Resistive Switching Behavior of Sol-Gel Spin Coated Zinc Oxide Thin Films on ITO Substrates

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Abstract- **This work focuses on the resistive switching behavior of sol-gel spin coated zinc oxide (ZnO) thin films on ITO substrate. The deposited ZnO thin films were annealed at various temperatures from 350°C to 500°C in a furnace for 60 minutes in order to study the effect of annealing temperature on the memristive behavior of ZnO thin film. The electrical property of the thin film was characterized using 2-point probe current-voltage (I-V) measurement. The surface morphology and film thickness were examined and measured using AFM and surface profiler respectively. It was found that the samples were followed the memristive behavior as shown in I-V measurement graph.**

Keywords – Zinc Oxide, Spin Coating, ITO, annealing

I. INTRODUCTION

In 1971, the memristor was originally found by circuit theorist Leon Chua as a missing non-linear passive two terminal electrical component relating electric charge and magnetic flux linkage [1]. The special behavior of memristor is when current flows in one direction through a memristor, the electrical resistance increases and vice versa [2]. When the current is stopped, the memristor retains the last resistance that it had, and when the flow of charge starts again, the resistance of the circuit will be what it was when it was last active [3]. Resistive switching happened when a dielectric suddenly changes its (two terminal) resistance under the action of a strong electric field or current. The change of resistance is non-volatile and reversible. An interesting application of resistive switching is the fabrication of novel non-volatile resistive random-access memories (RRAM). This effect is also at the base of the behavior of the so called memristor devices and neuromorphic memories [4,5,6,7].

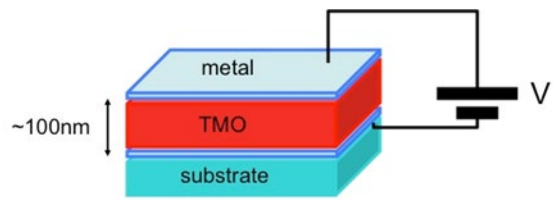


Figure 1. Schematic diagram of a memristor device structure with Pt and ITO used as top and bottom electrode respectively.

For this project, the metal is platinum , the TMO is zinc oxide. Lastly the substrate is ITO. In fact, TMOs usually exhibit high dielectric constants, which is considered a desirable feature towards dense electronic integration. A few types materials are reported to exhibit resistive switching for a typical resistive switching device. The electrode may be Au, Pt, Al, Ag, SrRuO3, etc. Next is the dielectric may be TiO2 , HfO2 , NiO, SrTiO3 , PCMO, LSMO, YBCO, ZnO, etc. There is a huge number of combinations, however, not all combinations work. Zinc oxide [ZnO] has the properties of wide bandgap (approximately 3.4 eV), adjustable doping, and low synthetic temperature. Therefore, the ZnO thin films have been investigated for the applications of transparent electrodes, light-emitting devices, photodiodes, thin film transistors, sensors, solar cells [8,9], and piezoelectric devices [10]. Recently, the resistive switching behaviours of ZnO have been reported [11,12,13,14,15]. Although the resistive switching characteristics and reliability were studied,the spacing between trap sites, the trap energy levels, as well as the electron mobility in ZnO films have not been addressed in detail. ZnO thin films have been prepared using sol-gel method. This is because the sol-gel method does not require expensive and complicated equipment but provides maximum control in doping level, the concentration of the solution, homogeneity, and easy to be coated and handled on substrate.

In this project, spin coating technique have been used to deposit uniform thin films. Basically the process involves dispersing a few drops of ZnO solution onto ITO, the substrate which is rotating with high speed. The speed set is 3000 rpm for 60 seconds. This technique is used in various applications that need to yield flat substrate that are coated with thin layers of materials.

The ZnO thin films are affected by several factors such as annealing temperature [16], annealing time, annealing ambient [17], and type of substrate [18]. It is important to get the right hysteresis loop during I-V characterization taken. Not all the samples able to produce a perfect hysteresis loop. Some of them only produce a loop on positive side and vice versa. It is happens that some of them only react to positive or negative voltage. Next is, since the project is varying the temperature of annealing, the surface profiler also important to analyze the difference of thin oxide growth.

II. METHODOLOGY

Fig. 2 shows the flowchart for ZnO fabrication process. Initially the ITO substrate was cleaned using acetone, methanol and distilled water, followed by drying process with nitrogen gases.

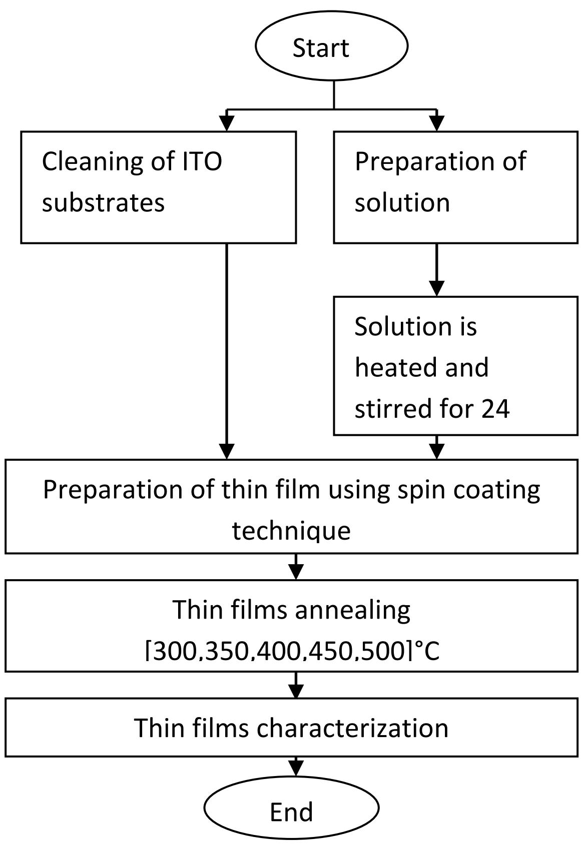


Figure 2. Flowchart of ZnO thin film fabrication process.

In this work the ZnO solution was simultaneously prepared with the substrate cleaning. In the solution preparation for zinc acetate dehydrate, 2-methoxyethanol and etanolamine were used as precursor, solvent and stabilizer respectively. Firstly the zinc acetate dehydrate was dissolved into 2-methoxyethanol. To stabilize the solution, the stabilizer was then added into the solution. In order to obtain 0.4 molar solution, the remaining solvent was added into the solution. The solution was then sonicated for 30 minutes at 50°C. Followed by stirring and heating process at 80°C for 3 hours to increase reaction process between all the materials in the solution. Then it was stirred at room temperature for another 24 hours to reinforce gel network and yield clear solution.

The next step is the preparation of thin films by using spin coating technique. In the thin film preparation process, ZnO solution is deposited onto the ITO substrate using spin coating technique. The solution was dropped onto substrate while spin at 3000 rpm for 1 minute. Then the substrates undergo drying process. In this process the substrates is heated at 150°C for 10 minutes to evaporate solvent and eliminate organic component in the film. The deposited ZnO thin films were then subjected to annealing process at various temperatures of 300, 350, 400, 450 and 500°C for 60 minutes. In order to form the MIM structure (Pt/ZnO/ITO/glass), Pt with the thickness of 60 nm was sputter coated onto the deposited ZnO thin film.

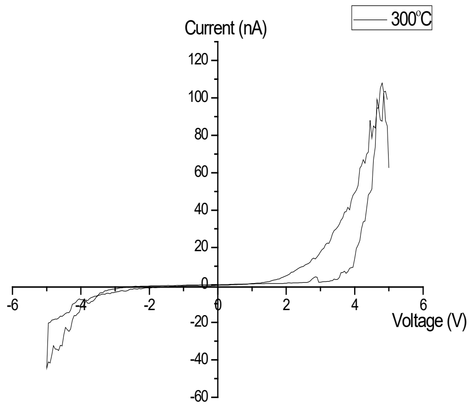
The electrical characterization was performed using 2-points probe I-V measurement system. To study the Pt/ZnO/ITO/glass memristive behavior, the bias voltage was swept from 0 V to 5 V, then 5 V to -5 V and back to 0 V while measuring the current simultaneously. The structural property and film thickness were examined and measured using atomic force microscopy and surface profiler respectively.

III. RESULTS AND DISCUSSION

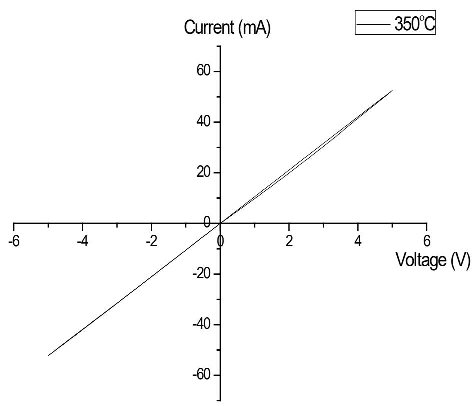
A. Electrical properties

Fig. 3 (a) to (e) show the current-voltage (I-V) measurement for ZnO thin film on ITO substrate annealed at 300 to 500°C. It was found that the ZnO thin film annealed at 300°C resulted in a rectifying I-V curve with the maximum current measured at 3 V was about 110 nA. The increase of current of about 50 mA was observed when the thin film was annealed at 350°C. The thin film was also found to exhibit ohmic behavior suggesting that the ZnO was more conductive. This is presumably due to the existence of oxygen vacancies in

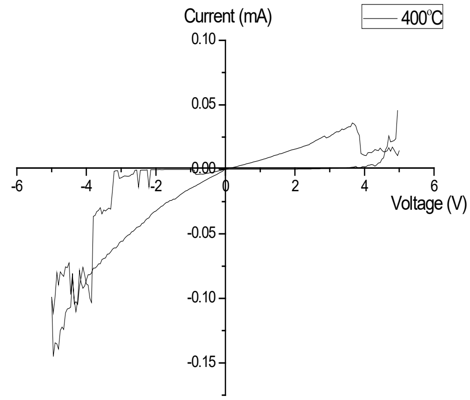
ZnO thin film as found in TiO_2 [19]. However, as the annealing temperature increased to 400°C the rectifying I-V characteristic was again observed. At this time the current decreased to 0.05 mA. Further increasing of annealing temperature resulted in the reduction of current. As can be seen in Fig. 3 (d) and (e), the switching loop only occurs at negative biasing voltage. This indicates that the device is more insulative with the application of positive voltage.



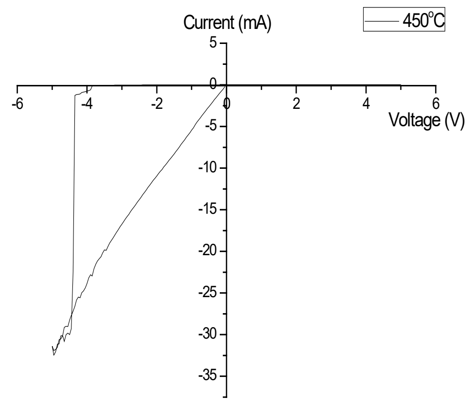
(a)



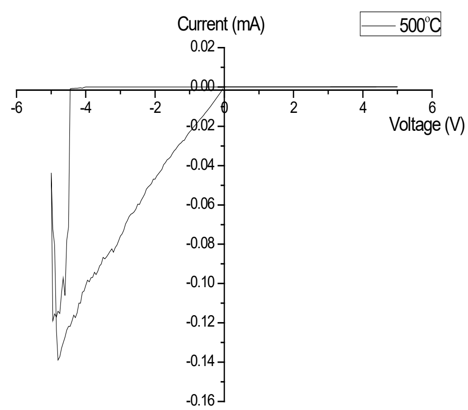
(b)



(c)



(d)

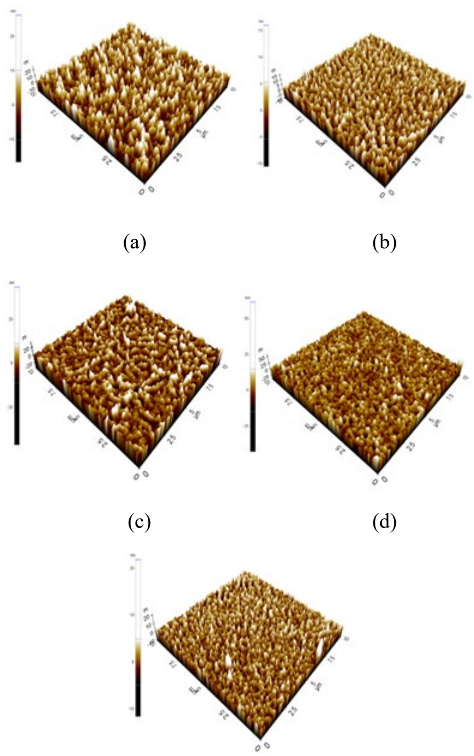


(e)

Figure 3. Current-Voltage measurement for Pt/Zno/ITO memristive device for (a) 300°C (b) 350°C (c) 400°C (d) 450°C (e) 500°C

B. Physical Properties

Fig. 4 (a) to (e) show the structural properties of ZnO thin films on ITO substrates annealed at 300 to 500°C examined by atomic force microscopy. It was observed that the structural of the thin films changed as the annealing temperature increased. As can be seen, the grains are getting denser as the annealing temperature is increased. The roughness of ZnO thin films was summarized in Table I.



(a) (b) (c) (d) (e)

Figure 4. The surface morphology of ZnO thin films on ITO substrates annealed at 300°C to 500°C

Table I. The roughness of the ZnO thin films.

Temperature (°C)	Roughness (nm)
300	4.151
350	2.223
400	3.338
450	5.055
500	1.961

Table II summarized the thickness of ZnO thin films on ITO substrate annealed at 300 to 500°C. As can be seen the minimum ZnO thickness of 80.2 nm was obtained when the thin film was annealed at 400°C. As indicated by [20] in order to exhibit memristive behavior, the thin film thickness should be in nanometer range thick.

Table II. The average thickness of the ZnO thin films.

Temperature (°C)	Thicknes (nm)
300	106.85
350	93.7
400	80.6
450	94.05
500	95.95

IV. CONCLUSION

As a conclusion, the samples that have been fabricated by sandwiching the ZnO thin films between ITO substrates and Pt electrodes followed memristive behavior. It was observed that the temperature of annealing has influenced the characterization of the samples. The higher of the annealing temperature results in the better memristive behavior which might be due to oxygen vacancies. It also exhibits that the grains are denser at higher temperature. The thickness of the thin films also as expected as the value was around 100 nm and below. Lastly, the sample annealed at high temperature show higher conductivity when negative voltage is applied.

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