangular shape structure appeared in the FE-SEM image. Those structure were covered the FTO substrate and were believed to be in a Cu₂O material which can be match with earlier [9]. The pyramidal and triangular structure can be referred to the orientation plane of [111] which been mentioned previously in the XRD result, respectively [15]. Other than that, the sample without annealed (as-deposited) has more meagre grain compared to the annealed sample. Thus, the decrement of the small grain after being exposed to the annealing treatment may be attributing the intensification of the morphological properties of the n-Cu₂O thin film. This is due to the small grain sample were agglomerated together to structure a further cluster of large grain of the pyramidal

structure[2]. Hence, it proved that annealing treatment did improve the performance of n-type cuprous oxide thin film.

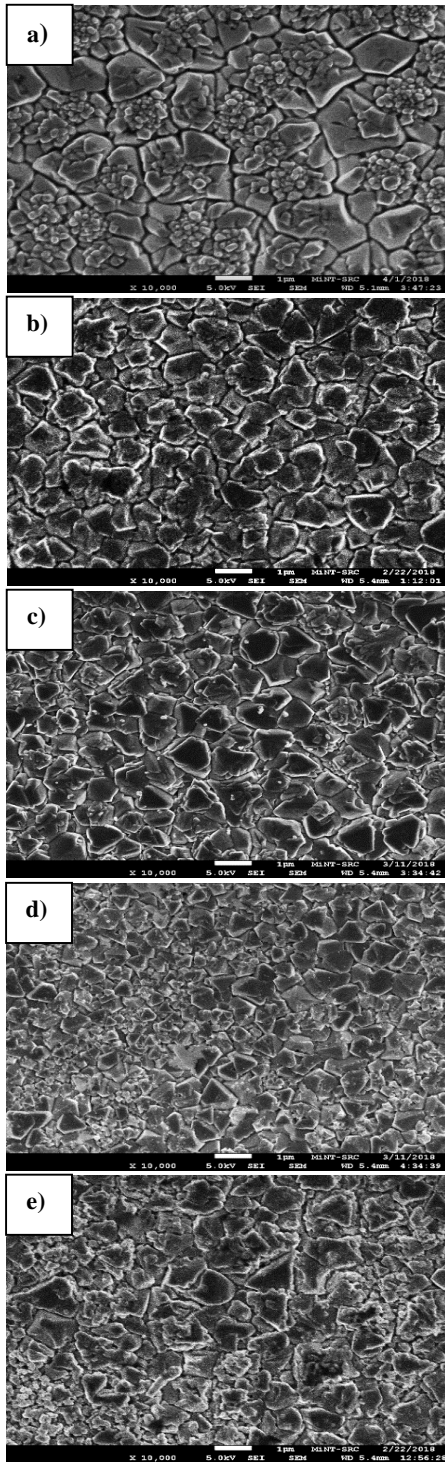


Figure 2: Morphological images of n-Cu₂O thin films prepared by different annealed duration of (a) as-deposited, (b) 40, (c) 50, (d) 60 and (e) 70 minutes, respectively

3.3 Topological properties

Topological properties of effective thin film can be determined by examine the sample with atomic force microscope (AFM).The value of each average surface

roughness was portrayed in the Table 1. The pattern of the that can be seen from the table is that the surface roughness of the sample decreased as the annealing duration increased. However this pattern only valid up to annealed duration of 50 minutes, beyond that the surface roughness start to increased. The value of average roughness of surface of the annealed n-type cuprous oxide thin film was smaller compared to the as-deposited sample. This is due to annealing treatment did lessen the forming of meager grain with flowering shape in the surface of thin film [11].This result in topological properties were support by the previous result which has been discussed in the morphological part earlier. Thus, the small grain that appeared in the FE-SEM image give a crucial effect to the average surface roughness the sample [1]. Hence, it proven that topological properties can be upgraded by exposing sample to the treatment of annealing.

Table 1: Average surface roughness of the n-Cu₂O thin films

Sample	Surface roughness(nm)
As-deposited	128.000
40 minutes of annealed	71.006
50 minutes of annealed	64.240
60 minutes of annealed	65.810
70 minutes of annealed	67.624

3.4 Optical properties

The optical properties of the thin film were achieved through ultraviolet visible spectroscopy (UV-Vis).Fig. 3 shows absorption coefficient graph for the five different samples of annealing duration and as-deposited to be compared with. Based on Fig. 3, the sample shows an absorption coefficient around 600nm in no difference to the as-deposited and annealed sample [18]. While, Fig. 4 represent the energy bandgap graph for the n-type cuprous oxide thin film. Based on the observation, all sample exhibits the same energy band gap even after and before annealing treatment. Thus, the value of bandgap was 1.9 eV which very similar with the previous finding which stated that bandgap Cu₂O should be in the ranging of 1.9 to 2.2 eV. [1][6][4].

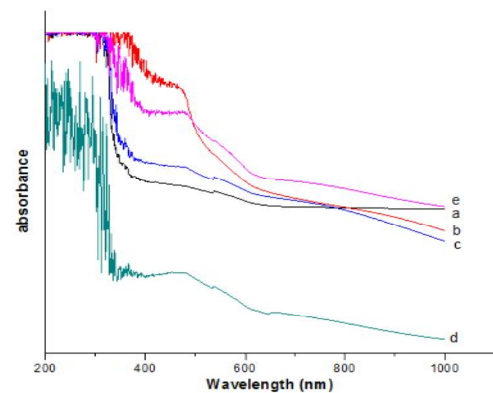


Figure 3: Absorption coefficient of n-Cu₂O thin films prepared by different annealed duration of (a) as-deposited (b) 40, (c) 50, (d) 60 and (e) 70 minutes, respectively

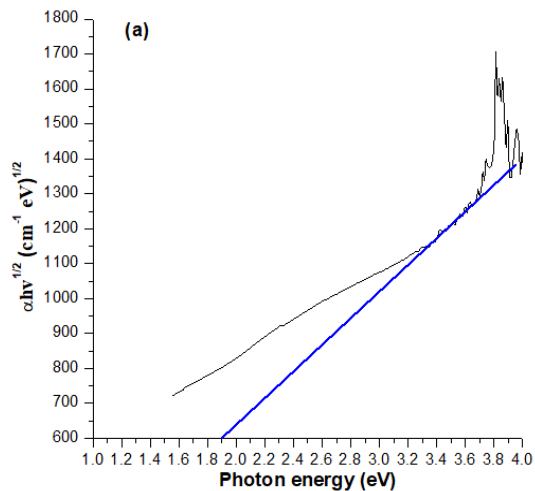


Figure 4: Extrapolated band gap of the n-Cu₂O thin films.

3.5 Electrical properties

The electrical properties n-Cu₂O thin film can be determined through testing sample with four point probe measurement. In electrical properties, the resistivity value of each sample were collected and been compared. The resistivity value of each sample was portrayed in the Table 2. The pattern that can be seen from the table is that the resistivity of the as-deposited sample started to decreased as annealing treatment being introduced. Then, the resistivity value decreased along with the increased of annealing duration. However, the pattern only valid up to annealed duration of 50 minutes and the resistivity value started to increased onwards. Thus, it showed that 50 minutes was the optimum condition for annealing treatment of 200°C. The different in resistivity value may due to the enlargement of grain size since formation of larger grain may be occurred during annealing treatment. The result can be related with the FE-SEM image in the morphological result earlier. Hence, the electrical properties can be enhanced by implementing the annealing treatment in n-Cu₂O homostructure solar cell.

Table 2: Resistivity of the n-Cu₂O Thin Films

Sample	Resistivity (x 10 ² Ω·cm)
As-deposited	1.73
40 minutes annealed	1.52
50 minutes annealed	1.27
60 minutes annealed	1.55
70 minutes annealed	1.58

3.6 Photoelectrochemical properties

n-type cuprous oxide thin film properties of photoelectrochemical can be determine using photoelectrochemical (PEC). In PEC measurement, only two sample were involved and being compared. First, the as-deposited sample and second was the optimum sample for

annealing treatment of n-type cuprous oxide thin film which was sample of 50 minutes.

During measurement, when both samples were being exposed with visible light, it will generate certain value of photovoltage. The photovoltage graph for both sample against recorded time was shown in Fig. 5 (a) and (b). From the graph it can be seen that when the sample were exposed to light, the photovoltage value started to decreased and the photovoltage value started to increased when illuminated light was turned off [19]. This is due to the case when the visible light started to on, the electron in the electrolyte has gained energy which caused the electron to drift from the electrolyte to the thin film of Cu₂O deposited. Thus, a negative sign value of photovoltage will be generated from the accumulation of electron.

Next, the as-deposited sample were less performed in terms of stability in the PEC performance in comparison with annealed sample. The performance of PEC for n-type cuprous oxide thin film was corresponds to the result on morphological and structural properties earlier. Without being said, the annealed sample has larger grain size and good growth crystallinity within the phase of [111]. This can be related with the sample tend to induced higher photovoltage production and greater photo-absorption for the annealed n-type cuprous thin film.

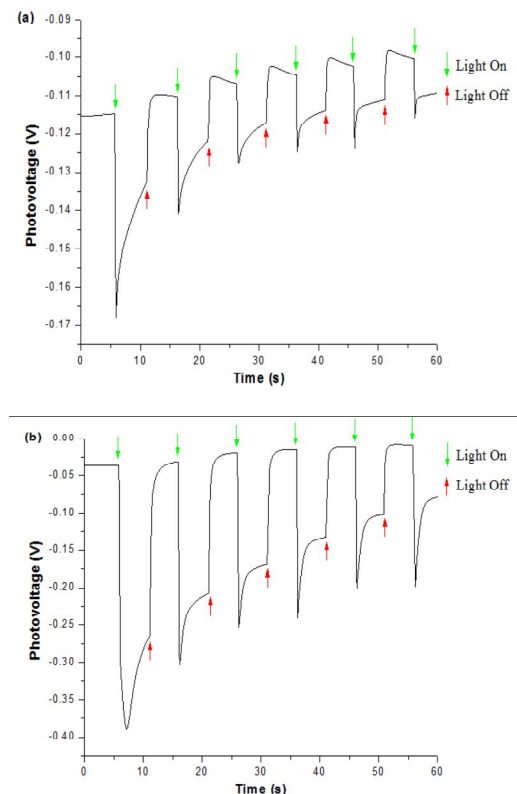


Figure 5: Graph of photovoltage for n-Cu₂O thin films of (a) as-deposited sample and (b) annealed sample at a duration of 50 minutes.

4. CONCLUSION

For the conclusion, homostructure solar cell can be formed by the n-type of cuprous oxide thin film. To construct the n-type

cuprous oxide thin film on FTO substrate, electrodeposition process was chosen. The electrodeposition process were occurred in a solution of acidic precursor. For the electrodeposition parameter, the temperature of precursor solution and pH value was put up continual to 60°C and 6.5. Next, the deposition potential and time were also fixed, -0.1V vs. Ag/AgCl and 30 minutes. To enhance the performance of n-type cuprous oxide thin firm in term of its properties, annealing treatment were introduced. It convinced that annealed sample exhibits better properties compared to the as-deposited sample. This may be seen by adjusting and varying the annealing duration lead to the improvement in structural, morphology, optical, topological and electrical properties, respectively. Lastly, 50 minutes of annealed duration was the optimum condition for annealing treatment of n-Cu₂O thin film since it possesses a good result in every characterization test compared to others.

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