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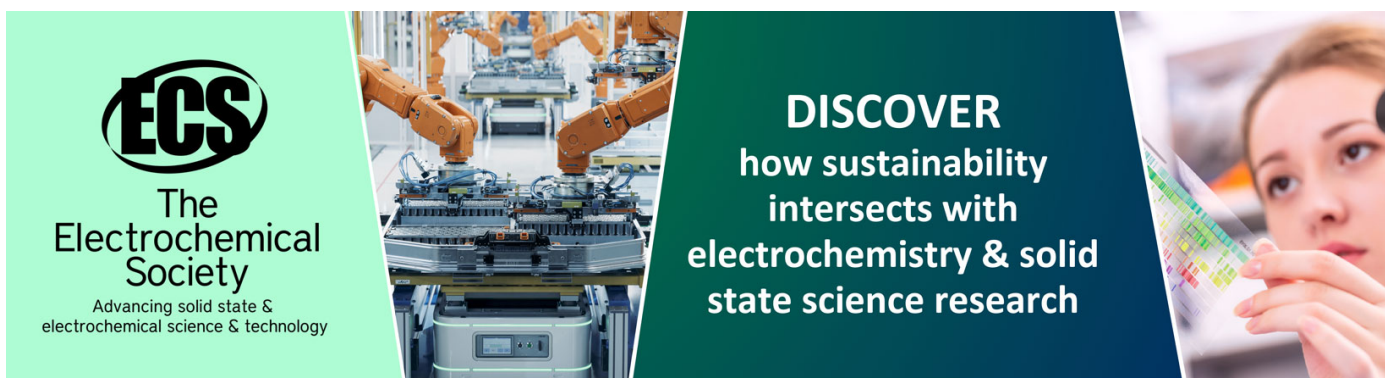
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Influence of Different Sol-gel Spin Coating Speed on Memristive Behaviour of Pt/TiO₂/ZnO/ITO Device

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Abstract. Composite titanium dioxide (TiO₂) and zinc oxide (ZnO) thin films were deposited on indium tin oxide (ITO) substrates using sol-gel spin coating technique. The electrical and physical characterizations of three different sol-gel spin coating speed were investigated using two-probe current-voltage (I-V) measurement, field emission scanning electron microscopy (FESEM) and surface profiler (SP) respectively. The I-V measurement results showed the pinched hysteresis loop for every single of devices thus indicate that all the devices are memristive. R_{OFF}/R_{ON} ratio which was defined from the hysteresis loop of device with higher spin speed was slightly higher compared to others.

1. Introduction

Memristive device which was introduced mathematically in 1971 [1] and physically was fabricated in 2008 [2] is known as the one of fundamental passive circuit elements. This two terminal device is constructed from metal-insulator-metal (MIM) structure where metals are represent as top and bottom electrodes and insulator is the thin film as well as the active layer of the device. The thin film can be deposited using several methods such as RF magnetron sputtering [3], chemical vapor deposition (CVD), spray pyrolysis, electrochemical anodization [4], atomic layer deposition (ALD) and sol-gel process. In this work, sol-gel process was selected due to it inexpensive, ease of handling and require no complex step to coat small or large desired area [5]–[7].

In memristive device, the thickness of thin films and dopant mobility give significant effect on the performance of the device. The correlation between these variables is show in equations (1) which was found by HP Lab researchers [2].

$$M(q(t)) = \left[R_{ON} \frac{w(t)}{D} + R_{OFF} \left(1 - \frac{w(t)}{D} \right) \right] \quad (1)$$



and

$$w(t) = \mu_V \frac{R_{ON}}{D} q(t) \quad (2)$$

where R_{ON} is the lowest resistance in doped region, R_{OFF} is highest resistance in undoped region, D is the overall film thickness, $w(t)$ is state variable, $q(t)$ is charge and μ_V is the dopant mobility. By substituting equation (2) into equation (1) and consider on $R_{ON} \ll R_{OFF}$ for the higher R_{OFF}/R_{ON} ratio the memristance can be simplifies to

$$M(q) = R_{OFF} \left(1 - \frac{\mu_V R_{ON}}{D^2} q(t) \right) \quad (3)$$

Equation (3) shows that the thinner film thickness in nanoscale will gives the significant memristance by referring to the factor of $1/D^2$. In sol-gel spin coating method, the film thickness is inversely proportional to the spin speed and spin time. Therefore, higher speed of spin coating will give thinner film thickness.

Three different speeds of sol-gel spin coating technique were applied to deposit composite bilayer TiO_2 and ZnO thin films on ITO/glass substrate in order to perceive the effect of spin coating speed toward the performance of device. The higher spin speed should give the thinner thin film thus contribute to better memristive performance.

2. Experimental

2.1. Substrates Preparation

The substrates were sonicated in ethanol for 10 minutes, followed by using deionized (DI) water with the same step to rinse the substrates. Then substrates were blown-dried under nitrogen gas, N_2 .

2.2. Solutions Preparation

2.2.1. ZnO solution. Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3$) were dissolved into solvent 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$). Zinc acetate and aluminium nitrate were used as precursor. Then, monoethanolamine (MEA, ($\text{C}_2\text{H}_7\text{NO}$)) which act as a stabilizer was added into the solution. At 80°C , the solution was stir-heated for 3 hours and continued stirred for another 24 hours in room temperature before ready to be deposited.

2.2.2. TiO_2 solution. Two separated solutions which was labelled as Solution A and Solution B were prepared initially. Solution A consists of absolute ethanol, glacial acetic acid (GAA, $\text{CH}_3\text{CO}_2\text{H}$) and titanium (IV) isopropoxide (TTIP, $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) where absolute ethanol performed as solvent, GAA as stabilizer and TTIP as precursor. While Solution B is a mixture of absolute ethanol which act as solvent, DI water as a substance to add O_2 element and triton X-100 as the stabilizer. Both solutions were stirred for 200 rpm in ambient temperature for 1 hour then they had been mixed up and subsequently stirred at the same speed for another 1 hour.

2.3. Thin Films Deposition and Interconnection

The spin coater was set to have two levels of spin speed. The first spin speed was set to be low at 500 rpm for 10 seconds to spread the solution evenly over the substrate and the second speed was set higher in order to have the required final thickness. In this work, 10 drops of solution were deposited on the substrate during spinning at the low speed then continued to higher speed at 1000 rpm, 2000 rpm and 3000 rpm. These steps were implemented for both TiO_2 and ZnO solutions deposition. ZnO

thin film is the first layer to be coated on substrate was annealed in air ambient at 450°C for 1 hour then followed by TiO₂ at 250°C for 20 minutes in air ambient as well.

For the metal contact, Pt was selected because it may give the smooth memristive behaviour and wider hysteresis loop compared to other metal [3]. RF sputtering technique was used to deposit 60 nm Pt on top of thin films as sputtering is the suitable method for high melting point metal (Melting point of Pt: 1769°C).

Figure 1 illustrates the final structure of memristive device with Pt on the top as top electrode, then TiO₂ and ZnO thin films as well as active layer of the device deposited on ITO for the bottom electrode which was coated on glass.

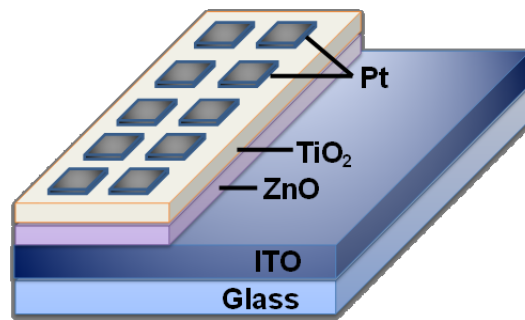


Figure 1. Final structure of Pt/TiO₂/ZnO/ITO/Glass memristive device

2.4. Measurement and Characterizations

Surface morphology and thicknesses of individual thin films were defined using the field effect scanning electron microscope (FESEM) and surface profiler respectively. Surface morphology was defined to prove the existence of thin films while for the thin films thickness itself, the thicknesses for individual layer with different speed of spin coating were measured in order to observe the changes of thin films thickness. For electrical characterization, I-V measurement was performed to get memristive behavior of the device. In order to get the pinched hysteresis loop, the bias voltage was swept from 0 V to 5 V, then from 5 V to -5 V and back to 0 V.

3. Result and Discussions

Single layer of TiO₂ and ZnO films thickness and composite TiO₂/ZnO which were deposited at 1000, 2000 and 3000 rpm were measured using surface profiler was plot in Figure 2. It can be seen that film thickness of both TiO₂ and ZnO as well as composite TiO₂/ZnO are inversely proportional to the spin coating speed [8] which mean the higher spin speed applied, the thinner film thickness will produce. Besides, both thin films were presented in exponential meet the spin coat theory, where thickness is inversely proportional to the square root of angular velocity, $t \propto (\sqrt{\omega})^{-1}$. By comparing of TiO₂ and ZnO thicknesses, it can be said that viscosity of TiO₂ solution is lower than ZnO solution since TiO₂ thin films is thinner even same spin speed were setup for both deposition [9]. Single layer of TiO₂ and ZnO films thickness were measured from different samples which were prepared separately with the composite TiO₂/ZnO but same parameter were applied. Sample with single TiO₂ and ZnO thin films was coated on ITO substrate and annealed in air ambient at 250°C for 20 minutes and 450°C for 1 hour respectively.

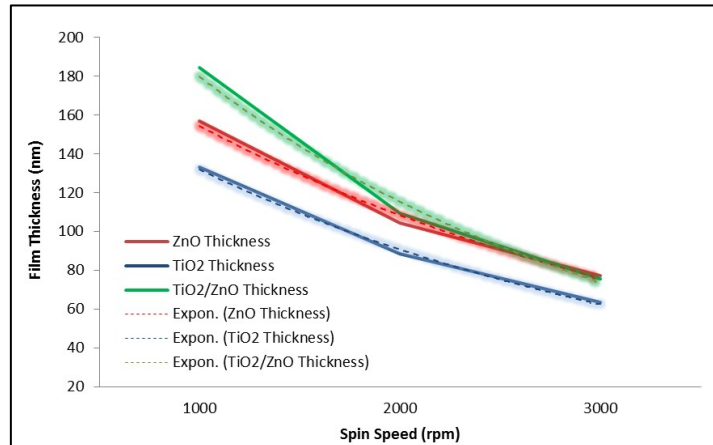


Figure 2. Film thicknesses of TiO₂ and ZnO for sample deposited at different spin speed.

Figure 3 shows the I-V measurement results for Pt/TiO₂/ZnO/ITO/Glass samples deposited with 1000 rpm, 2000 rpm and 3000 rpm spin speed in linear and semilog scale. The results were taken from 2nd measurement and above by considering the first measurement initially performs to create a path for ions movement [7]. This process can be considered as electroforming where high voltage bias will be applied to the virgin sample in order to conduct ions movement through the active layer. All samples successfully exhibited the pinched hysteresis. Sample with 1000 rpm spin speed was plot in blue triangle line has a wider loop at positive side compared to negative side while sample with 2000 and 3000 rpm in red circle and green square line respectively give wider loop at negative side.

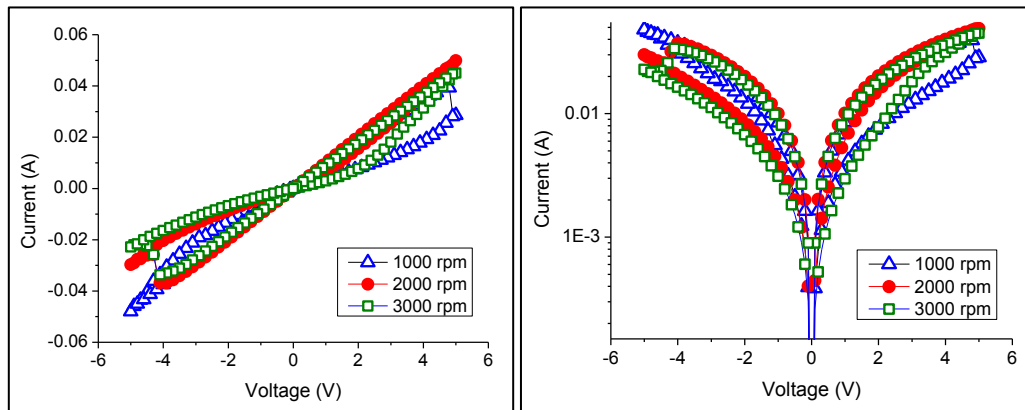


Figure 3. I-V characteristics of Pt/TiO₂/ZnO/ITO/Glass memristive device for samples deposited at different spin speed.

Table 1 was tabulated to show the R_{OFF}/R_{ON} ratio of the samples. The values of R_{OFF}/R_{ON} ratio was calculated based on

$$\text{Ohm's law: } V = IR \quad (4)$$

Substitute in

$$\frac{R_{OFF}}{R_{ON}} = \frac{V/I_{OFF}}{V/I_{ON}} = \frac{I_{ON}}{I_{OFF}} \quad (5)$$

The I_{OFF} and I_{ON} values were taken after several times of measurement to ensure the I-V characteristics are wider and stable enough to be used after electroforming process. Table 1 shows that R_{OFF}/R_{ON} ratio of deposition at 3000 rpm is slightly higher 2.07 compared to 1000 rpm and 2000 rpm with ratio 1.84 and 1.95 respectively. These results seem to be consistent with other research [7] which found that device with thinner film thickness will give the higher R_{OFF}/R_{ON} ratio thus better memristive behavior as the loop is wider which also obeys Equation (3).

Table 1. R_{OFF}/R_{ON} ratio for samples deposited at different spin speed

Spin Speed	Thickness	Voltage at Maximum R_{OFF}/R_{ON} ratio	R_{OFF}/R_{ON} Ratio
1000	184.386	4.1 V	1.84
2000	109.417	-3.7 V	1.95
3000	75.8	-4.0 V	2.07

Several recent studies performing surface morphology characterization to define the effect of annealing temperature [6], [10], [11], doping [12], different type of metal oxide or substrate use [13] towards the structure, surface roughness and film thickness. Here, the surface morphology characterization was carried out to observe the existence of TiO_2 and ZnO thin film on top of the substrate regardless the effect on surface structure and roughness. Figure 4 shows the surface morphology of samples deposited at 2000 rpm and 3000 rpm with grain diameters between 80 nm and 110 nm. It can be seen that sample with 3000 rpm gave cleared agglomerate structure compared to sample with 2000 rpm spin speed but these changes of spin speed not really impact the size of the grain. Same results were reported by other researcher where the grain size was not so being affected compared to film thickness when the spin coating time was varied [14]. Previous studies show that it will be more significant if cross-section image could be performed as it will specify the film structure and thickness of the sample [15], [16].

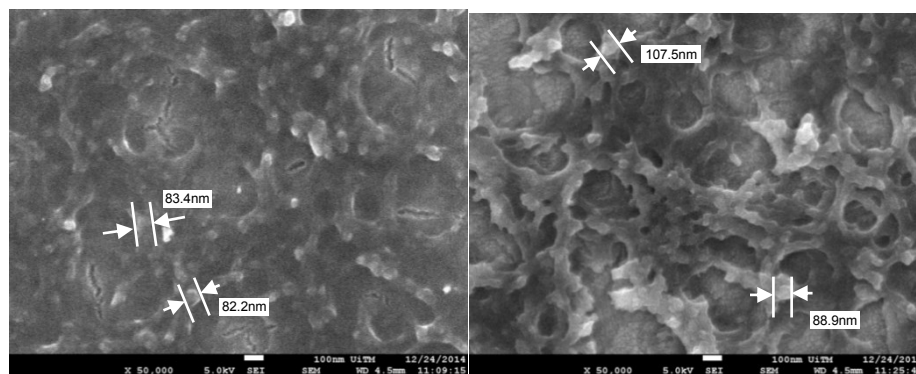


Figure 3. Surface morphology of sample deposited at 2000 rpm and 3000 rpm respectively.

4. Conclusion

Three samples which were deposited at different spin coating speed 1000, 2000 and 3000 rpm were fabricated on ITO coated glass to study on the influence of film thickness towards memristive behavior. Sample deposited with higher spin coating speed gave thinner film thickness as per proven by the thickness measurement on single TiO_2 and ZnO layer and composite TiO_2/ZnO . The results shown that all samples exhibit the characteristics of memristive device but sample with 3000 rpm spin speed gives a wider hysteresis loop with $2.07 R_{\text{OFF}}/R_{\text{ON}}$ ratio compared to samples deposited at 1000 and 2000 rpm which have 1.84 and 1.95 respectively. Thus, we can conclude that memristive device with thinner film thickness may give the better memristive behavior.

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