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## Resistive switching of Cu/Cu<sub>2</sub>O junction fabricated using simple thermal oxidation at 423 K for memristor application

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Abstract. Recently, extensive researches have been done on memristor to replace current memory storage technologies. Study on active layer of memristor mostly involving n-type semiconductor oxide such as TiO<sub>2</sub> and ZnO. This paper highlight a simple water vapour oxidation method at 423 K to form Cu/Cu<sub>2</sub>O electronic junction as a new type of memristor. Cu<sub>2</sub>O is a p-type semiconductor oxide, was used as the active layer of memristor. Cu/Cu<sub>2</sub>O/Au memristor was fabricated by thermal oxidation of copper foil, followed by sputtering of gold. Structural, morphological and memristive properties were characterized using XRD, FESEM, and current-voltage, I-V measurement respectively. Its memristivity was indentified by pinch hysteresis loop and measurement of high resistance state (HRS) and low resistance state (LRS) of the sample. The Cu/Cu<sub>2</sub>O/Au memristor demonstrates comparable performances to previous studies using other methods.

#### 1. Introduction

The fourth fundamental circuit element, memristor (memory resistor) proposed by Leon Chua in 1971 is a suitable candidate to replace current memory technologies [1]. Feature size of memory device such as DRAM and FLASH has been successfully decreased while increasing its memory density. However, it will no longer be able to decrease sooner or later. Specifically, when the memories shrink down to 21nm, it will reach miniaturization limit and cannot be shrink down any further [2]. In 2008, Hewlett-Packard (HP) research laboratory has produced the first physical memristor. It has a metalinsulator-metal (MIM) structure using platinum for both of its electrode and n-type semiconductor oxide of titanium dioxide, TiO<sub>2</sub>, as the active layer [3]. Since then researchers have use different material for the active layer and mostly consist of other n-type semiconductor oxide such as TaO and ZnO [4]. While only a few does on p-type semiconductor oxide such as SnO and CuO [5].

Cuprous oxide ( $Cu_2O$ ) is a p-type semiconductor oxide with a band gap energy of 2.1 eV and it has a wide range of application such as photovoltaics, gas sensing, catalysis, dilute magnetic semiconductors and as active layer of memristor [6]. Cu<sub>2</sub>O is cheap and fairly easy to be fabricated compared to TiO<sub>2</sub>. N-type semiconductor oxide, for example ZnO, contain oxygen vacancies due to lack of oxygen while p-type semiconductor oxide such as Cu<sub>2</sub>O contain copper vacancies due to

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excess in oxygen [7]. It is expected that copper vacancies will contributes to the formation of resistive switching in Cu<sub>2</sub>O.

In this research,  $Cu_2O$  was prepared using simple thermal oxidation in a water vapour environment at 432 K [6, 8, 9]. This method is favourable as it can be done at low temperature and cheaper than other methods. The memristive performance of the electronic junction was compared and evaluated.

#### 2. Experimental procedures

Thin layer of  $Cu_2O$  was produced by oxidising a copper foil in a water vapour environment at temperature of 423 K. The temperature was chosen to avoid the oxide layer from being porous. Copper foil were cut into 1cm x 1cm and polished. The sample was then sonicated using ultrasonic cleaner (Branson 3510) to remove any residue.

Figure 1 shows the furnace set up specially to oxidise copper foil in a water vapour environment. The argon gas flowrate were fix to 100 sccm. Once the heater and electric furnace has achieved their intended temperature, sample were insert and place in the middle of the furnace followed by vaccumisation of the furnace using vaccum pump to remove air trapped inside the furnace. The sample was oxidised at 423 K for 25 seconds and 1 hour.

The fabricated  $Cu/Cu_2O$  junction was analysed using XRD (PANalytical X'Pert PRO) to confirm the existance of oxide layer. The surface morphology of the junction was characterized using FESEM (JOEL JFC-6700F).

Gold was sputtered on top of Cu<sub>2</sub>O using auto fine coater (JEOL JFC-1600) to produce a Cu/Cu<sub>2</sub>O/Au memristor. I-V characteristics of the memristor was then measured using a 2-point probe connected to AUTOLAB Potentiostat (PGSTAT302N) at room temperature. The voltage sweep was  $0V \rightarrow 2V \rightarrow 2V \rightarrow 0V$  repeated 10 cycles for each measurement.

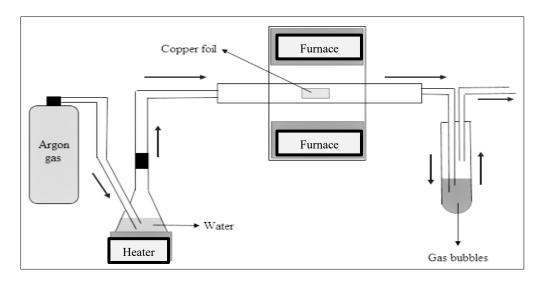


Figure 1 : Tube furnace setup

#### 3. Results and Discussion

Figure 2 shows a diffraction peaks of copper foil after thermal oxidation in water vapour environment for 25 seconds. XRD result shows a (221) Cu<sub>2</sub>O diffraction peaks at 66 degree angle and (321) Cu<sub>2</sub>O diffraction peaks at 86 degree angle. Due to thin oxide layer, substrate Cu was also detected at respective peak angle with facet orientation of (111), (200) and (220). CuO diffraction peak was not detected. This is due to oxygen partial pressure during the reaction is higher than dissociation pressure of Cu<sub>2</sub>O but lower than dissociation pressure of CuO.

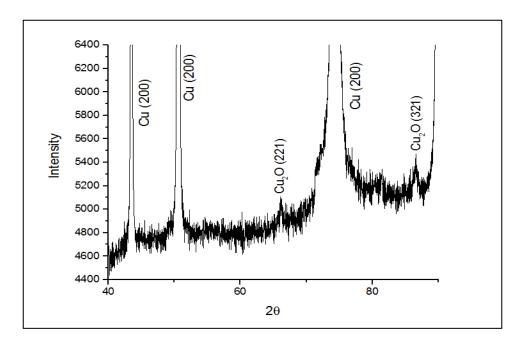


Figure 2 : Diffraction peaks of sample oxidized for 25 seconds

Figure 3 shows FESEM micrograph of the sample at various magnification. The oxide layer was uniformly formed on the surface and show almost no void / porosity. We are unable to detect any form of microstructure such as rod-like and flakes as normally observed using other deposition techniques. It is postulated that water vapor somehow facilitates to the formation of dense and even surface.

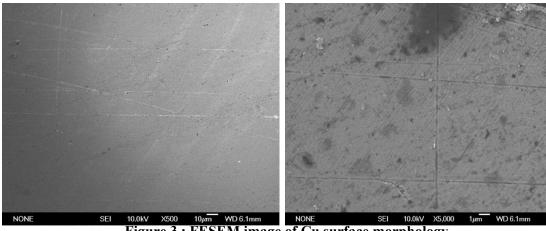


Figure 3 : FESEM image of Cu surface morphology

The *I-V* measurements of the samples show the pinched hysteresis loops as shown in Figure 4 which follows the characteristics of a memristor. Calculated HRS value for sample oxidised for 25 seconds is  $15.80\Omega$  and the LRS value is  $14.85\Omega$ , while the HRS for sample oxidised for 1 hour is  $15.56\Omega$  and the LRS is  $14.74\Omega$ . The ratio of HRS and LRS for both sample was determined to be 1.064 for sample oxidised for 25 seconds and 1.056 for sample oxidised for 1 hour. The higher the ratio of HRS and LRS the better as higher ratio means that the distinction between HRS and LRS value is bigger. A memristor required to have big hysteresis loop and a clear distinction between HRS and LRS and LRS value so that it can be read by voltage signals.

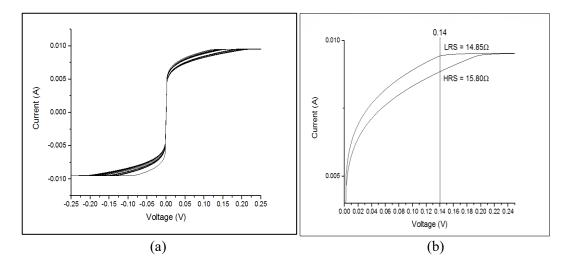


Figure 4 : (a) hysteresis loop of sample oxidized in 25 seconds, (b) its' HRS and LRS value

The polarity dependence of the resistance to voltage is called bipolar resistive switching. Resistive switching behavior is where the current changes from high resistance state, HRS to low resistance state, LRS at a set voltage from '0 V to 2 V' path to '2 V to 0 V' path. The difference of HRS and LRS creates the hysteresis loop in *I-V* curve. HRS/LRS ratio of Cu/Cu<sub>2</sub>O/Au junction shows results that is within the range of our previous findings as reported in [4], [10] and [11]. The difference between HRS and LRS in memristor occurred because of the diffusion of defect vacancy in oxide layers when polarized. The formation of metal vacancy defects in transition metal oxide produces pinched hysteresis loop in memristor. We conclude that Cu/Cu<sub>2</sub>O/Au junction is a promising memristor, and its memristive ability relies on the existence of metal vacancy defects in Cu<sub>2</sub>O active layer.

#### 4. Conclusion

Cu/Cu<sub>2</sub>O/Au memristor has successfully been fabricated by thermal oxidation of copper foil in water vapour environment, and gold sputtering technique. The I-V measurement of a Cu/Cu<sub>2</sub>O/Au memristor show a hysteresis loop, proving its resistive switching behaviour. The thinner the oxide layer produced the better the performance of memristor and the sample produce by oxidation of copper foil for 25 seconds have the higher HRS/LRS ratio of 1.064.

#### Acknowledgement

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