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The Effect of Annealing Treatment on n-Cu_2O Thin Film Fabrication

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Abstract: This experiment is about fabrication of homojunction n-type cuprous oxide (Cu_2O) thin film by using electrodeposition method. The Cu_2O thin films 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 of 30 minutes. Annealing treatment was introduced to enhance the properties of the thin films. The quality of Cu_2O thin films were studied in varied the annealing duration. Morphological, structural, optical and electrical properties were characterized using X-Ray Diffractometer, Field Emission-Scanning Electron Microscopy, Ultraviolet-visible Spectroscopy and Four Point Probe, respectively.

Keywords: Electrodeposition, annealing treatment, Cu_2O thin film

1. Introduction

Cuprous oxide (Cu_2O) is an example of semiconductor material which potentially attractive for solar cell and sensor application. In order to fabricate highly efficient solar cells, the heterojunction process is introduced and this is proven by researches, that solar cells can be fabricated using the heterojunction process [1]. In 2013, Minami, T. and her coworkers concluded, through rigorous researching, the highest efficiency of heterojunction solar cells in their research, is 5.38% [2]. However, with energy conversion efficiency of 5.38% in heterojunction is still considered to be small compared to the theoretical limit of a Cu_2O solar cell. With that, homojunction was introduced to increase the efficiency of the energy conversion.

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Homojunction has been proven that it was able to perform better than heterojunction in relevant applications [3]. The optimum ways to improve the efficiency of the solar cell are by achieve the n-type semiconductor Cu_2O [4]. The difficulty comes when it hard to achieve the n-type Cu_2O because of the challenges to improve the quantity of copper and oxygen vacancies in Cu_2O which can be related to the conductivity of the film [5]. However by implement the electrodeposition method, the problem can be solve due to the conduction type of the electrodeposit cuprous oxide can be control by the solution of the pH [4]. Other than electrodeposition method, there has a various technique to deposit Cu_2O thin film such as thermal oxidation [6], solvothermal method [7], radio frequency magnetron sputtering [8], pulsed laser and deposition [9]. Between these methods, electrodeposition was mainly used to fabricate Cu_2O thin film due to its low cost and low processing temperature which is also act as a simple process [10]. As a Comparison from previous study, the suitable deposition temperature in the range of 45 to 77°C. By using electrodeposition, the thickness of the production of Cu_2O thin film can be precisely control [11]. In addition, Cu_2O film can be easily deposit into the desired substrate which the thickness of the film can be control by adjusting the electrodeposition parameter [12]. Hence, this can answered the first objective of this research which was to fabricate the n-type of Cu_2O thin film by using electrodeposition method. Annealing treatment is introduced to enhance the properties of the cuprous oxide thin film which to increase the quality of energy conversion [10]. The structural, morphological, optical and electrical characteristic of n-type cuprous oxide 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

In this study, Cu_2O thin films were electrodeposited on fluorine doped tin oxide (FTO) substrate in an electrochemical cell that contained an aqueous solution of cupric sulphate, lactic acid and sodium hydroxide that act as a pH regulator. The working, counter and reference electrode were FTO substrate, platinum electrode and Ag/AgCl, respectively. Cu_2O thin films were prepared at mixture of pH solution 6.3 and bath temperature 60ºC. The deposition potential was fixed to 30 minutes at -0.125 V with the presence of Ag/AgCl as reference electrode.

In order to enhance the properties of the fabricated Cu_2O thin film, the cuprous oxide thin film were annealed in air with a fixed temperature and different duration of annealing treatment. The annealing temperature was set up to 300ºC. The duration of annealing treatment was varied in 20, 30, 40, 50 and 60 minutes. The preparation of cuprous oxide thin film which not involved any annealing process called as-deposited was fabricated in order to compare the performance between the samples. Table 1 shown the fixed deposition parameter and Table 2 various annealing process parameter of each samples.

XRD was used to analyse the structural properties of Cu_2O thin film. Next, FE-SEM was used to characterize the sample in term of their morphology. In order to obtain the optical energy band gap, UV-visible spectrometer was used. Four point probe was also used in order to determine the electrical properties of the sample.

Table 1 - Deposition parameter

Deposition parameter	
Potential (V vs. Ag/AgCl)	0.125
Bath temperature (ºC)	60
pH value	6.3
Deposition Time (min)	30

Table 2 - Annealing time

Sample	Annealing time (min)
1	0
2	20
3	30
4	40
5	50
6	60

3. Experimental Results

3.1 Structural Properties

By using XRD, the structural states of the deposited cuprous oxide thin film on FTO substrate in different annealing time were characterized. From Fig. 1, the stacked of the XRD pattern for all samples can be observed. The XRD peaks for the entire sample were persistent with the standard peak in JCPDS no. 050667 that the determined the accomplishment structure Cu_2O [13]. The XRD peak were detected in plane (111), (200) and (220) corresponding at the position of 36.45°, 42.30° and 61.45°, respectively shown in Table 3. The peak that clearly observed for the Cu_2O thin film was the reflection at (111) formation. For this studied, the sample 4 indicate the highest peak [14]. This can reveal the structural enhancement of Cu_2O crystallinity [10]. The intensity improved with the increment of annealing duration up to 40 minutes and decreased onwards. The decrement of intensity can be relates from previous study which mentioned that the peak has a kind mixed of Cu_2O - CuO phase due to annealing treatment which Cu_2O will be converted to CuO in the presence of oxygen [15]. After annealing treatment, the peak did not shift and stay at their position of 2θ. The similar research has reported by Kim, T.G and his co-worker [10] which prove that annealing treatment do not affect the position peak of 2θ. With the result above, annealing treatment improved the cyrstallinity of n- Cu_2O and 40 minutes duration was the optimize value.

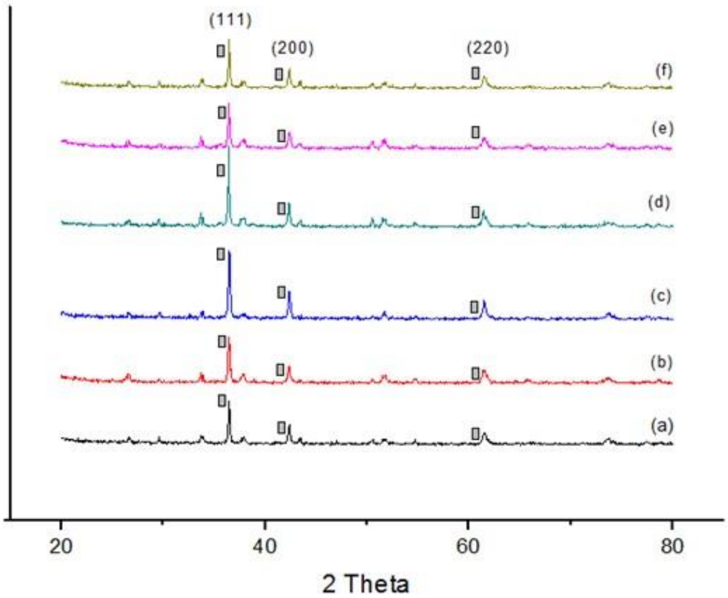

Fig. 1 - XRD patterns for (a) as-deposited Cu_2O and annealed-Cu_2O with duration of (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60 minutes, respectively

Table 3 - Corresponding plane for Cu_2O reflection peaks

2 Theta (Degree)	Phase [h k l]
36.46	[111]
42.30	[200]
61.45	[220]

3.2 Morphological Properties

In this study, Field Emission-Scanning Electron Microscope (FE-SEM) was used to examine the morphological properties of the sample deposited. From the results obtained, there were formations of Cu_2O on the FTO substrate. Figure 2 shows the FE-SEM images for six samples that used to determine the effect of annealing on Cu_2O over time. All samples exhibits an average thickness of 706 nm which been measured by FE-SEM through cross section measurement. For as deposited sample, the triangular and pyramidal shapes can be observed in the FE-SEM image. In addition to that shape, small grain structure also present in the image. After annealing treatment, the quantity of the small grain reduced and totally disappeared at the annealing duration of 40 minutes. This can be related to the theory that mention about after annealing treatment, the enhancement of the morphological properties will lead to the decreasing of the small grain on the Cu_2O thin film [16]. While for grain size, its start to increase as annealed duration increased but only up to 40 minutes. However, when the duration of annealing up to 50 onwards, different type of structure was appeared. Then, the structure was downgraded (less formation of triangular structure) the quality of the Cu_2O which has been observed in structural characterization. This statement has been proved in the XRD analysis that can be related to the intensity of the peak.

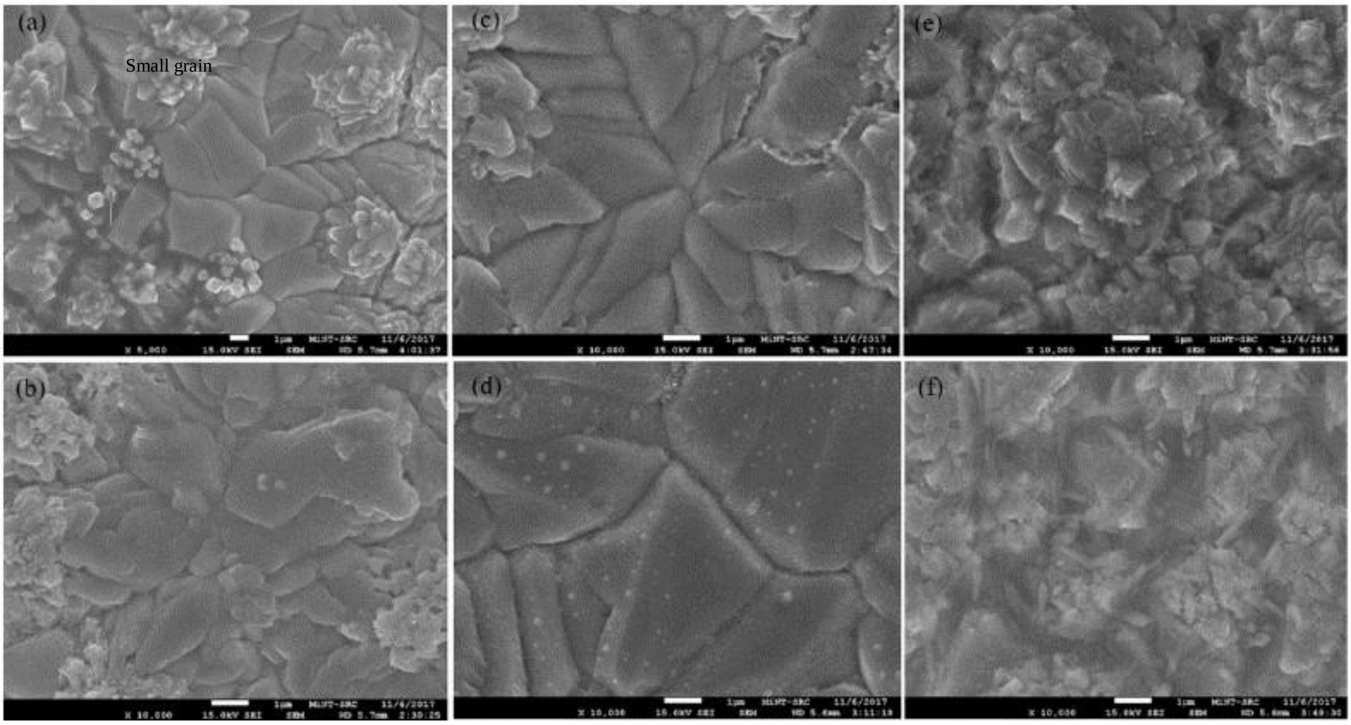

Fig. 2 - XRD patterns for (a) as-deposited Cu_2O and annealed- Cu_2O with duration of; (b) 20; (c) 30; (d) 40; (e) 50; (f) 60 minutes, respectively

3.3 Optical Properties

Ultraviolet Visible Spectrometer (UV-Vis) was used to examine the absorbance and energy band gap of the thin films. In order to determine the band gap of the deposited Cu_2O thin films, the absorbance of the sample is taken into account. The absorbance of the Cu_2O thin films that has been annealed for 40 minutes are shown in Figure 3. The figure shows that, there is an increment of wavelength at 600nm and it is represented by band gap energy of 1.9eV as shown in Figure 4. According to previous study, Cu_2O has a band gap range between 1.9eV to 2.2eV [10]. The extrapolation line from the Figure 4 can be defined as the energy band gap of the Cu_2O thin films. All six samples that deposited at pH 6.3 obtained the value of the energy band gap of 1.9eV, respectively. This results are very similar and can be relates with the previous study that mentioned the bandgap for electrodeposition of cuprous oxide is unaffected by the annealing treatment [17].

3.4 Electrical Properties

The sheet resistivity of the Cu_2O thin films can be determined by using Four Point Probe. The resistivity for as deposited of the Cu_2O thin film was 7.42 Ω/sq. From Table 4, the resistivity of the Cu_2O thin film was found to have decreased after annealing treatment. Similar results had been reported by one finding which said that after the annealing treatment the resistivity of copper will be decreased [18]. Also, another trend can be observed in the Table 4, where the resistivity started to increase when the annealing time at 50 and 60 minute. This result can be inferred with one finding which said that the increased in resistivity was due to the decreased in carrier concentration [19]. Hence, from the results in Table 4, 40 minutes of annealed time was the optimum duration since it reduced resistivity of Cu_2O thin film.

Table 4 - Resistivity of Cu_2O thin film

Sample	Resistivity (Ω/sq)
As deposited	7.42
Annealed 20 minutes	7.25
Annealed 30 minutes	6.09
Annealed 40 minutes	5.02
Annealed 50 minutes	7.48
Annealed 60 minutes	7.55

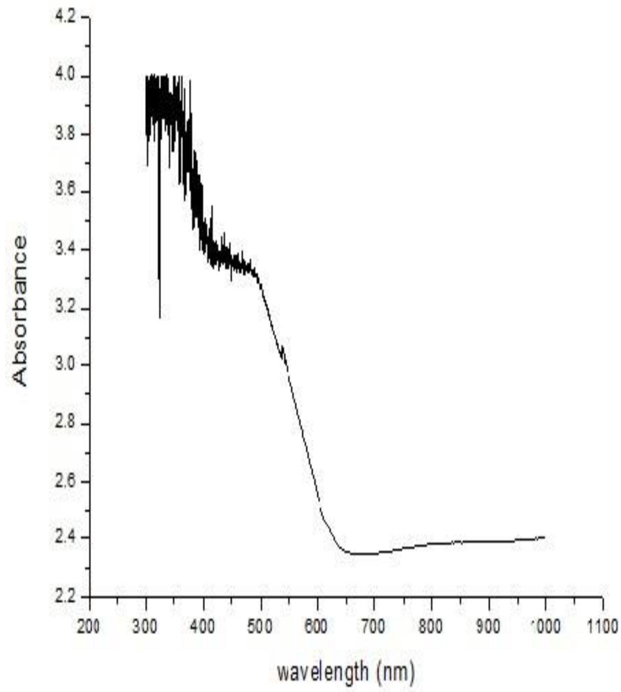

Fig. 3 - The absorbance of the duration of 40 minutes.Cu_2O thin film at annealed

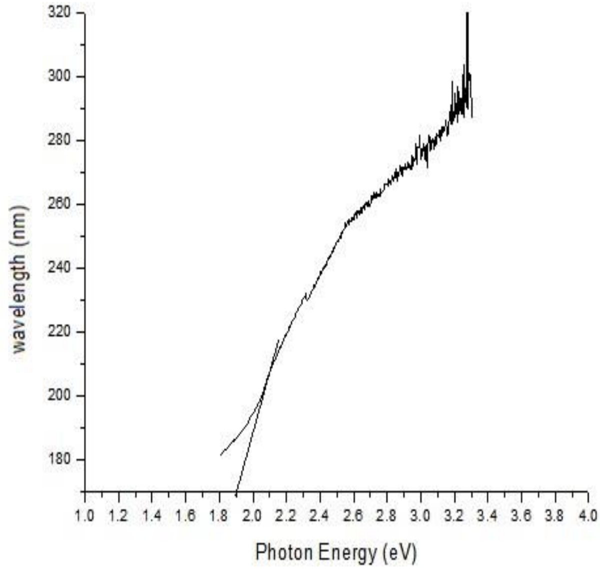

Fig. 4 - The energy band gap of the Cu_2O thin film at annealed duration of 40 minutes

4. Conclusion

n-type Cu_2O thin film were successfully fabricated onto FTO glass substrate by using electrodeposition method. The deposition potential was fixed to 30 minutes at 0.125 V vs. Ag/AgCl deposition potential. Cu_2O thin films were prepared at mixture of pH solution 6.3 and bath temperature 60ºC. Annealing treatment was introduced to improve the properties of Cu_2O thin film. Results of different annealing duration with fixed temperature of 300ºC were studied. The sample were grown on FTO glass substrates with typical triangular shape of Cu_2O except sample 1 that exhibited small grain of Cu_2O and sample 5 and 6 exhibited other structure of Cu_2O. The structural properties of Cu_2O were analysed and all sample possessed (111) preferred orientation. Among these samples, sample 4 shown an optimum structural properties. This sample also absorbed light at wavelength 600 nm with the band gap energy of 1.9 eV.

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