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Thin cuprous oxide films prepared by thermal oxidation of copper foils with water vapor

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Abstract

We present an improved preparation method of high quality crystals of cuprous oxide films grown by thermal oxidation of copper foils with water vapor. This method proved to be good for preparing cuprous oxide films with high purity and large grain size. X-ray diffraction studies revealed the formation of Cu₂O films with (111) preferred orientation. The cuprous oxide diodes fabricated by the above technique have been studied using current-voltage method.

Keywords: A1.Surfaces; B1.Oxide; B2.Semiconducting materials

1. Introduction

Cu₂O is spontaneously a p-type semiconductor since it contains negatively charged copper vacancies and probably interstitial oxygen [1]. Various attempts have been made to fabricate solar cells utilizing cuprous oxide as an active layer. Because this semiconductor shows many interesting characteristics useful for solar cells production such as low cost, non-toxicity, good mobility, fairly high minority carrier diffusion length and direct energy gap with a direct band gap of 2.1 eV. Although the theoretical limit of the energy conversion efficiency of a cuprous oxide solar cell is about 20 % (just considering radiative recombination), the highest efficiency obtained up to now on this substrate is 2 % [2]. Cuprous oxide thin films have been prepared by various techniques such as thermal oxidation [3], chemical vapor deposition [4], anodic oxidation [5], reactive sputtering [6], pulse laser deposition [7], electro-deposition [8] and plasma oxidation [9]. But thin films

prepared by these methods are usually deposited on specific substrates, such as a quartz plate.

In this paper we report a method to obtain self-supporting Cu_2O films with high quality. Cu_2O films can be obtained by using thermal oxidation of copper foils with water vapor. Copper oxidized in air or oxygen forms two thermodynamically stable oxides CuO and Cu_2O depending on the thermodynamic stability of the oxides [10]. For water vapor used in our experiments, only Cu_2O is formed. These will allow the study of various kinds of electric junction other than the extensively studied $\text{Cu}_2\text{O}/\text{Cu}$ structure, and may hopefully lead to better rectifying junctions for use as photovoltaic cells with improved efficiency. The Cu_2O based schottky diodes have been investigated by current-voltage (J - V) measurements.

2. Experimental

Thin Cu_2O films have been synthesized by thermal oxidation of copper foils in air and water vapor. Experimental detail of oxidation in air as reported in [11]. Figure 1 shows the schematic diagram of the experimental setup for oxidation with water vapor. The ultrasonic nebulizer is connected to quartz tube and N_2 gas cylinder. Copper foils (0.1 mm thick, 4N6) were used as substrates. The copper foils were cut into standard sizes of $1\text{cm} \times 1\text{cm}$. The substrates were first cleaned in dilute hydrochloric acid to remove the native oxide layer and adsorbed impurities, and then they were cleaned with acetone, methanol, and deionized water under an ultrasonic bath for 5 min. Finally, they were dried by N_2 flow. The cleaned Cu substrate is placed onto a quartz boat. The quartz boat is positioned in the center of a quartz tube that is mounted in the middle of a horizontal tube furnace. The one end of the quartz tube was attached to a nebulizer and other to the gas bubble. A flow of N_2 gas is introduced into the quartz tube at a flow rate of 1 L/min for 20 min to remove air from the system, and then this is adjusted to 0.5 L/min. The tube furnace is heated to the set-point temperature. After being held at the set-point temperature, the N_2 gas flow is kept at a rate of 0.5 L/min. The system is allowed to cool naturally to room temperature to prevent the thin film from cracking, caused by thermal stress and further oxidized in air if the film is directly taken out of the high temperature furnace. The substrate is pulled out of the furnace for further analysis. The crystal structure and phase composition were identified by X-ray diffraction (XRD, Rigaku RINT-2100) using a 40 kV, 30 mA, $\text{Cu-K}\alpha$ X-ray. A scanning step of degree of 0.02° was applied to record the XRD patterns in the 2θ range of degree of $20 - 60^\circ$. The morphology of the Cu_2O was characterized by scanning electron microscope (SEM, Hitachi S-3000H) operated at 15 kV. Cu_2O

based schottky diodes were fabricated to characterize electrical properties of the thin films. Because Cu_2O is reported as p-type semiconductor [12], Au and Cu were used as ohmic and schottky contact materials, respectively. Au (100 nm) was deposit on the surface of Cu_2O thin films prepared at 800 °C in water vapor. The oxide layer of the other side was removed by polishing to expose the surface of the copper foil. The exposed copper was used as a schottky electrode. The current-voltage (J - V) characteristics of the Au / Cu_2O / Cu diodes were measured using a semiconductor parameter analyzer.

3. Results and discussion

3.1. Growth of Cu_2O thin films by thermal oxidation with water vapor

Figures 2(A) and (B) show the SEM images of the copper thin films after being heated in air and water vapor at 700 °C for 2 h, respectively. Figure 2 (A) shows that CuO nanowires are formed on the surface of the copper foils annealed in air [11]. On the other hands, as shown in figure 2(B), Cu_2O thin films having rugged rock like morphology are obtained by thermal oxidation in water vapor. In order to study the influence of the oxidation temperature on the growth of Cu_2O thin film in water vapor, three samples have been prepared at 700, 800 and 900 °C for 2 h, as shown in figures 3 (A) – (C). A large amount of oxide grains with size of about 3 μm were observed in the sample prepared at 700 °C. Figure 3 (B) shows that the sample prepared at 800 °C, have a large amount of oxide grains with non uniform size. In this process the large oxide grains with size ranging from 2 to 12 μm are formed. As shown in figure 3(C) the oxide grains with size of about 15 μm were observed in the sample prepared at 900 °C. From the morphology of these samples, it is observed that the size of oxide grain increases with increasing the oxidation temperature.

A SEM cross-section image of the sample heated at 700 °C reveals that the sample consists of two layers as shown in Figure 3(D). The top layer is a Cu_2O thin layer with thickness of about 5 μm that lies directly above the copper substrate. However, when copper thin film is oxidized in air, at first, the major product is Cu_2O , and then CuO is formed through a second step of oxidation of Cu_2O [11].

3.2. XRD characterization of Cu_2O thin films

Figure 4 (A) shows the XRD pattern of the samples oxidized at 700, 800 and 900 °C for 2 h in air. As

reported in Ref [11], both Cu_2O and CuO phases are present when copper substrates are oxidized in air. In this study, both Cu_2O and CuO are also observed as shown in figure 4 (A). XRD peak at $2\theta = 35.5^\circ$ and $2\theta = 38.7^\circ$ can be readily indexed as $(\bar{1}11)$ and (111) crystal plane of monoclinic CuO . These two peaks become strong with increasing the heating temperature. But (111) plane of Cu_2O becomes weak while CuO is formed through a second step of oxidation of Cu_2O . Other weak peaks corresponding to Cu_2O and CuO phases have also been observed. When the temperature rose to 900°C , CuO became the main oxidation product with a small Cu_2O peak. This indicates a conversion from Cu_2O to CuO , and this is also confirmed by the fact that the colors of the samples changed from brick red (Cu_2O) to black (CuO). However, as shown in figure 4 (B), only Cu_2O is observed after the samples after oxidation at 700 , 800 and 900°C for 2 h with water vapor. The XRD results show that Cu_2O is the only oxidation products with a small amount of Cu after the oxidation at 700 and 800°C . XRD peak at $2\theta = 36.3^\circ$ and $2\theta = 29.7^\circ$ corresponding to (111) and (110) plane of cubic Cu_2O structure, in addition (111) plane is the most prominent peak in the sample. The weak two peaks at $2\theta = 43.8^\circ$ and $2\theta = 50.9^\circ$ can be readily indexed as (111) and (200) crystal plane of cubic Cu . When the temperature rose to 900°C , almost copper phases were all oxidized. This indicates a conversion of copper to cuprous oxide which is evidenced by a color change from reddish brown color (Cu) to brick red (Cu_2O). Cu_2O can be obtained by oxidation in water vapor at higher temperature.

When air is used, the O_2 concentration decreases locally with the reaction near the thin film surface because the oxidation rate is larger than the diffusion rate. Employing a N_2 gas flow with water vapor one is able to keep a relatively low O_2 concentration near the film that helps to convert the entire copper thin film into Cu_2O . The Cu-O phase diagram [13] shows that two types of oxide, Cu_2O and CuO may form during oxidation. Thermodynamically oxides form only if the ambient oxygen partial pressure (P_{O_2}) is larger than the dissociation pressure ($P_{\text{O}_2\text{-dis}}$) of the oxide in equilibrium with Cu . The environmental oxygen partial pressure is higher than the dissociation pressure ($P_{\text{O}_2\text{-dis}}$) of Cu_2O and CuO . Therefore, both CuO and Cu_2O can form in air [11]. If traces of oxygen are present in the water vapor, with oxygen partial pressure above the dissociation pressure of Cu_2O , but below that of CuO , formation of the former, but not the latter will occur. This is consistent with our results that only Cu_2O and not CuO are formed on samples oxidized in water vapor.

3.3. *J-V* characteristic of Cu₂O based diodes

Figure 5 shows the *J-V* characteristic of an Au/Cu₂O/Cu Schottky diode. The dark *J-V* data shows a typical rectification behavior. For the case of the diode with a high series resistance and ideality factor, the relation between the applied forward bias *V* and the current *I* can be written as [15],

$$I = I_s \left[\exp \left(\frac{q(V - IR_s)}{nkT} \right) \right] \quad (1)$$

When $V_D > 3kT/q$ [16]. Where *q* is the electronic charge, *V* the voltage applied across the diode, *k* the Boltzmann constant, and *T* the absolute temperature, *I_s* the reverse saturation current. The diode parameter obtained with an electrode area of 0.01cm² were *R_s* = 20 Ω and a saturated reverse current density *J_s* = 0.33 mA/cm² with a diode factor *n* = 3.8. The measured value of *n* is larger than two and therefore tunneling, recombination and generation currents in the depletion region and recombination through interface states at the Cu₂O/Cu junction are expected to play important roles [14].

4. Conclusion

In the present work, we developed a new process to prepare Cu₂O films and studied the properties of the films. Cu₂O thin films are formed in water vapor in which the oxygen pressure is less than the dissociation pressure of CuO. It is observed that the diameter of oxide grain increases with increasing the oxidation temperature. X-ray diffraction studies indicate that the film is Cu₂O and Cu₂O is the only oxidation products. The cupric oxide (CuO) phase is absent. The current-voltage characteristics of the Au/Cu₂O/Cu diodes exhibit rectification. The method is recommended as a fairly easy way for fabrication Cu₂O films. It can serve as a starting material for studying Schottky or metal insulating semiconductor diodes with better characteristics based on contacts of Cu₂O with various metals or compound semiconductors.

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Figure caption

Figure 1 Schematic representation of the experimental setup.

Figure 2 SEM images of the sample surface oxidized at 700 for 2 h: (A) in air and (B) in water vapor.

Figure 3 SEM images of the sample surface oxidized at (A) 700, (B) 800 and (C) 900 °C for 2 h in water vapor. (D) SEM image of cross-section of the sample oxidized at 800 °C for 2 h in water vapor

Figure 4 XRD patterns of the sample oxidized in air (A) and water vapor (B) at 700, 800 and 900 °C for 2 h..

Figure 5 Current-voltage characteristics of an Au/Cu₂O/Cu diode.

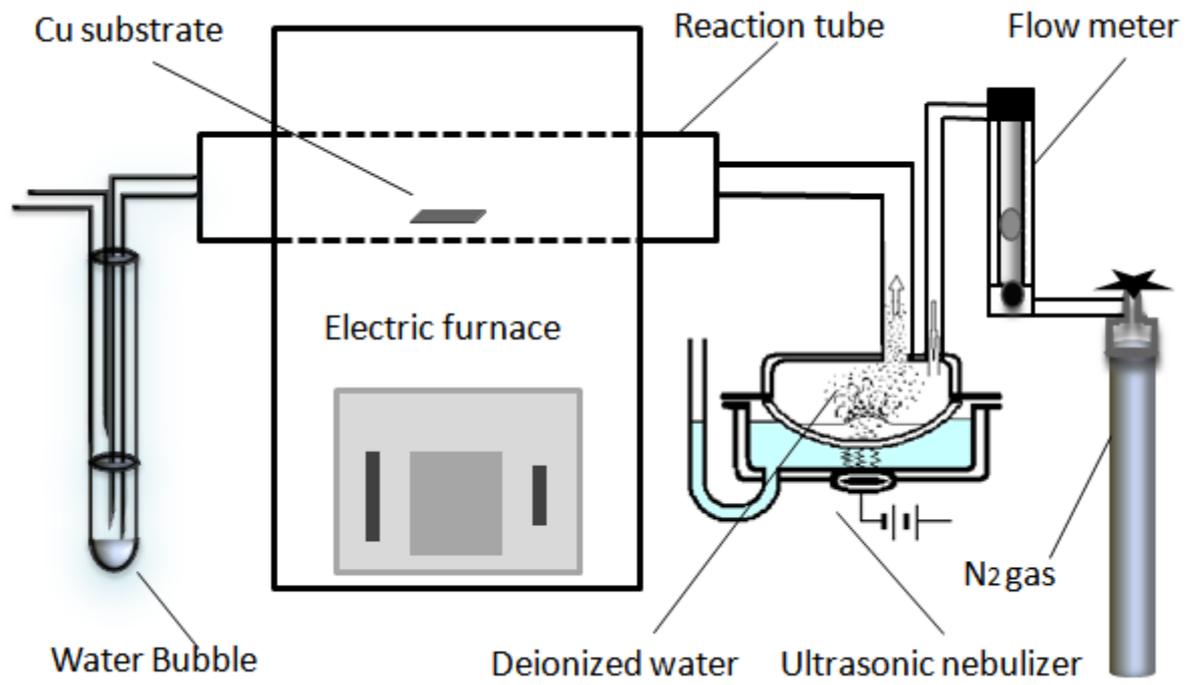


Figure 1 J.B. Liang et.al.

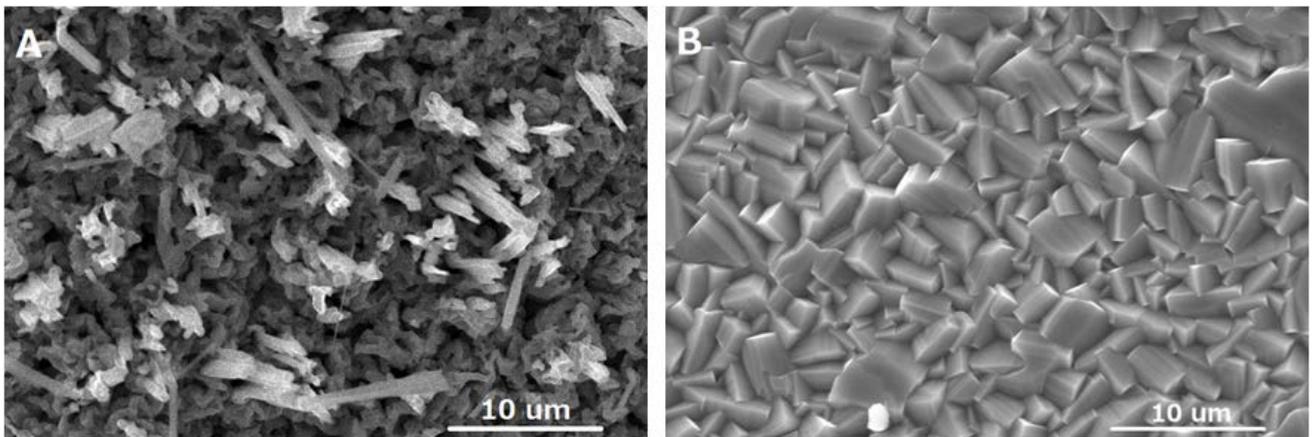


Figure 2 J.B. Liang et.al.

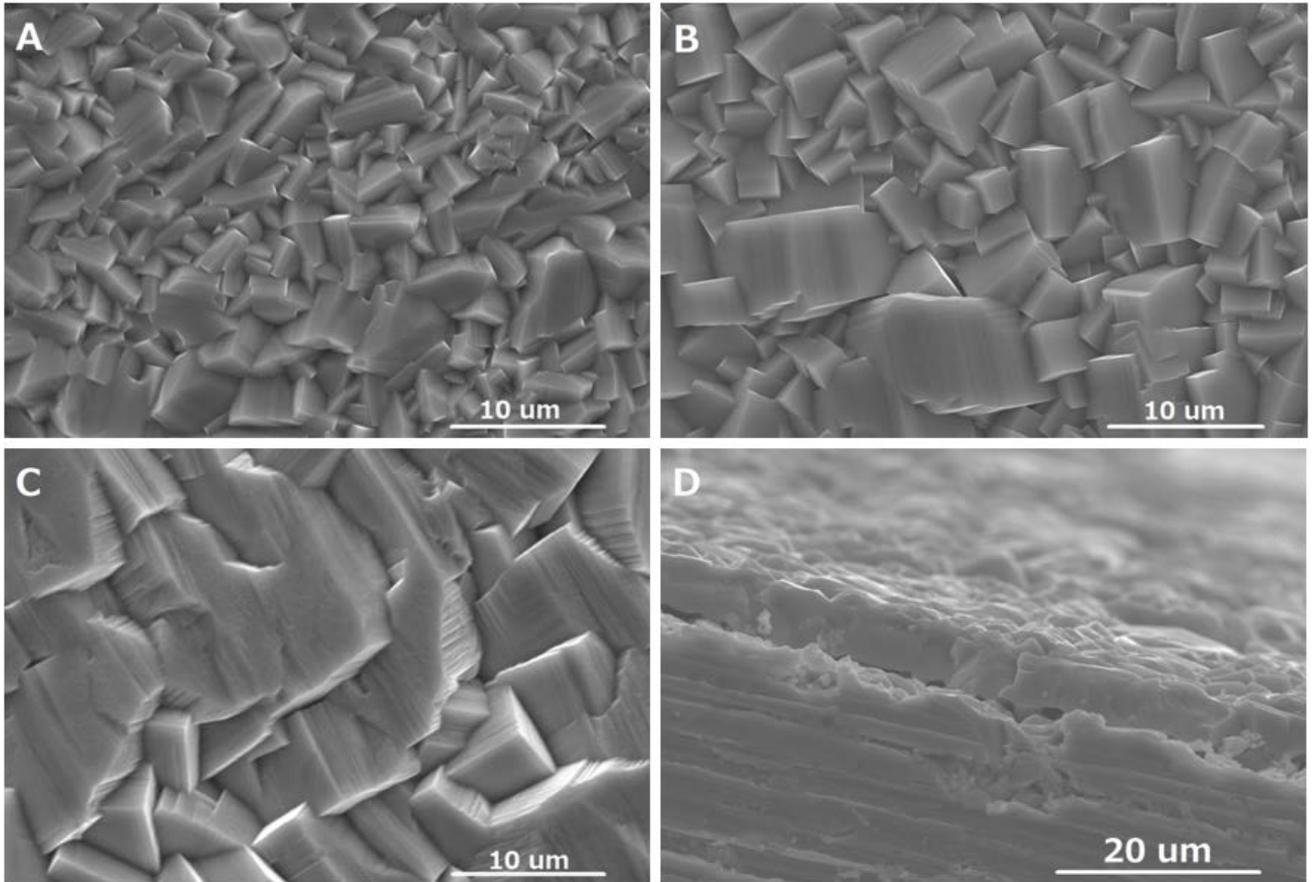


Figure 3 J.B. Liang et.al.

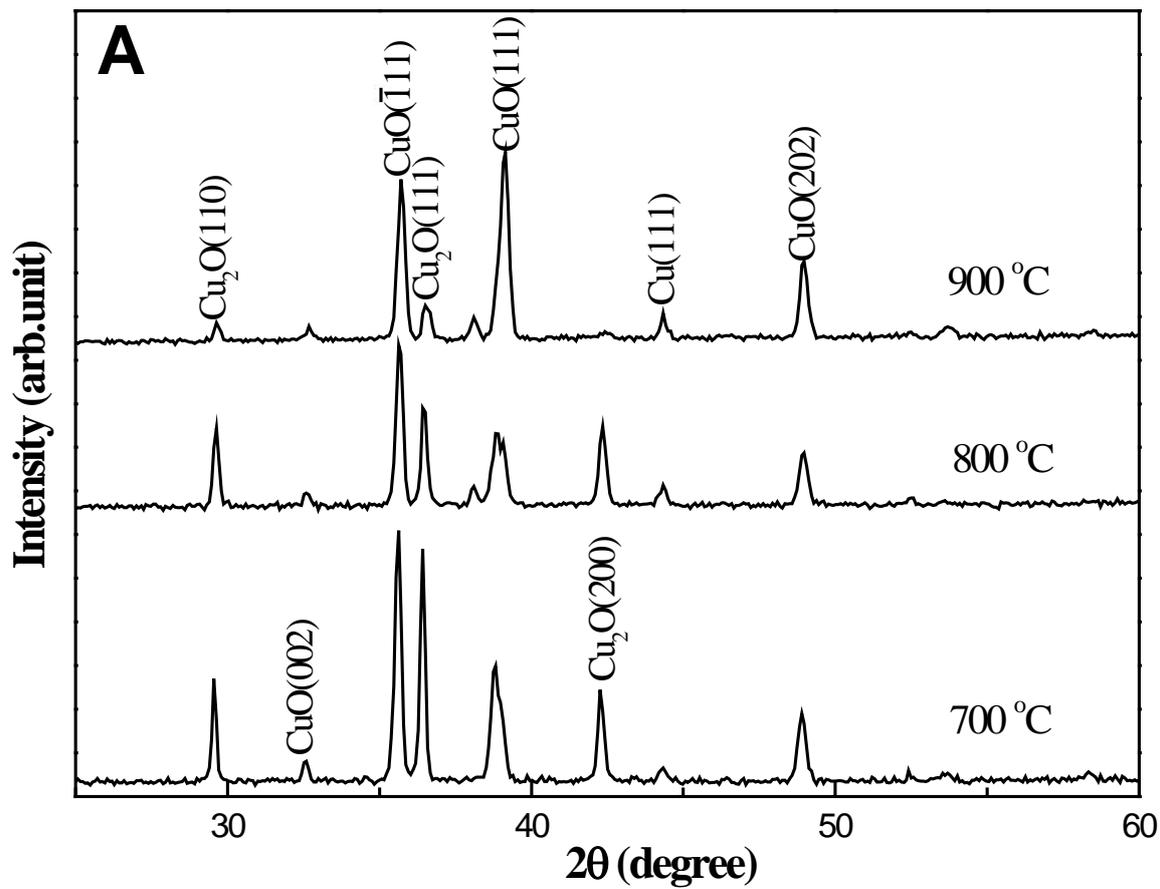


Figure 4 (A) J.B. Liang et.al

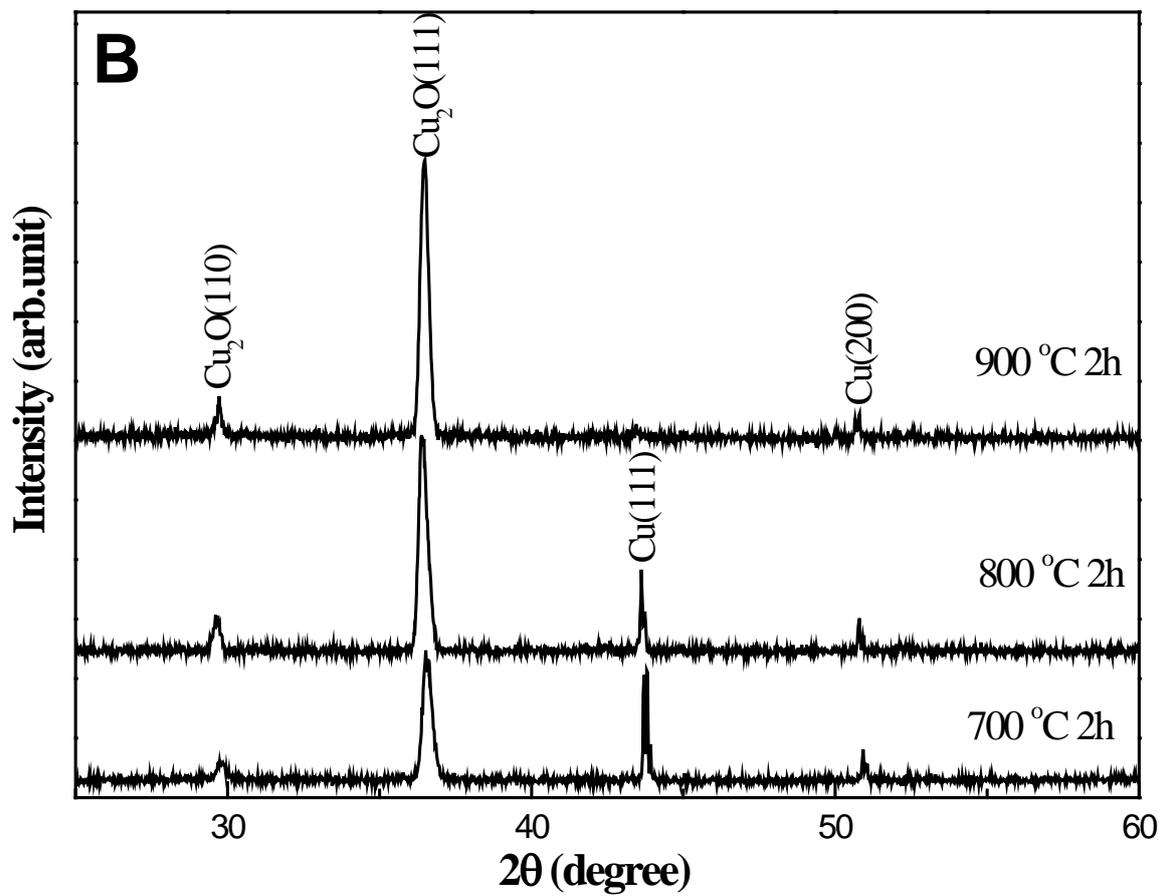


Figure 4 (B) J.B. Liang et.al.

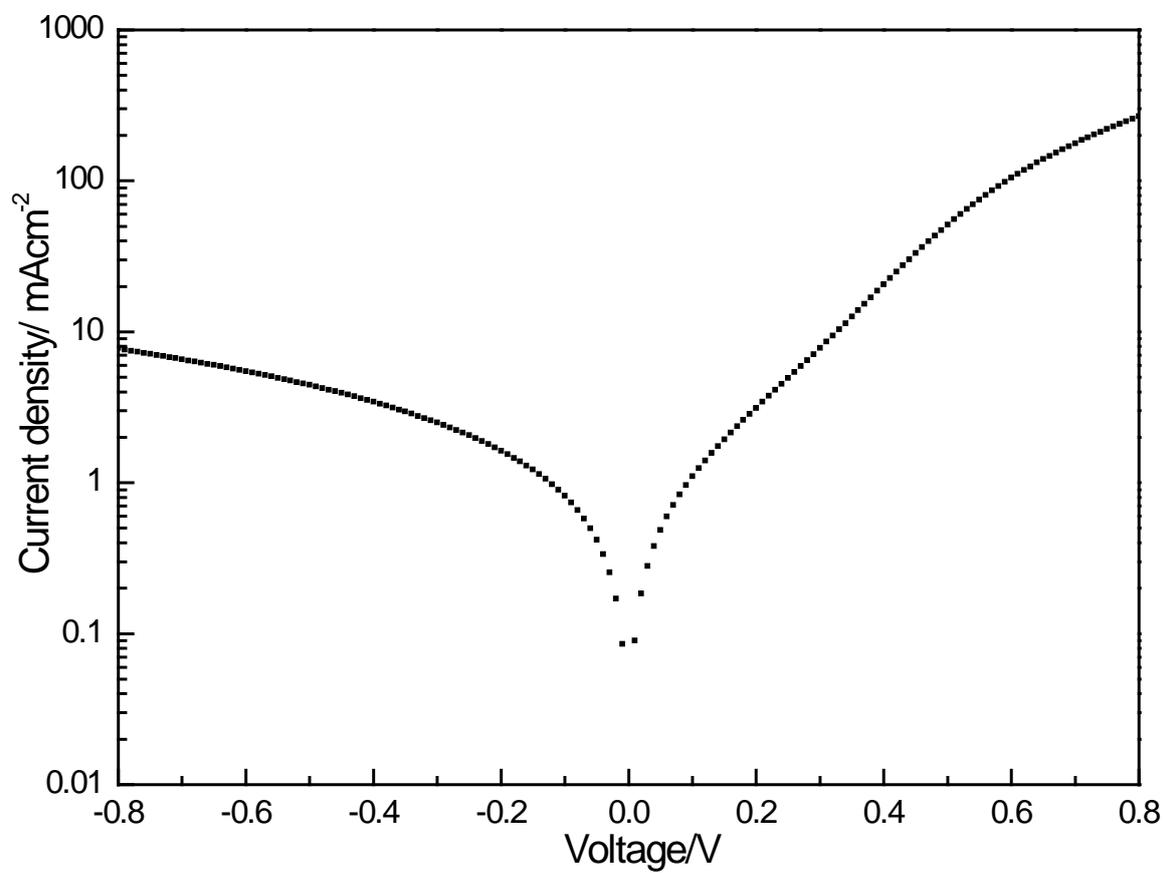


Figure 5 J.B. Liang et.al.