The Effect of the Sol-gel Spincoating Deposition Technique on the Memristive Behaviour of ZnO-based Memristive Device

N.A.A. Shaari1*, S.M.M. Kasim1, N.S.M. Sauki1, and S.H. Herman1,2
1NANO-Electronic Centre (NET) Faculty of Electrical Engineering UiTM Shah Alam.
2CoRe of Frontier Materials & Industry Applications, UiTM Shah Alam.

*noraziraakma.shaari@yahoo.com.my

Abstract. This paper presents the memristive behavior of zinc oxide thin films deposited on ITO substrate by sol-gel spin coating technique. The spin coating speed was varied from 1000 rpm to 5000 rpm to study the effect it has on the memristive device fabricated. The electrical properties were characterized by using a two-point probe IV (current-voltage) measurement system (Keithley 2400). The thicknesses of the thin films were measured by Veeco Dektak 150 Surface Profiler and it shows that the thickness decreased with the spin coat speed. The lowest thickness was obtained from thin film deposited at 5000 rpm which is 17.47 nm. The highest resistance $R_{off}/R_{on}$ ratio was obtained from thin film spin coated at 3000 rpm which is 1.346 with visible ZnO nanoparticle characterized by FESEM (JEOL JSM 6701F). This indicated that the optimum spin coat speed for the zinc oxide-based memristive device is 3000 rpm as it exhibited the best switching behavior.

Keyword: spin coat, speed, memristive, ZnO, resistance ratio

1. Introduction

Memristor is a two terminal device that is memory dependent and non-volatile, which means it has the ability to store resistance value indefinitely. It was proposed by Professor Leon Chua back in 1971[1]. Since the thickness of the active layer needs to be in nanometer scale, its physical state only been discovered in HP lab in 2008 with advancing nanotechnology that enabled the fabrication of nanoscale devices [2]. It is also reported to be viable to use in microscale as well [3]. Memristor is considered as the fourth fundamental circuit element. It extends the fundamental passive circuit elements which are revolved around capacitors, resistors and inductors. The memristive device is defined by its IV characteristic that exhibits a hysteresis loop in a shape of bow tie and that loop is necessarily crossing the origin point [4].

The most commonly used material as the active layer of the memristive device is titanium dioxide ($\text{TiO}_2$) since it is compatible with standard complementary (CMOS) technology. For this study, zinc oxide is chosen instead as an active layer for the memristive device. It has similar bandgap compared to $\text{TiO}_2$ but it is a direct semiconductor. ZnO has shown to be a promising material in memristive device as it has been widely used in other applications such as blue and ultraviolet light emitter, solar cell windows, photovoltaic device [5], flexible memory application (RRAM) [6] and surface acoustic wave device [7].
In this paper, ZnO solution was prepared by using sol-gel spin coating technique to deposit the ZnO solution onto the ITO substrate. The spin coating speed is varied from 1000 rpm, 3000 rpm and 5000 rpm to study its effect on the memristive behavior. Sol-gel is chosen as it is cheap and easy to coat the substrate in whichever shape and area[8].

2. Methodology

2.1. Memristor Fabrication
The ITO substrate as a bottom electrode would first go through the cleaning process. Acetone, methanol and deionized water are used to clean the substrate, followed by drying it off with nitrogen gas. This cleaning process is crucial to get rid of all the contamination that could affect the properties of the thin films. The sol-gel was prepared by mixing together zinc acetate dehydrate (Zn(CH$_3$COO)$_2$H$_2$O) as a precursor material, 2-methoxyethanol (C$_3$H$_8$O$_2$) as solvent and monoethanolamine (C$_2$H$_7$NO, MEA) as stabilizer. The solution was then sonicated for 30 minutes under 50°C temperature. After that it will be stirred on the hot plate stirrer for 3 hours at 80°C. It was then left to age for 24 hours to produce the clear homogeneous solution.

The thin film deposition is then carried out by spin coating technique. This is where the speed of spin coater is varied. The thin films are spin coated at 1000rpm, 3000rpm, and 5000rpm in 1 minute each while 10 drops of ZnO solution is dropped. After the spin coating process, the thin films are left to dry for 10 minutes at 150°C to evaporate the solvent and remove the residuals. Finally the thin films were then annealed in the furnace for 1 hour at 350°C temperature.

2.2 Memristor Characterization
The memristive device was characterized for both electrical and physical properties. For the physical properties, the thin films thickness was characterized by using Surface Profiler, the surface morphology was characterized by FESEM. The electrical characterization for current-voltage measurement was done by using two-point probe Keithley 4200 semiconductor characterization system connected to the probe station. The main purpose of this characterization was to obtain the memristive behavior of ZnO thin films by sweeping the voltage from 0V to -5V, -5V to 5V, 5V to 0V. The Figure 1 shows the memristive device structure for its IV measurement technique used in this work.

![Figure 1: The cross section diagram of IV measurement for memristive device structure of Au/ZnO/ITO](image-url)
3. Result and Discussion

![Figure 2: IV Characteristics of Au/ZnO/ITO memristive device spin coated at a) 1000rpm, b) 3000rpm, and c) 5000rpm](image)

From Figure 2(a) the thin film annealed at 1000rpm, the IV characteristic graph resulted in asymmetrical IV characteristic with only hysteresis loop exists in negative biased. This can be observed clearly from the semilog asymmetrical IV characteristic graph as shown in Figure 3(a).

The result shows that the ZnO spin coated at 3000rpm and 5000rpm show memristive behavior with resistance ratio of 1.346 and 1.125 respectively as tabulated in Table 1. This switching behavior may be resulted from the filament formation within the oxide layer that contains movement of oxygen vacancies that allows the electrons to drift towards the cathode [9]. In Figure 2(b) it can be said that the thin film’s conductivity is increasing compared to thin film in Figure 2(a) as a result of better oxygen vacancies created in the ZnO active layer [10]. Further increment of spin coat speed to 5000rpm as shown in Figure 2(c) resulted in thinning loops of memristive behavior and decreasing resistance ratio to 1.125. The symmetrical semilog IV characteristic graph as shown in Figure 3(b) and 3(c) shown the existent of hysteresis loops in both negative and positive biased. Spin speed is somewhat contributed to the change in film thickness. It was proven that the forming of metallic gold filaments passing through the thin ZnO layer contributed to an ohmic resistance switches for sample spincoated at 5000 rpm as shown in Figure 3(c). These filaments could be disrupted by Joule heating. The gold was also reported to give a fuse-like behaviour, which contributed to poor memristive behaviour [11].

The higher the spincoating speed, the thinner thin film gets, causing the ZnO particles to be scattered
in the substrate. This is proven in Table 1. Thinnest film makes contributes better resistance ratio with memristive behavior. As seen from Figure 2, although 5000 rpm has lowest resistance ratio compared to samples spincoated at 1000rpm and 3000rpm, it shows symmetrical memristive behavior with loops on negative and positive sides. The sample spin coated at 1000rpm is not symmetry, Figure 3(a) only shows loop on the negative side, since it has the thickest film. It was reported that the increase in film thickness contributed to defects in oxygen-related [12]. It is suspected that the fall in resistance is due to disruption in gold bridge [11].

![Figure 3: Semilog IV Characteristic for thin films spincoated for a) 1000rpm, b) 3000rpm and c) 5000rpm](image)

The resistance ratios were calculated from the IV characteristic graph as shown in Figure 4 by using the formula (1) and the results are tabulated in Table 1 along with thin film thicknesses measured by Veeco Dektak Surface Profiler.

\[
R_{ON} = \frac{V}{I_{ON}}, \quad R_{OFF} = \frac{V}{I_{OFF}} \]

\[\text{.................................(1)}\]
TABLE 1. Thin film thicknesses and resistance ratio for different spincoat speed

| Spincoat Speed (rpm) | Thin Film Thickness (nm) | Resistance Ratio |
|----------------------|--------------------------|------------------|
| 1000                 | 76.52                    | 1.178            |
| 3000                 | 34.48                    | 1.346            |
| 5000                 | 17.47                    | 1.125            |

Based on the thin film thicknesses tabulated in Table 1, it can be seen that the thicknesses decreased as the spin coating speed increasing [13]. As the spin coating speed increased, the more ZnO particles will be scattered away from the ITO substrate, thus leaving the thinner films [14].

Figure 5(a)-(c) shows the FESEM image of surface of ZnO thin films spin coated at 1000 rpm, 3000 rpm and 5000 rpm respectively. It can be seen that the nanoparticles were formed on the thin films. The images show the height difference possibility in the structures. From the figure 5(b), the ZnO thin film spin coated at 3000 rpm shows less dense structure compared to ZnO thin film spin coated at 1000 rpm. However, the grain becomes more uniform, denser and reduced grain size for ZnO thin film annealed at 5000 rpm as it has the thinnest layer as proven in Figure 5(c).
4. Conclusion
The work was carried out to study the effect of spin coating speed on the resistive switching behavior of ZnO thin films. It is known that the film thickness decreases as the spin coating speed increasing. The higher spin coat speed is what improving the grain size of the ZnO nanoparticles by reducing it and making it uniform. The spin coat speed of 3000 rpm has the memristive behavior with the highest resistance ratio of 1.346 and also the optimum spin coating speed for this study. For thin film spin coated at 5000 rpm speed was seen to drop slightly in term of the resistance ratio by 1.125 due to the metallic gold filaments forming passing through the thin ZnO layer as it is proven to have the thinnest, densest structure of ZnO nanoparticles for the surface morphology characteristic.

5. Acknowledgment
This work is partially supported by the Ministry of Education (MOE) Malaysia under the Niche Research Grant Scheme NRGS (Project Code: 600-RMI/NRGS 5/3 (7/2013)), Research Acculturation Grant Scheme (Project Code: 600-RMI/RAGS 5/3 (198/2014)) and Universiti Teknologi MARA Shah Alam.

References

[1] L. O. Chua, “Memristor The Missing Circuit Element,” *IEEE Trans. Circuit Theory, vol. 5*, no. CT-18, pp. 507–519, 1971.

[2] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, “The missing memristor found.,” *Nature*, vol. 453, no. 7191, pp. 80–3, May 2008.

[3] T. Prodromakis, K. Michelakis, and C. Tournazou, “Switching mechanisms in microscale memristors,” *Electron. Lett.*, vol. 46, no. 1, p. 63, 2010.

[4] R. S. Williams, ““How We Found the Missing Memristor,”” *IEEE Spectr.*, vol. 45, no. 12, pp. 28–35, 2008.

[5] M. H. Mamat and M. Z. Sahdan, “Electrical Characteristics of Sol-Gel Derived Aluminum Doped Zinc Oxide Thin Films at Different Annealing Temperatures,” *Electron. Devices, Syst. Appl.*, no. 100, pp. 408–411, 2010.

[6] S. Kim, H. Moon, D. Gupta, S. Yoo, and Y.-K. Choi, “Resistive Switching Characteristics of Sol–Gel Zinc Oxide Films for Flexible Memory Applications,” *IEEE Trans. Electron Devices*, vol. 56, no. 4, pp. 696–699, Apr. 2009.

[7] Z. Sin, N.D.M, Mamat, M.H.; Rusop, M.; Zulkifli, “Electrically Conductive Zinc Oxide (ZnO) Nanostructures Prepared By Sol gel Spin-coating,” *Enabling Sci. Nanotechnol. (ESciNano)*, 2010 Int. Conf., vol. 3, no. 9, pp. 9–10, 2010.

[8] A. A. A. Halim, H. Hashim, M. Rusop, M. H. Mamat, and A. S. Zoolfakar, “Study on Electrical Properties of Zinc Oxide Thin Film,” *Innov. Technol. Intell. Syst. Ind. Appl*. 2008. CITISIA 2008. *IEEE Conf.*, no. July, pp. 123–126, 2008.
[9] R. Dong, X. Yan, Z. Zhang, and M. Wang, “Memristive behavior and forming mechanism of homogeneous TiOx device,” *Mater. Res. Bull.*, vol. 61, pp. 101–104, 2015.

[10] R. A. Bakar, A. Faiz, M. Zohaimi, U. T. Mara, and S. H. Herman, “Annealing Temperature Dependence of Resistive Switching Behavior for Sol-gel Spin Coated Zinc Oxide Thin Films,” *ICSE 2014 IEEE Int. Conf. Semicond. Electron.*, pp. 0–3, 2014.

[11] E. Gale, D. Pearson, S. Kitson, A. Adamatzky, and B. D. L. Costello, “The effect of changing electrode metal on solution-processed flexible titanium dioxide memristors,” *Mater. Chem. Phys.*, vol. 162, p. 29, 2011.

[12] Q. Mao, Z. Ji, and J. Xi, “Realization of forming-free ZnO-based resistive switching memory by controlling film thickness,” *J. Phys. D. Appl. Phys.*, vol. 43, no. 39, p. 395104, Oct. 2010.

[13] W. Wang, R. Dong, X. Yan, B. Yang, and X. An, “Memristive Behavior of ZnO/Au Film Investigated by a TiN CAFM Tip and Its Model Based on the Experiments,” *IEEE Trans. Nanotechnol.*, vol. 11, no. 6, pp. 1135–1139, Nov. 2012.

[14] N. S. Kamarozaman, M. a. R. M. Rashid, M. Z. Musa, S. H. Herman, R. a Bakar, W. F. H. Abdullah, and M. Rusop, “Effect of film thickness on the memristive behavior of spin coated titanium dioxide thin films,” *RSM 2013 IEEE Reg. Symp. Micro Nanoelectron.*, pp. 155–158, Sep. 2013.