

Effect of annealing temperature on construction of CuO layer on electrodeposited-Cu₂O layer by annealing

S M Zainal¹, M.Zamzuri^{1,2}, M.Hasnulhadi¹, Z.Nooraizedfiza¹, M.Marina¹, Fariza Mohamad³, N. Hisyamudin³ and M.Izaki⁴

¹ School of Manufacturing, Universiti Malaysia Perlis, Pauh Putra Main Campus, 02600, Arau, Perlis, Malaysia.

² Institute of Nanoelectronic Engineering, Universiti Malaysia Perlis, Block A, Taman Pertiwi Indah, Seriab, 01000, Kangar, Perlis, Malaysia

³ Faculty of Electrical & Electronic Eng. Universiti Tun Hussein Onn Malaysia, 86400, Parit Raja, Batu Pahat, Johor, Malaysia

⁴ Department of Mechanical Eng., Toyohashi University of Technology, 1-1 Hibari Gaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan

E-mail: fuzah2525@gmail.com

Abstract. We report the annealing effects on the morphological and structural properties of Cu₂O films electrodeposited on Cu substrates from an aqueous solution containing copper acetate and lactic acid. The Cu₂O/CuO layers has been constructed by electrodeposition of p-Cu₂O layer on the modified surface of Cu substrate followed by formation of the CuO layer by annealing from 100°C to 300°C. The morphology and structural analysis was performed using optical microscope, AFM and XRD respectively. The result showed that increasing the annealing temperature resulted in the increment of the Cu₂O grain size from about 96 to 201 nm. AFM reveals the precipitation of CuO grains on the Cu₂O layer by annealing in air at 300°C, and completely covered the surface of Cu₂O layer.

1. Introduction

Cuprous oxide (Cu₂O) is naturally p-type semiconductor with a direct band gap of 2.1eV [1], that acts as a light absorber layer in the solar cell. Over the year, Cu₂O has gained a broad attention due to its excellent optical and electronic properties [2,3]. The advantage of Cu₂O in optoelectronic applications includes its direct-transition band structure that suitable for solar radiation absorption with the theoretical photovoltaic conversion efficiency approximately 20% [4]. Cu₂O thin film can be prepared by various deposition techniques such as atomic layer deposition (ALD) [5], thermal oxidation of Cu sheets [6], molecular beam epitaxy [7], sputtering [8] and electrodeposition technique [9,10]. Electrodeposition is a common method used for deposition of Cu₂O thin film on a substrate. It is a low cost and simple electrochemical technique that give the opportunity for the broad area for thin film manufacturing [11].

On the other hand, cupric oxide (CuO), also a p-type semiconductor is used as another metal oxide candidate for solar applications. CuO has a direct band energy of 1.4 eV to 1.7 eV [12], with a large absorption coefficient that makes them active in the wide range of visible light. CuO has different crystal structures, colors, and physical properties with the Cu₂O [13]. Both the Cu₂O and CuO are used as a good candidate for photovoltaic applications because of their low cost, nontoxic, abundantly available on earth, excellent electrical and high optical properties [14]. The high-quality of CuO as



well as Cu_2O can be prepared by thermal oxidation because of its simplicity and low-cost [15]. The thermal oxidation process is usually performed by annealing the Cu sheet at the temperature range from 300°C to 1000°C in air or oxygen gas (O_2). The two major products are CuO and Cu_2O , whose formation depends on conditions under which the oxidation takes place. Fan et al. successfully prepared the CuO/ Cu_2O on fluorine-doped tin oxide (FTO) substrate by simply annealing the electrodeposited Cu_2O layer [13]. They reported that the photocurrent density and photoelectrochemical (PEC) stability of the p-type heterostructure CuO/ Cu_2O was improved greatly compared with the pure Cu_2O , which was greatly affected by annealing time and temperature.

In solar cell system, particularly the photovoltaic device, carrier mobility refers to both electron and hole mobility where this mobility depends on several factors such as the temperature, electron and hole concentrations. The low mobility relating to the diffusion length of minority carrier can affect the performance of the solar cell by reducing the conversion efficiency [16]. Also, the smaller grain size and inferior crystalline structure of the photovoltaic cell can affect the movement of an electron which directly reduced the efficiency of the device.

Here, we demonstrate the preparation of the CuO layer on electrodeposited Cu_2O layer. We applied the electrodeposition method for fabrication of Cu_2O layer followed by annealing method for construction of CuO layer, and report the effects of the annealing temperature towards the properties of the Cu_2O /CuO layer on modified Cu surface. The structural and morphology characterizations for Cu_2O /CuO layer were carried out by X-ray diffraction (XRD), optical microscope and atomic force microscopy (AFM).

2. Experimental Section

The Cu sheet (Emsys Sdn. Bhd. Malaysia) with a dimension of 2 cm (length) x 1 cm (width) was used as a substrate, and prior to the electrodeposition, the Cu sheet surface was polished with 2000-grit silicon carbide sandpaper using (MoPao TM 260E) Grinder Polisher machine to modify the surface before immersed with acetone for 3 minutes and then rinsed with distilled water. Next, the Cu_2O layer was deposited potentiostatically at 0.5V referenced to Ag/AgCl electrode on the Cu substrate at a constant electric charge of 1.7 C/cm^2 with a potentiostat (HOKUTO DENKO HABF-501A) in an alkaline aqueous solution containing a 0.4M copper(II) acetate monohydrate, $\text{Cu}(\text{CH}_3\text{COO})_2$ and 3M of lactic acid, $\text{C}_3\text{H}_6\text{O}_3$ (Kanto Chemical, Co., Inc.) at 328K. The solution was prepared with 500ml of deionized (DI) water with a resistivity of $18 \text{ M}\Omega\cdot\text{cm}$ and potassium hydroxide, KOH was added for the pH adjustment to 12.5. A platinum, Pt plate was used as the counter electrode. Annealing of the electrodeposited Cu_2O layer was performed at 100°C , 200°C and 300°C for 2 hours in air condition using a heating furnace (NABERTHERM N 11/H Furnace). During annealing, the Cu_2O samples were placed on an alumina plate.

The surface roughness of the Cu sheet was determined with MITUTOYO FORMTRACER CS-3100 Surface Roughness Tester with a scan speed of 0.02mm/s and sample length of 4mm. The appearance of the Cu substrate before and after surface modification was observed by optical microscopy (MOTICAM 1000 1.3M Pixel Optical Microscope) with a 20x magnification. Structural characterization was carried out by X-ray Diffractometer (XRD BRUKER D2 PHASER), operated at 30kV and 10mA using Cu $K\alpha$ radiation (wavelength of $K\alpha_1=1.5406\text{\AA}$) that linked with DIFFRAC.SUITE EVA Software. The crystallite size (D) can be calculated using Debye-Scherrer equation ($D = 0.9\lambda/(\beta \cos \theta)$), where λ is the wavelength of X-radiation, β is the full width at half maximum (FWHM) of the highest intense peak and θ is the diffraction angle in radian.

3. Results and discussion

3.1 Characteristic of Cu_2O /CuO layer prepared on the Cu substrate

Fig.1(a) shows the schematic illustration of the cell configuration of Cu_2O /CuO on Cu substrate. The Cu_2O layer was deposited on Cu substrate followed by construction of CuO layer by annealing in air. The surface of the as-received Cu substrate before and after surface modification are shown in **Fig.1(b,c)**. The surface roughness of the Cu substrate was modified from $0.369 \mu\text{m}$ to $0.077 \mu\text{m}$ after polishing. **Fig.2** shows the transition of the physical appearance of the Cu_2O layer on Cu substrate before and after annealing at different temperature. The red brown color of Cu substrate changed to

maroon color after deposition of Cu_2O layer. Furthermore, the color of Cu_2O layer became darker as the temperature increases. At 300°C , the Cu_2O layer changed to black color film indicating the formation of CuO layer [3]. The surface morphology of the $\text{Cu}_2\text{O}/\text{CuO}$ layers was further examined by AFM.

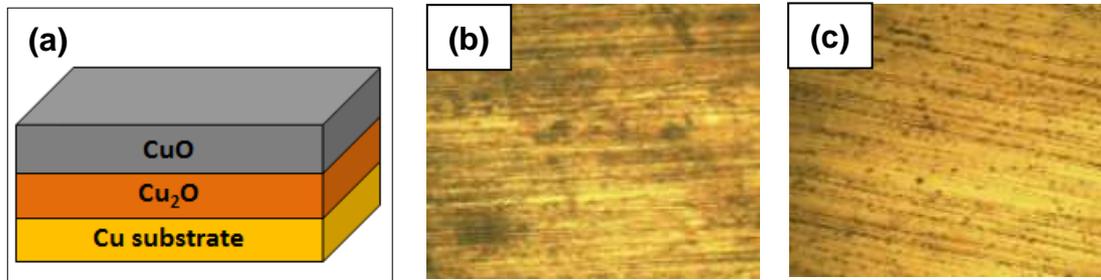


Figure 1: (a) Schematic illustration of cell configuration of $\text{Cu}_2\text{O}/\text{CuO}$ on Cu substrate and (b) optical micrograph of the Cu sheet before and (c) after polishing.

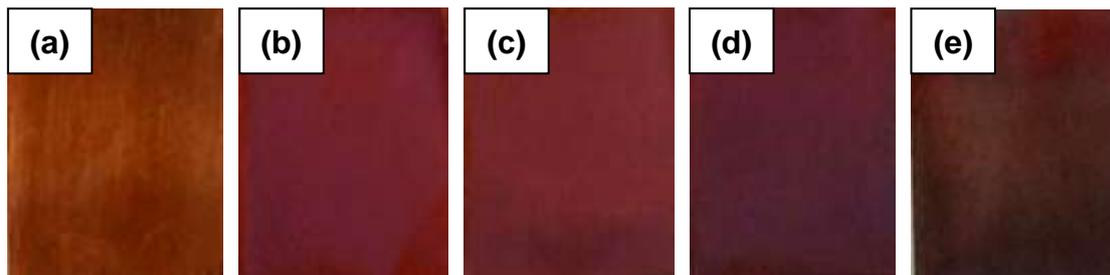


Figure 2 : The physical appearance of (a) as-received Cu substrate, (b) as-deposited Cu_2O layer on Cu substrate, and Cu_2O layer on Cu annealed at (c) 100°C , (d) 200°C and (e) 300°C respectively.

Fig.3 (a,b) displays the three-dimensional and plan view topography of electrodeposited Cu_2O on Cu substrate, respectively. The Cu_2O layers deposited on the Cu substrate were composed of pyramid-like Cu_2O particles grown in a direction perpendicular to the Cu substrate surface [17]. The triangular facet of the Cu_2O crystal was obviously observed in the plan view (**Fig.3b**). Meanwhile, the annealed Cu_2O layers at different temperature are shown in **Fig.4 (a-f)**. From **Fig. 4**, it shows that Cu_2O grains had changed significantly with the annealing temperature. The correlations between Cu_2O grain size and surface roughness of the as-deposited Cu_2O layer before and after annealing are presented in **Fig. 5**. As the annealing temperature increase up to 200°C , the Cu_2O grain size has increased gradually from 96.151 nm to 201.206 nm and the surface roughness also increased from $0.023\text{ }\mu\text{m}$ to $0.034\text{ }\mu\text{m}$. However, the Cu_2O grains size as well as surface roughness decreased to 173.440 nm and $0.017\text{ }\mu\text{m}$ respectively as the annealing temperature reached 300°C . Therefore, the thickness of CuO layer was estimated to be around 20 nm . At 300°C , the surface of the pyramid-like structure was covered completely to a compact irregular structure indicating the formation of CuO grains as shown in **Fig.4(c,f)** [18].

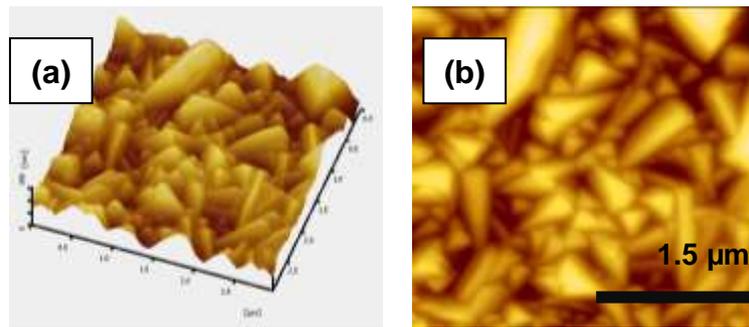


Figure 3: The surface topography of the deposited Cu_2O on Cu substrate without annealing (a) 3D View (b) plan view

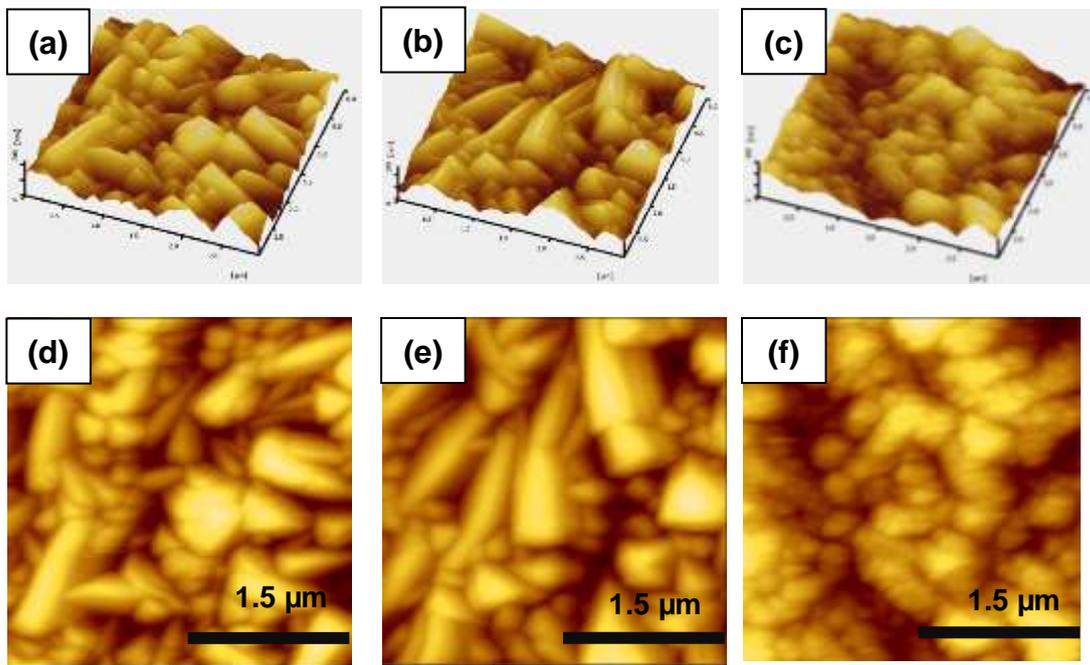


Figure 4 : The 3D view and plan view of AFM images of the deposited Cu_2O on Cu substrate annealed at (a,d) 100°C, (b,e) 200°C and (c,f) 300°C.

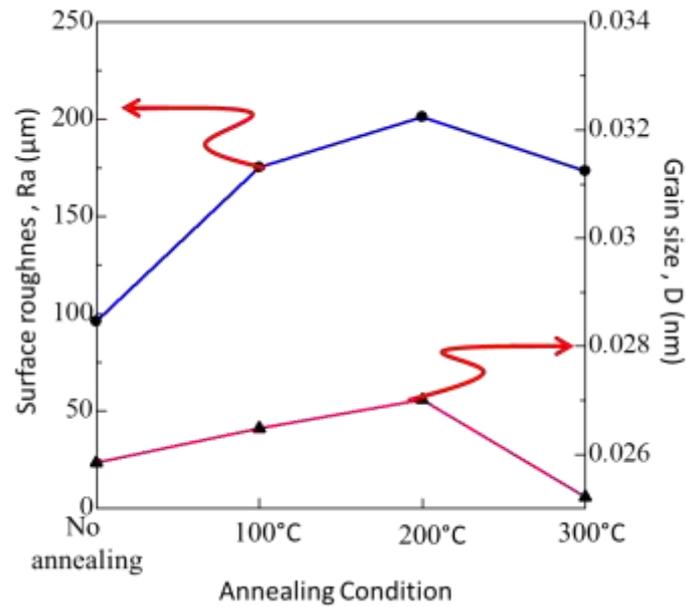


Figure 5 : The surface roughness and grain size of the deposited Cu_2O on Cu substrate.

3.2. Structural analysis of the $\text{Cu}_2\text{O}/\text{CuO}$ layer prepared on the Cu substrate

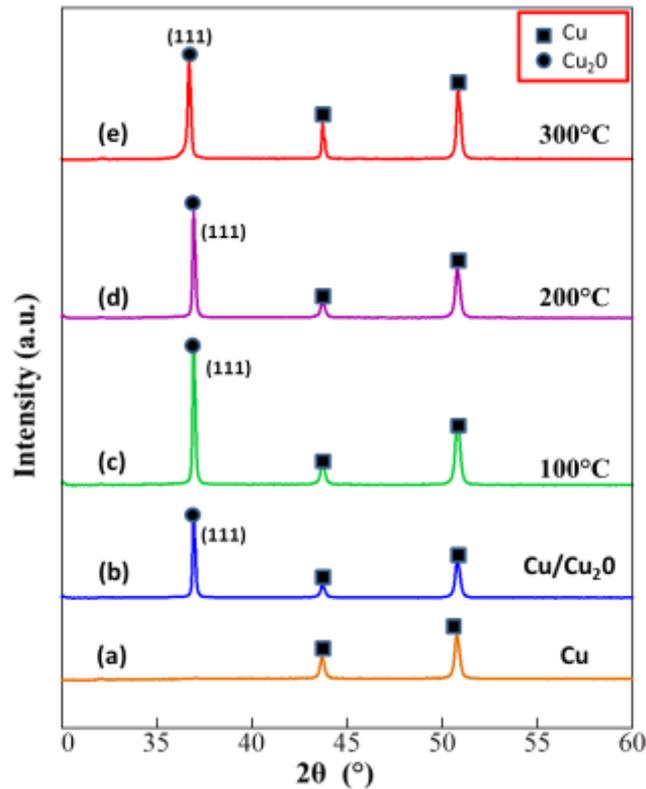


Figure 6 : XRD patterns of the (a) Cu and (b) deposited Cu_2O layer prepared on Cu substrate without annealing, Cu_2O annealed at (c) 100°C, (d) 200°C and (e) 300°C.

X-ray diffraction (XRD) analysis was carried out to examine the orientation and crystal structure of the Cu₂O/CuO layers. **Fig.6** shows the XRD patterns for as-deposited Cu₂O layer and annealed Cu₂O layer at different temperature from 100°C until 300°C. The as-deposited Cu₂O layer revealed single orientation which was indexed to (111) at diffraction peaks of 36.4°. The Cu₂O orientation was corresponding to cubic Cu₂O pattern (PDF 01-071-3645) and the intensity increase as the annealing temperature increased up to 300°C. No obvious peak of CuO layer could be seen as the Cu₂O layer was annealed in air at 200°C and 300°C irrespective with the changed in the microstructure as shown in the **Fig.4 (c,f)**.

However, the peaks of CuO layer become visible in the diffraction pattern when the annealing temperature was slightly increased to 350°C [13]. Based on the changes in the appearance (**Fig. 2e**) and microstructure of annealed Cu₂O layer observed by AFM (**Fig. 4 (c,f)**), it is speculated that the CuO layer could be constructed by annealing of Cu₂O layer in air at temperature as low as 300°C.

4. Conclusions

The Cu₂O/CuO layer has been constructed by electrodeposition of the p-Cu₂O layer on the Cu substrate followed by formation of the CuO layer by annealing at different temperature. The Cu₂O layer was prepared by electrodeposition on Cu substrate in an alkaline aqueous solution containing copper (II) acetate and lactic acid. The thickness of Cu₂O layer was maintained by controlling the electric charge during the electrodeposition process. The results obtained from AFM showed that increasing the annealing temperature resulted in the increment of grain size of Cu₂O layer and led to the formation of CuO layer on its surface. The thickness of CuO layer was found to be around 20 nm. Although further improvement is needed, these results show the importance of the crystalline structure of the Cu₂O/CuO layer to the improvement of the photovoltaic device performance.

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