

Effect of Deposition Time on the Electrodeposited n-Cu₂O Thin Film

Asyikin Sasha Mohd Hanif^{1, a}, Siti Aisyah Azmal^{1, b}, Mohd Khairul Ahmad^{1, c},
and Fariza Mohamad^{1, d}

¹Microelectronic and Nanotechnology – Shamsuddin Research Centre (Mint-SRC), Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400, Batu Pahat, Johor, Malaysia

^aasyikinsasha@gmail.com, ^baisyah157@yahoo.com, ^ccahairul@uthm.edu.my,
^dfarizamd@uthm.edu.my

Keywords: cuprous oxide, electrodeposition, n-type semiconductor, deposition time

Abstract. This work demonstrates the fabrication of Cu₂O thin film onto a fluorine-doped tin oxide (FTO) glass substrate via electrodeposition method which was conducted in a solution containing copper (II) acetate monohydrate and lactic acid. While varying the deposition time ranging up to 80 minutes, the solution was kept constant at solution temperature of 40°C, solution pH 6.5 and current density -0.3 mA/cm². The characteristics of electrodeposited Cu₂O were investigated via x-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), current-voltage (I-V) test and surface profiler. The XRD results showed the intensity peak of Cu₂O corresponded to reflection (111) increased when the deposition time increased. The topological characteristics from AFM characterization showed the increment of surface roughness decreased as the time increased from 5 to 60 minutes. However, the surface roughness decreased when the time reached 70 and 80 minutes. I-V characteristics of all electrodeposited Cu₂O showed Ohmic behaviours indicating the successful fabrication of n- Cu₂O thin film. From this study, the significant effect of deposition time of Cu₂O was clearly observed and plays an important role in providing mechanism growth of the film.

Introduction

Solar energy is energy that is produced by the sun. Sunlight from the sun can be used directly to generate electricity using the photovoltaic technology [1,2]. This type of energy is used to run the electricity at homes, offices and can also be used to run the machineries. Basic idea of a solar plate cell is to convert light energy into electrical energy and it is typically and usually made up of silicon material. Silicon is the substance that can absorb sunlight and changes it into electrical energy. The high cost of using the silicon solar cells to capture light energy have forced the development in creating new photovoltaic devices that utilize cheap and non-toxic materials prepared by energy-efficient process [3].

Cuprous oxide (Cu₂O) is one of the metal oxide semiconductors that received attention in solar cell applications. The synthesized Cu₂O is typically a p-type semiconductor with a direct band gap of around 2.17eV which makes it a potential candidate for light energy absorbing layer in solar cells plate. Besides, Cu₂O is attractive due to its high absorption coefficient, comes in abundance, non-toxicity and low cost fabrication [4,5].

There are many methods have been applied to synthesize Cu₂O which include sol-gel approach [6], thermal oxidation [7], chemical vapor deposition [8], sputtering [9] and electrochemical method [5,10]. Compared to mentioned methods, electrochemical method is chosen because the deposition process is simple, inexpensive, producing controllable film thickness, producing large scale deposition and can be done at low temperature [11]. Moreover, it has the facility to control the surface morphologies, phase compositions and other elements by adjusting the deposition parameters [12].

In this work, the electrochemical deposition method was used to prepare the n-type Cu₂O where the deposition of n-type films show the importance of growing p-n homojunction of Cu₂O for applications in thin film solar devices [5]. In developing the electrodeposited Cu₂O as a solar energy material, it is very important to identify parameters that could control the conduction type of the

film where in this study, the effect of deposition time towards n-type Cu_2O thin film was investigated. It was revealed that the compositions and microstructure of the films were strongly affected by the deposition time. In addition, the pyramidal columnar grains were obtained at the end of this study by controlling several deposition times.

Experimental

Cu_2O thin films were deposited on FTO substrates. Prior to the deposition process, substrates were cut (2.5cm x 1cm), cleaned with acetone in ultrasonicator for 5min and finally rinsed with distilled water. The substrates were further cleaned by using polarization process in 1M NaOH at current density $+10\text{mA}/\text{cm}^2$ for 60s. Films were deposited by using galvanostat in 200ml aqueous solution containing 0.4M copper (II) acetate monohydrate and 3M lactic acid. Solution pH was set at 6.5 by adding potassium hydroxide in the solution. The temperature of the solution was maintained at 40°C in water bath. Electrodeposition was carried out under a galvanostatic condition of $-0.3\text{mA}/\text{cm}^2$ with platinum plate as the counter electrode and FTO substrate as working electrode. Deposition time was varied from 5min to 80min. The electrodeposited samples were then characterized via x-ray diffractometer (Bruker, Model D8 Advance), field emission scanning electron microscopy (JEOL, Model: JSM-7600F), atomic force microscopy (Tenko, Model XE-100), current-voltage (I-V) test and surface profiler (KEITHLY, Model: Series 2400 SourceMeter).

Results and Discussion

A. Structural characterization

By using XRD, the structural states of Cu_2O electrodeposited on FTO substrate in different deposition time were characterized. The deposition time was ranging from 5min to 80min with solution temperature and solution pH at 40°C and 6.5, respectively. The result was shown as in Fig 1. The XRD peaks were consistent with the standard peaks in JCPDS no. 050667 which determined the success of Cu_2O formation [13]. The focused peak was the reflection of Cu_2O at (111) formation which as the deposition time increased, the peak was also increased. The increment of the intensity indicated the structural improvement of Cu_2O where the crystallinity increased as the deposition time increased.

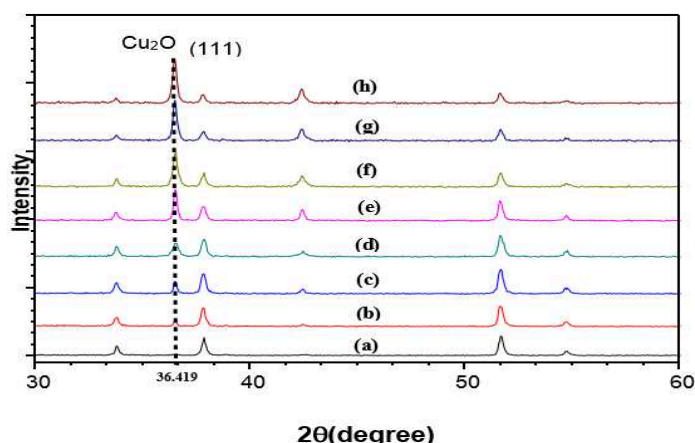


Fig. 1: XRD pattern of electrodeposited Cu_2O thin films at different deposition time, (a)5, (b)10, (c)15, (d)30, (e)45, (f)60, (g)70 and (h)80 minutes.

B. Morphological characterization

Fig. 2 shows the systematic morphological evolution of FESEM images of Cu_2O thin films that were deposited under different deposition time. FESEM images revealed the strong effect of deposition towards composition and microstructure of Cu_2O thin films. Triangular and pyramidal shapes can be observed in all FESEM images which confirmed the successful fabrication of Cu_2O on FTO substrate. These results were consistent with XRD results where the higher intensity of Cu_2O peaks showed more compact and closer particles as the deposition time was increased.

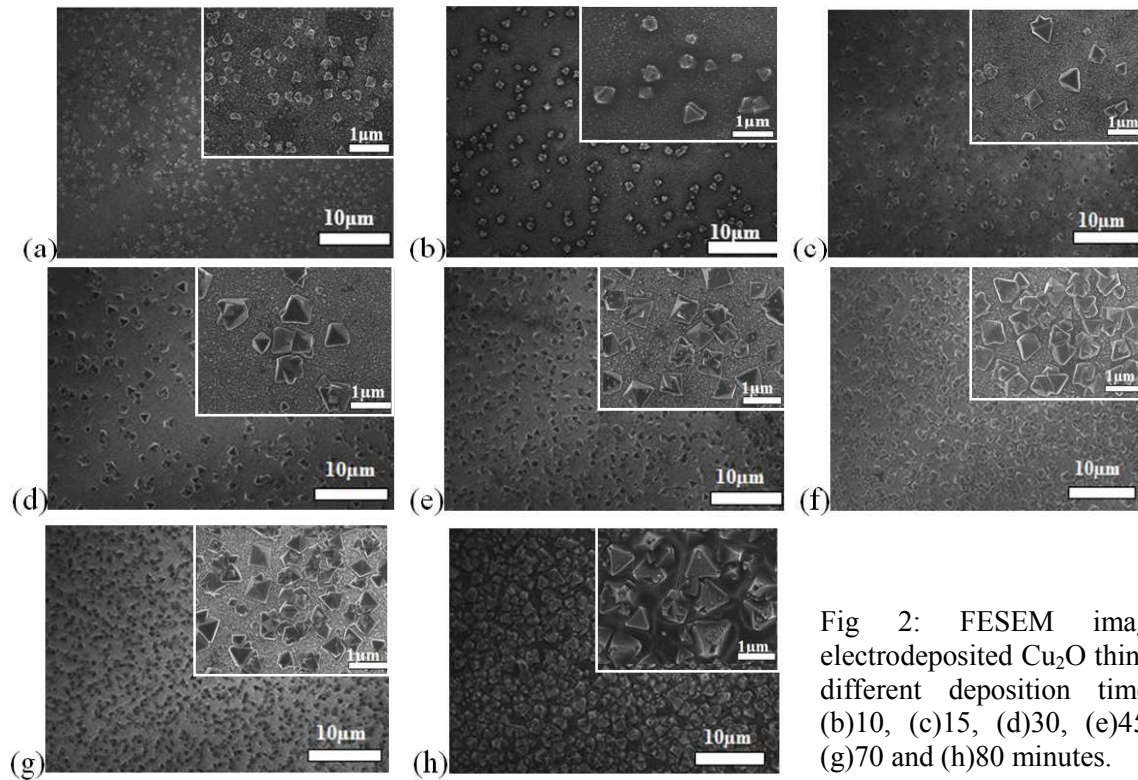


Fig 2: FESEM images of electrodeposited Cu_2O thin films at different deposition time, (a)5, (b)10, (c)15, (d)30, (e)45, (f)60, (g)70 and (h)80 minutes.

C. Topological characterization

Table 1 shows the roughness of electrodeposited Cu_2O thin films fabricated at different deposition time taken using AFM. It was observed that the roughness increased from 5 to 60min and decreased in 70 and 80min. These results can be related to FESEM images where the surface of FTO substrate started to become denser with the growth of Cu_2O as the time increased. However, when the time was increased to 70 and 80min, the surface was more compact and dense which made the roughness decreased.

Table 1: The average roughness of electrodeposited Cu_2O thin films.

Deposition Time Taken (Minutes)	Roughness (nm)
5	153.662
10	182.524
15	242.068
30	289.000
45	320.973
60	338.000
70	287.000
80	235.506

D. Electrical characterization

Fig. 3 shows the acquired I-V characteristics from the electrodeposited Cu_2O thin film. It indicates that the deposited Cu_2O has ohmic contact with FTO substrate [14]. The result is one of the evidence that the fabricated Cu_2O thin film was an n-type since it was known that the FTO on glass substrate is n-type substrate [15].

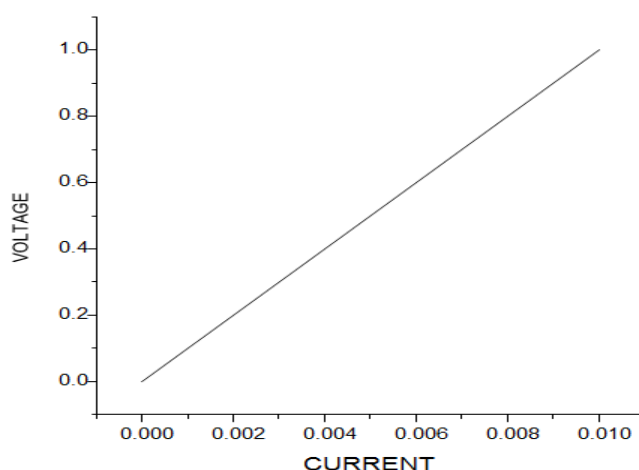


Fig. 3: I-V characteristics of electrodeposited Cu_2O thin films.

E. Thickness measurement

Table 2 shows the average thickness of electrodeposited Cu_2O thin films that have been analyzed using surface profiler machine. The result showed that as the deposition time increased, the thickness of thin film was also increased. This was parallel with other characterizations that showed as the time was prolonged, more Cu_2O particles were formed on FTO substrate.

Table 2: The average thickness of electrodeposited Cu_2O thin films.

Effect Of Deposition Time (Minutes)	Average Thickness (μm)
5	0.21379
10	0.34786
15	0.37193
30	0.70861
45	0.71309
60	1.28853
70	1.81190
80	1.96496

Conclusion

The n-type cuprous oxide (Cu_2O) thin film were deposited using electrodeposition method. The main objective of this research is to determine the effect of deposition time on the fabrication of n- Cu_2O thin film. The deposition time is varied to 5,10,15,30,45,60,70 and 80 minutes. In this study, the n- Cu_2O was successfully deposited on a fluorine-doped tin oxide (FTO) glass substrate from a simple aqueous solution containing copper (II) acetate monohydrate aqueous, lactic acid and potassium hydroxide by galvanostatic electrochemical process. The samples were then undergone the analysis of x-ray diffraction (XRD), field emission scanning electron microscope (FESEM), atomic force microscopy (AFM), current-voltage (I-V) measurement and thickness measurement. XRD results obtained from this investigation explains that the intensity peak of composition Cu_2O (111) increased with the increasing of deposition time. The FESEM images of Cu_2O nanostructure deposited on the thin films became more compact and closer to each other which related to the intensity composition of Cu_2O (111) obtained from XRD. From AFM analysis, the roughness of the thin films was increasing up to 60 minutes but decreasing in the time of 70-80 minutes. The reason was the nanostructure of the thin films was dense and more compact with the increasing of deposition time. Next the I-V characteristics showed an Ohmic behavior of the representative of all deposition time at the thin films and the thickness increased with respect to the increment of

deposition time. It can be concluded that deposition time affected the properties of n-Cu₂O thin films in terms structural, morphological, topological and so on.

Acknowledgement

The authors would like to acknowledge Microelectronic and Nanotechnology Shamsuddin Research Center (MINT-SRC), Universiti Tun Hussein Onn Malaysia for providing laboratory apparatus and characterization equipment. This work was supported by FRGS Vote No. 1223.

References

- [1] A. Goetzberger, C. Hebling, H. W. Schock, *Materials Science and Engineering: Reports*, **40**(1), 2003, pp. 1-46.
- [2] A. Goetzberger, J. Luther, G. Willeke, *Solar Energy Materials and Solar Cells*, **74**(1-4), 2002, pp. 1-11.
- [3] D. Wöhrle, D. Meissner, *Advanced Materials*, **3**(3), 1991, pp. 129-138.
- [4] C. A. N. Fernando, S. K. Wetthasinghe, *Solar Energy Materials and Solar Cells*, **63**(3), 2000, pp. 299-308.
- [5] K. Han, M. Tao, *Solar Energy Materials and Solar Cells*, **93**(1), 2009, pp. 153-157.
- [6] O. Akhavan, H. Tohidi, A. Z. Moshfegh, *Thin Solid Films*, **517**(24), 2009, pp. 6700-6706.
- [7] A. O. Musa, T. Akomolafe, M. J. Carter, *Solar Energy Materials and Solar Cells*, **51**(3-4), 1998, pp. 305-316.
- [8] S. Jeong, E. S. Aydil, *Journal of Crystal Growth*, **311**(17), 2009, pp. 4188-4192.
- [9] K. Akimoto, *Solar Energy*, **80**(6), 2006, pp. 715-722.
- [10] J. Xue, *Surface and Coatings Technology*, **216**, 2013, pp. 166-171.
- [11] S. Bugarinovic, M. Rajcic-Vujasinovic, Z. Stevic, V. Grekulovic, *Cuprous Oxide as an Active Material for Solar Cells*, in: L. A. Kosyachenko (Ed.), *Solar Cells: New Aspects and Solutions*, Intech, Croatia, 2011, pp. 167-186.
- [12] L. C. Chen, *Materials Science in Semiconductor Processing*, **16**(5), 2013, pp. 1172-1185.
- [13] S. Laidoudi, *Semiconductor Science and Technology*, **2**(11), 2013, pp. 115005.
- [14] P. Samarasekara, *Georgian Electronic Scientific Journals: Physics*, **2** (4), 2010, pp. 3-8.
- [15] A. N. Banerjee, S. Kundoo, P. Saha, K. K. Chattopadhyay, *Journal of Sol-Gel Science and Technology*, **28** (0), 2003, pp. 105-110.