Dilute electrodeposition of TiO$_2$ and ZnO thin film memristors on Cu substrate

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Abstract. Memristor has become one of the alternatives to replace the current memory technologies. Fabrication of titanium dioxide, TiO$_2$ memristor has been extensively studied by using various deposition methods. However, recently more researches have been done to explore the compatibility of other transition metal oxide, TMO such as zinc oxide, ZnO to be used as the active layer of the memristor. This paper highlights the simple and easy-control electrodeposition to deposit titanium, Ti and zinc, Zn thin film at room temperature and subsequent thermal oxidation at 600°C. Gold, Au was then sputtered as top electrode to create metal-insulator-metal, MIM sandwich of Au/TiO$_2$-Cu$_2$O-CuO/Cu and Au/ZnO-Cu$_2$O-CuO/Cu memristors. The structural, morphological and memristive properties were characterized using Field Emission Scanning Electron Microscopy, FESEM, X-Ray Diffraction, XRD and current-voltage, $I$-$V$ measurement. Both Au/TiO$_2$-Cu$_2$O-CuO/Cu and Au/ZnO-Cu$_2$O-CuO/Cu memristivity were identified by the pinched hysteresis loop with resistive ratio of 1.2 and 1.08 respectively. Empirical study on diffusivity of Ti$^{4+}$, Zn$^{2+}$ and O$^{2-}$ ions in both metal oxides show that the metal vacancies were formed, thus giving rise to its memristivity. The electrodeposited Au/TiO$_2$-Cu$_2$O-CuO/Cu and Au/ZnO-Cu$_2$O-CuO/Cu memristors demonstrate comparable performances to previous studies using other methods.

1. Introduction
Memristor is a promising alternative for the next generation non-volatile memory system. The limitations on size and manufacturing cost of the current memory storage especially for dynamic random access memory, DRAM has closely reached their maximum limit and has driven a tremendous amount of research on memristor. Memristor was first discovered as the fourth fundamental element by Chua [1] in 1971 and it was experimentally demonstrated in 2008 by William et al. [2]. Memristor is a non-volatile memory which is also known as a resistive random access memory, RRAM made from a simple structure of MIM sandwich. The advantages of memristor are its fast switching speed, low power consumption and high density [1]. The uniqueness of the memristor is that it will remember the most recent resistance even when the voltage is off [3]. Previous researches discovered that transition metal oxides, TMO such as TiO$_2$ [3]-[6], ZnO [7]-[9], nickel (II) oxide, NiO [10], perovskite oxides [11] and
cuprous oxide, Cu₂O [12] have the ability to create memristive effects when used as the intermediate active layer of memristor.

The most popular material used in memristor is TiO₂ due to its simple structure and compatibility with the Complementary Metal-Oxide-Semiconductor, CMOS manufacturing process [4]. Ti is an expensive material and very complicated to handle due to its reactivity to oxygen. In recent years, many methods have been used to fabricate memristive devices. So far the most common methods used have been radio frequency, RF sputtering [13–19], thermal oxidation [4], [7], chemical vapor deposition, CVD [20], [21], pulsed laser deposition, PLD [22], sol gel [6], [23], atomic layer deposition, ALD [24] and electrodeposition [7], [8], [25]. Recently, ZnO has attracted a lot of attention due to its non-toxicity and prevalence in semiconductor electronic devices applications such as light emitting diodes, LED, photodetectors, sensors, and solar cells.

In this paper, thin films of TiO₂ and ZnO were fabricated on copper, Cu substrate by using electrodeposition and thermal oxidation methods that yields comparable results to the expensive, complex and time consuming existing methods. Cu substrate has been chosen due to its resistance to corrosion, high electrical conductivity and its wide use in electronic devices. The memristive performance of Au/TiO₂-Cu₂O-CuO/Cu and Au/ZnO-Cu₂O-CuO/Cu samples were compared and evaluated.

2. Experimental procedures

The electrodeposition setup consists of working electrode and counter electrode placed in a dilute solution of 0.06 M titanium trichloride, TiCl₃ and 0.005 M zinc chloride, ZnCl₂ electrolytic baths. The supporting precursor hydrogen peroxide, H₂O₂ was added to the TiCl₃ to pre-oxidize Ti³⁺ to Ti⁴⁺. TiCl₃ electrolyte bath was prepared as reported by Chang et al. [26] by adding 0.075 M of hydrochloric acid followed by addition of H₂O₂. 1 M ZnCl₂ stock solution was made by dissolving 13.65 g of ZnCl₂ from Ajax Finechem in 100 ml distilled water. Then, it was diluted to 0.005 M. A fixed voltage of 1 V was used during the electrodeposition process for Zn deposition, but a higher voltage of 10 V was needed for Ti deposition. The acrylic cell holder was used to clamp the plates with a fixed spacing, d of 20 mm and deposition diameter, a of 12 mm shown in Figure 1 (a) and schematic diagram of the electrodeposition setup shown in Figure 1 (b).

![Figure 1](image_url)

**Figure 1.** Schematic diagram for electrolytic cell holder (a) and electrodeposition setup (b).

The working electrode was Cu foil for both cases, while the counter electrode was Ti plate for Ti/Cu sample and Zn foil for Zn/Cu sample. Both thin films were deposited for 1 minute deposition time at its respective voltage. After the deposition, the samples underwent thermal oxidation process at a temperature of 600 °C for 60 minutes [27]. It was then coated with Au to form a simple MIM junction by using an auto fine coater (JEOL JFC-1600). Both deposited samples then underwent I-V measurements by applying DC voltage from -2 V to 2 V with a step voltage of 0.1V. FESEM (JEOL JSM-6700F), XRD (SHIMADZU XRD-6000) and potentiostat (PGSTAT302N, AUTOLAB) were used to characterize the thin films for surface morphology, structure and I-V measurement. All experiments and measurements were performed at room temperature.
3. Results and Discussion

The XRD patterns of both thin films after thermal oxidation were illustrated in Figure 2 (a). Miller indices were included at each diffraction peak. Deposited Ti and Zn were fully oxidized to TiO$_2$ and ZnO. TiO$_2$ peaks were observed at 25.21° (101), 49.02° (200) and 61.21° (118) conforming to JCPDS Card 21-1272. ZnO peaks also matches the JCPDS Card 36-1451 at 2θ of 35.68° (101) and 44.26° (102). The existence of CuO (JCPDS Card 80-1917) and Cu$_2$O (JCPDS Card 5-0667) diffraction peaks indicated that the Cu (JCPDS Card 85-1326) was being oxidized as show in Figure 2 (b). Hence, not only TiO$_2$ and ZnO but also copper oxides were also possibly functioning as the active layer for the memristor.

As observed, there were peaks shifted to higher 2θ after thermal oxidation process. Thermal oxidation has resulted in the Cu peaks becoming broader and the intensity was increased. Their peaks also were shifted to a higher angle. This indicates the formation of copper oxides and at the same time inter-diffusion between atoms has occurred. The phase formation during thermal oxidation occurred through solid-state diffusion of ions. The 2θ values of Cu diffraction peaks corresponding to (111), (200) and (220) had shifted towards higher angle value thus indicating the reduction of the lattice parameter of Cu. This is due to the diffusion of Cu which during the formation of oxides. This lattice changes can be calculated by using Bragg’s Law in equation (3.1).

$$n\lambda = 2d \sin \theta$$ (3.1)

where $n$ is equal to 1, $\lambda$ is the wavelength of the x-ray, $d$ is the lattice distance and $\theta$ is the incident angle. The lattice distances, $d$ for corresponding (111), (200) and (220) after the thermal oxidation process was reduced by 2.5 x 10$^{-3}$ nm, 1.1 x 10$^{-3}$ nm, and 6.0 x 10$^{-4}$ nm respectively. From here, the shifted peak shows the reduction in lattice parameter of Cu which happened during the heat treatment where diffusion of ions occurred. Figure 3 shows the FESEM micrographs for surface morphologies of (a) TiO$_2$-Cu$_2$O-CuO and (b) ZnO-Cu$_2$O-CuO at high magnification (x60k). The microstructure of TiO$_2$-Cu$_2$O-CuO exhibits granular grains in contrast to ZnO-Cu$_2$O-CuO that displays a rod-like structure with similar length and diameter.
The $I$-$V$ measurements of both samples show the pinched hysteresis loops as shown in Figure 4 (a) and (b) which follows the characteristics of a memristor. Higher maximum and minimum current value for Au/ZnO-Cu$_2$O-CuO/Cu was bigger than the Au/TiO$_2$-Cu$_2$O-CuO/Cu sample. The maximum and minimum current measured were 52 $\mu$A, -61 $\mu$A for Au/TiO$_2$-Cu$_2$O-CuO/Cu and 93 $\mu$A, -103 $\mu$A for Au/ZnO-Cu$_2$O-CuO/Cu respectively.

The polarity dependence of the resistance to voltage is called bipolar resistive switching [11]. Resistive switching behavior was illustrated in Figure 4 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. Calculated HRS and LRS of both samples were tabulates in Table 1. Au/TiO$_2$-Cu$_2$O-CuO/Cu gave greater difference in between HRS and LRS of 8.83 k$\Omega$ with HRS/LRS ratio of 1.2. While Au/ZnO-Cu$_2$O-CuO/Cu have HRS and LRS difference of 2.02 k$\Omega$ with HRS/LRS ratio of 1.08.
Table 1. Calculated HRS and LRS.

| Sample                  | $\Delta I_{\text{max}}$ (µA) | HRS (kΩ) | LRS (kΩ) | HRS – LRS (kΩ) | HRS/LRS |
|------------------------|-------------------------------|----------|----------|----------------|---------|
| Au/ZnO-Cu$_2$O-CuO/Cu | 21.0                          | 27.05    | 25.0     | 2.02           | 1.08    |
| Au/TiO$_2$-Cu$_2$O-CuO/Cu | 5.0                        | 50.7     | 41.9     | 8.83           | 1.2     |

The diffusivity of cation possesses greater value than the diffusivity of anion by a factor of $10^3 \sim 10^4$ which creates metal vacancies instead of oxygen vacancies. The formation of metal vacancy defects in transition metal oxide produces the pinched hysteresis loop in memristor. We conclude that the ability of memristor to be used as memory device to store data relies on the existence of metal vacancy defects come from different diffusivities in the metal oxide active layer.

4. Conclusion

In summary, it can be demonstrate that TiO$_2$-Cu$_2$O-CuO and ZnO-Cu$_2$O-CuO thin films are successfully deposited using ultra-dilute solution on Cu substrates through the electrodeposition and thermal oxidation method. Both samples showed the hysteresis loop in the $I$-$V$ measurements where Au/TiO$_2$-Cu$_2$O-CuO/Cu has bigger HRS-LRS value of 8.83 kΩ compared to Au/ZnO-Cu$_2$O-CuO/Cu of 2.02 kΩ. However based on the HRS/LRS ratio, both Au/TiO$_2$-Cu$_2$O-CuO/Cu and Au/ZnO-Cu$_2$O-CuO/Cu have comparable memristive performances of 1.2 and 1.08 respectively. From the postulation of diffusivity, the memristive effects occurred due to the formation of metal vacancy defects as the diffusion of each ions are $D_{\text{Zn}}^{2+}$ in ZnO $> D_{\text{Ti}}^{4+}$ in TiO$_2$ $> D_{\text{O}}^{2-}$ in ZnO $> D_{\text{O}}^{2-}$ in TiO$_2$. The diffusivity of cation greater than anion in $10^3 \sim 10^4$ factor.
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