Memristive behaviour of spin coated titania thin film

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Abstract. This paper presents the memristive behaviour of spin coated titania thin films. The precursor molarity of titania thin film was varied from 0.05 to 0.4 M to study the effect of precursor molarity on the memristive behaviour of the thin films. From the observation, although the film thickness increased with the precursor molarity, the resistance ratios of the best switching loop for all samples showed no significant differences. However, it was found that the sample with less precursor molarity (device that having thinner film) required lesser time to produce the stable switching loop compared to the sample with higher precursor molarity (device that having thicker film).

1. Introduction
For over 150 years, there were only resistor, capacitor and inductor known as the fundamentals passive circuit element, until 1971, Dr Leon Chua argued that there should be the fourth element to complete the symmetry of the basic fundamental passive circuit element. The first physical modeled of a memristor was realized by HP Labs only in 2008 due to the advancement of nanotechnology [1]. The term ‘memristor’ is basically the simplified term of ‘memory resistor’ which indicates its ability to memorize the recent dynamic resistance even when the bias is turned off. The memristor exhibits I-V characteristics of bow-ties or known as pinched hysteresis loop that crosses at zero point [1, 2]. Basically, the memristor is based on metal-insulator-metal (MIM) structure. This simpler structure compared to transistors and its ability to be used as nonvolatile memory, switching devices and smart interconnects has attracted much attention from researchers recently [3, 4]. It has been reported that the memristive behaviour becomes noticeable at nano scale thickness [2-4], but then there are few studies reported that the switching behaviour can also be observed even in micro or millimeter scale thickness recently [5].

Titania is a promising active layer to be used in memristor due to its simple structure and compatibility with standard complementary metal-oxide semiconductor technology [6, 7]. It is easy to grow the films on various substrates using different deposition methods such as sputtering, atomic layer deposition (ALD), dip-coating, anodization and spin-coating method [7-10]. Furthermore, Debashis Panda et al., has stated that the TiO₂ shows different types of switching depending on the structures and stoichiometry of the films [11]. Due to that, TiO₂ is chosen as an active layer for the device in this work. Although sputtering and atomic layer deposition (ALD) are well-known methods used to fabricate the device due to the better control of the film thickness and oxygen content during deposition process, both methods require high cost [10, 12, 13]. Thus, a simpler and inexpensive method, sol-gel spin coating is chosen. Titania thin film was spin-coated on conductive
ITO-coated glass substrate followed by deposition of Pt metal contact to form a memristive device. The effect of precursor molarity differences on the switching behaviour of the memristive device was studied. The ITO was chosen as the bottom electrode because it was reported that it improves the reproducibility of I-V curve and shows non-volatile characteristics [12], while Pt as top electrode shows better memristive behaviour with titania layer compared to Au and Ti [14].

2. Experimental method

2.1. Memristive device fabrication

The ITO-coated substrate as a bottom electrode for the device was subjected to a standard cleaning procedure using methanol and deionized water (DI) for 10 minutes each in an ultrasonic bath. The titania solution was prepared using titanium (IV) isopropoxide, Ti[OCH(CH₃)₂]₄ (Sigma Aldrich) as a precursor, glacial acetic acid (GAA) as the stabilizer, Triton X-100 as the surfactant and ethanol absolute as the solvent. The precursor molarity was varied from 0.5 to 0.4M. The solutions were stirred at 2 rpm for 3 hour in room temperature. The solution was then deposited onto the ITO substrate by using spin coating method. The spin speed was set to 3000 rpm for 60 seconds. During this process, 10 drops of titania sol-gel were dropped onto the spinning ITO substrate. Next, the titania thin film was annealed for 20 minutes in the furnace with temperature of 250 °C. Lastly, Pt as a top electrode for the device was sputtered with 60-nm thickness.

2.2. Device characterization

The current-voltage (I-V) measurement was performed by the two point probe method using Keithley 2400 semiconductor characterization system connected to a probe station at room temperature. To test the memristive behaviour, the bias voltage is swept from 0V to 5V, then 5V to -5V and -5V back to 0V while simultaneously measuring the current. From the result, resistance (R_{OFF}/R_{ON}) ratio can be obtained as shown in figure 1. The surface morphology of the samples were observed by using Field Emission Scanning Electrode Microscope (FESEM, JEOL JSM 7600F) and the thickness of the TiO₂ thin film was measured by using Surface Profiler (VEECO DEKTAK 750 Profile System). The average thicknesses of the films were calculated by taking measurements at 5 different points on one sample.

![Figure 1. Resistance (R_{OFF}/R_{ON}) ratio estimation at a particular voltage](image)

3. Result and discussion

3.1. Memristive behaviour
Figure 2 shows the I-V characteristics for 5 samples which have different precursor molarity of 0.05M, 0.1M, 0.2M, 0.3M, and 0.4M, respectively. From figure 2, all samples show the bias-dependant switching characteristic that match the electrical behaviour reported for memristor [1, 3]. From the result, it is observed that all samples have almost similar resistance ($R_{OFF}/R_{ON}$) ratio ranging from 1.80 to 2.29 as shown in table 1, despite having deposited using different precursor molarity. The sample 0.4M gave the highest resistance ratio, while the sample 0.2M gave the lowest resistance ratio.

It has been reported that the resistance ratio is higher for thinner film thickness [1, 15]. However, in this work, it is observed that the sample with 0.4M with thin film of 120nm thickness still shows the memristive behaviour. This result is agreed with work reported by T. Prodromakis et al. which stated that the memristive behaviour still can be observed even in microscale memristor [5]. The reason why film thickness did not affect the memristive behaviour in this work will be investigated further.

**Table 1.** Resistance ratio and maximum current at low resistance state for all samples with different precursor molarity

| Precursor (TTIP) molarity (M) | Resistance ratio ($R_{OFF}/R_{ON}$) | Maximum current, $I_{max}$ at LRS (A) | Thickness (nm) |
|-----------------------------|-------------------------------------|-------------------------------------|----------------|
| 0.05                        | 1.96                                | 0.054                               | 21.5           |
| 0.1                         | 2.03                                | 0.079                               | 33.4           |
| 0.2                         | 1.80                                | 0.023                               | 62.2           |
| 0.3                         | 2.00                                | 0.056                               | 85.3           |
| 0.4                         | 2.29                                | 0.040                               | 120.0          |

3.2. Device performance

Figure 3 (a) to (e) shows the I-V characteristics of the samples that have different precursor molarity and the insets correspond to the FESEM surface morphology images. To test the repeatability of the results, the measurement was done three times for each sample.
Figure 3. I-V characteristics (taken three times) and inset FESEM image of surface morphology for samples deposited with (a) 0.05M (b) 0.1M (c) 0.2M (d) 0.3M and (e) 0.4M.
From figure 3, it was observed for samples of 0.05M and 0.1M, the same switching loop was reproduced during the second measurement. However, for sample 0.2M, 0.3M, and 0.4M, the stable switching loop is only obtained during third measurement. From the FESEM images of the surface morphology, it was observed that, sample 0.05M gave the smoothest surface morphology, while sample with precursor molarity of 0.4M, the grains that seen on the surface morphology are dense with agglomerate particles. It can be seen that the higher the precursor molarity, the thickness of titania thin film is increased as shown in table 1. Thus, we hypothesize that the thicker the titania thin film, the surface became more agglomerate, and the more time was taken to the memristor to achieve the stable switching loop. Note that the switching behaviour is dealing with the movement of positive charges, oxygen vacancies. Due to that, most have reported that the path creation of the oxygen vacancies in the active layer can be created by electroforming process [16-18]. However, this electroforming process requires high voltage to the virgin sample and might affect the device performance [17-19]. Thus, it is desirable to eliminate this process by controlling the oxide layer thickness and switching cycling [16, 20]. We found that the device with thinner film thickness takes a shorter time interval to get a stable switching loop compared to the device with thicker film thickness. Thus, from this work, it can be said that the conductive path is easier to be formed within device that having thinner film thickness without more measurement cycles compared to the device that having thicker film thickness.

4. Conclusion

We have successfully deposited titania thin film by applying sol-gel spin coating method. The titania was deposited onto several samples with variation of precursor molarity ranging from 0.05M to 0.4M. The variation of precursor molarity gave a little impact to the resistance ratio which can be conclude that, the memristive behaviour of all the samples were not affected despite of the precursor molarity differences. Nevertheless, it was observed that the sample with less precursor molarity (thinner film) required lesser time to obtain stable switching loop compared to the sample with high precursor molarity (thicker film).

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