Fabrication of Flexible Au/ZnO/ITO/PET Memristor Using Dilute Electrodeposition Method

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Abstract. DRAM has been approaching its maximum physical limit due to the demand of smaller size and higher capacity memory resistor. The researchers have discovered the abilities of a memristor, a Non Volatile Memory (NVM) that could overcome the size and capacity obstacles. This paper discussed about the deposition of zinc oxide (ZnO) on indium tin oxide (ITO) coated polyethylene terephthalate (PET) substrate by electrodeposition. Metallic Zn film was deposited on substrates with varying deposition time from 15 to 120 seconds in very dilute zinc chloride (ZnCl\textsubscript{2}) aqueous and subsequently oxidized at 150 °C to form ZnO/ITO coated PET junction. The deposited thin film was characterized via x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The results from $I$-$V$ measurement show the deposited ZnO exhibits pinched hysteresis loop. The hysteresis loop becomes smaller with increasing deposition time. The 15 seconds electrodeposition gave the largest hysteresis loop and largest value of resistive switching ratio of 1.067. The result of the synthesized ZnO on the flexible substrate can be one of the alternatives to replace the current memory system as the flexible memory system.

1. Introduction
The usage of organic materials in electronic device has shown a rapid growth as the size demand of devices is increasingly smaller and faster. Future electronics industry depends on the development of organic base semiconductor devices due to their advantages. Flexible electronics possesses a lot of advantages of excellent portability, lightweight, low cost and ease of manufacture \cite{1,2}. Many researches have been done on flexible electronic devices such as integrated circuits (ICs), organic light emitting diodes (OLEDs), and radio frequency identification (RFID) antennas. However, only few researches have been done on flexible memory resistor (memristor)\cite{3,4}. The flexible substrate (PET) is favorable to be used in line with the growing interest from device manufacturers in thin films at thinner thicknesses. Memristor, a fourth fundamental element found by Chua in 1971 becomes the possible answer to replace the current charge based memories such as dynamic random access memory (DRAM) and flash memory \cite{5}.
Experiments have proven that a memristor can be made through a phenomenon known as bipolar resistive switching, and mostly found in transition metal oxides [6]. Hence, the titanium dioxide (TiO$_2$) film which is extensively used in most experimentation as the active layer to exhibit the memristive characteristics [7]. However, improvement on the use of other materials and different fabrication techniques as an alternative is crucial to overcome the drawbacks of using TiO$_2$ which is expensive and moreover, it’s the fabrication process is complex, involving atomic layer deposition and other additional processes [8][9].

Owing to the similar resistive switching characteristics of the transition metal oxides (TMO), the TiO$_2$ thin film can be replaced by other TMO. For example, zinc oxide (ZnO) which has properties favorable for the electronics industry. ZnO is one of just several oxides that can be grown at low deposition temperatures as low as room temperature on various amorphous substrates [10][11]. Sauki et al. [12] has successfully deposited nanoparticle sized ZnO using RF sputtering method at low temperature. By optimizing the parameters, they are able to control the crystalline structure of ZnO. Yusoff et al. [11] has demonstrated that thin film ZnO is possible to be developed using simple electrodeposition method.

In this paper, thin film ZnO were fabricated on ITO coated PET substrate by using electrodeposition and thermal oxidation methods which replaces the expensive, complex and time consuming existing methods. Their memristive performance of Au/ZnO/ITO coated PET samples is evaluated.

2. Experimental procedures

Electrodeposition process consists of ITO coated PET substrate as working electrode, platinum foil as counter electrode and silver nitrate (Ag/AgCl) as the reference electrode. 0.005M zinc chloride solution (ZnCl$_2$) was choose as the electrolyte because of its high solubility in water thus important for producing low concentration of electrolyte solution while possessing good ionic conductivity. The flexible substrate was cut into 30 x 20 mm, cleaned in ultrasonic cleaner for 10 minutes followed by rinsing with ethanol and distilled water. 2.0 V DC voltage was set to generate voltage potential between anode and cathode using the AUTOLAB Potentiostat (PGSTAT302N). Figure 1 (i) show the schematic diagram of the electrodeposition process. Both electrodes were clamped in electrolytic cell holder made by acrylic with fixed distance of 20 mm and deposition area of 113 mm$^2$.

![Image](image.png)

Figure 1 The Schematic Diagram of Electrodeposition Process (i) and Au/ZnO/ITO coated PET Sample in The I-V Measurement (ii)

After the electrodeposition process, the samples were heated for 60 minutes at temperature 150 °C on a hot plate subsequently cooled to room temperature (RT). Sputter coater was used to coat gold on
top of the deposited ZnO thin film to create another metal contact between the ZnO insulators making an Au/ZnO/ITO coated PET sandwich structure of the memristor device. Before executing characterizations was performed using FESEM and I-V measurement. Figure 1 (ii) is a schematic diagram of I-V measurement of Au/ZnO/ITO junction. The measurement was conducted by applying DC voltage between −4 V and 4 V with scan rate of 0.1 V.

3. Results and Discussion

Figure 2 shows the X-ray diffraction (XRD) patterns of the 15 seconds deposited thin film before and after the thermal oxidation with the identification of Miller indices at each peak. The peak of Zn at 2-theta, 2θ of 29.1°(220), 31.8°(221), 32.9°(100) and 43.2°(101) were clearly seen right after the electrodeposition. After the thermal oxidation process, Zn was fully oxidized to ZnO as indicated by the formation of peaks, 2θ of 47.2°(102). There also the appearance of gold (Au) peak at 38.9° because of the gold coating on top of ZnO/ITO sandwich. The corresponding peaks of the ITO coated PET substrate were found at 23.6° and 54.1°. The metal was slowly oxidized entirely in air with slow heating rate under the setting condition of thermal oxidation process. The result shows that the ZnO is well synthesized on flexible substrate.

Figure 2 XRD Results Of 15 Seconds Deposited Zn Before And After Thermal Oxidation

Figure 3 (i) and (ii) show the morphology of surface for Zn, ZnO structures before and after thermal oxidation respectively at different deposition time. Fig 3 i) (a)-(d) exhibits a granular shape of Zn microstructures. Longer deposition time increased the number of small pallet structure of Zn. After the thermal oxidation process, the size of grain particles of ZnO become larger as shown in Fig 3 ii) (a)-(d). The increased of size in synthesized ZnO morphology are due to sintering of Zn during thermal oxidation. It is clearly shown that surface morphology has changed after the thermal oxidation. ZnO microstructure has different shape from the deposited metallic Zn.
Figure 4 (i) show the $I-V$ characteristics on the Au/ZnO/ITO coated PET memristor at deposition time from 15 to 120 seconds. The result show pinched hysteresis loops which describe the characteristic of a memristor. The size of pinched hysteresis loop gets smaller with the increase of the deposition time. 15 seconds of deposition time gave the biggest $I-V$ curve with highest maximum current reading at 4 V. Figure 4 (ii) shows the reproducible of the memory switching characteristic of 100 cycles in semi log scale. The Au/ZnO/ITO coated PET memristor demonstrates good reproducibility memristic behaviour of the device because it can successfully performed 100 cycles without obvious deterioration. The pinched hysteresis loop is actually a bipolar resistive switching where the resistance depends on the polarity of the applied voltage [11].

![Figure 3 Surface Morphology Of Synthesized Zn Before Thermal Oxidation (i), Zno After Thermal Oxidation (ii) For Depositing Time at 15 (a), 30 (b), 60 (c) And 120 (d) Seconds at 20k Magnification](image)

![Figure 4 I-V Hysteresis Loops From Synthesized ZnO Thin Films at 15 (a), 30 (b), 60 (c) and 120 (d) Seconds (i), Semi Log Scale of I-V Curves in 100 Cycles (ii)](image)

The existence of resistive switching characteristic could be seen from the changes of current due to changes of resistance from high resistance state (HRS) to low resistance state (LRS) from the curve. The metal vacancy defects inside the transition metal oxide of the active layer gives significant effect to the for memristive behaviour of the memristor. The ratios of $R_{OFF}/R_{ON}$ (HRS/LRS) of Au/ZnO/ITO
coated PET memristor are plotted in figure 5 (i). From the graph, it is observed that the $R_{OFF}/R_{ON}$ ratio is decreases when the deposition time increased. This could easily understand because memristance is a function of thin film thickness. Memristance defined in the equation expressed by William et al. [13] below.

$$M(q) = R_{OFF} \left( 1 - \frac{\mu_v R_{ON}}{D^2} \cdot q(t) \right)$$  \hspace{1cm} (1)

Where, $R_{ON}$ and $R_{OFF}$ are the low resistance state (LRS) and high resistance state (HRS), $\mu_v$ is the dopant mobility, $q(t)$ is charge-dependent with time and $D$ is the thin film thickness. The $R_{OFF}/R_{ON}$ ratio of 15 seconds Au/ZnO/ITO coated PET is 1.067 and 120 seconds Au/ZnO/ITO coated PET is 1.051. Figure 5 (ii) shows compilation of HRS-LRS from previous works on ZnO thin film memristor and comparison with this work [14][15]. Suitability of the method reproduces the comparable results with the previous study. In order to obtain higher $R_{OFF}/R_{ON}$ ratio, thinner scale of thin film is required which means in this technique it can be done by the controlling the deposition time and the concentration of electrolyte.

4. Conclusion
An Au/ZnO/ITO coated PET thin film memristor was synthesized using electrodeposition and thermal oxidation method. XRD analysis shows that deposited metallic Zn was successfully oxidized into ZnO. The increment in particles size of the deposition surface structure proves that Zn was fully oxidized to ZnO after the thermal oxidation process. From the $I-V$ measurement, a pinched hysteresis loop was observed proving the resistive switching behavior of Au/ZnO/ITO coated PET memristor. The measured $I-V$ curve becomes smaller with the increase of deposition time. The largest size of hysteresis loop was obtained at 15 seconds deposition time with the largest HRS/LRS ratio, 1.067. It can be concluded that the results obtained from the synthesized ZnO of this work is comparable and demonstrated a good agreement with previous work using rapid, low cost and simpler ultra-diluted electrodeposition method. Furthermore, we believe this is the first reported attempt on fabrication of memristive device by electrodeposition method on a flexible substrate.

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