Precursor Molarity Effect on the Memristive Behaviour of Spin Coated Titania Thin Film

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***Abstract*- This paper presents the memristive behaviour of the titania thin film. The precursor molarity of titania thin film was varied to 0.05M, 0.1M, 0.2M, 0.3M, and 0.4M to study the effect of precursor molarity on the memristive behaviour of titania thin film. From the observation, despite of the precursor molarity differences, the resistance ratios of the best switching loop for all the samples shows no significant changes. However, it was found that the sample with less precursor molarity required lesser time to produce the stable switching loop compared to the sample with higher precursor molarity.**

I. INTRODUCTION

For nearly over 150 years, there were only resistor, capacitor and inductor known as the fundamentals passive circuit element. Then, in 1971, Dr Leon Chua, a professor of Electrical Engineering at the University of California, has predicted and theorized the fourth fundamentals passive element which he called it as 'memristor'[1]–[6]. It is been called 'memristor' due to its special attributes which it can memorize the recent dynamic resistance value when the power supply is turned off for a short or long period of time [2], [4]. Basically, memristor is a two-terminal device whose resistance depends on the magnitude and polarity of the voltage applied to it and the length of time that voltage has been applied [1], [3], [7].

Besides, resistor, capacitor and inductor are the only well known fundamentals basic circuit elements which gave us three basic relationships. Those three are, resistor relates with voltage and current ($dv=R.di$), capacitor relates between charge and voltage ($dq=C.dv$), and inductor relates with flux and current ($d\varphi =L.di$). However, there are a missing link between the charge and magnetic flux [8]. However, as shown in Fig. 1, the missing link between charge and magnetic flux are successfully found and called as memristence, ($Mq = d\varphi/dq$) [8], [9].

In the other hand, Moore's law states that the number of transistor that can be placed in one single chip will double in every one or two years[10], [11]. But, this law will eventually come to the end and it has been predicted that it only can last for the next five to fifteen years [2]. It is because, in order to increase the performance, the number of transistor should be increased. Then, to increase the number of transistor in one single chip, the size of transistor should be reduced. But, it cannot go further when the size of the transistor is as small as the size of an atom. So, the electronics design need to shift by using increasingly capable devices instead of increasing infinitesimal devices [2]. In search of this device, Dr. Stanley Williams group at Hewlett-Packard Laboratories has physically found the most suitable candidates for increasingly capable device which is the memristor that had been theorized by Dr Leon Chua for almost 40 years ago[2], [3], [6].

Basically, memristor with $Pt/TiO_2/Pt$ structure exhibit a good memristive behavior as reported [12]–[14]. However, in this work we are focusing on investigating the switching behaviour of memristor using $Pt/TiO_2/ITO$ structure instead. Indium thin oxide (ITO) acts as the bottom electrode which posses several advantages such as excellent transparency in visible light, improve functional reproducibility, and also shows a bipolar switching behaviour which it has a good prospect for many applications in future electronic devices [13], [14].

In this paper, several samples of memristor which having a different precursor molarity of TiO_2 thin film was fabricated by using sol-gel spin coating method. Sol-gel spin coating method was choosen due to inexpensive and the processing parameters were easy to maintain [15]. The effect of precursor molarity differences on the switching behaviour of the memristive device was studied in this work.

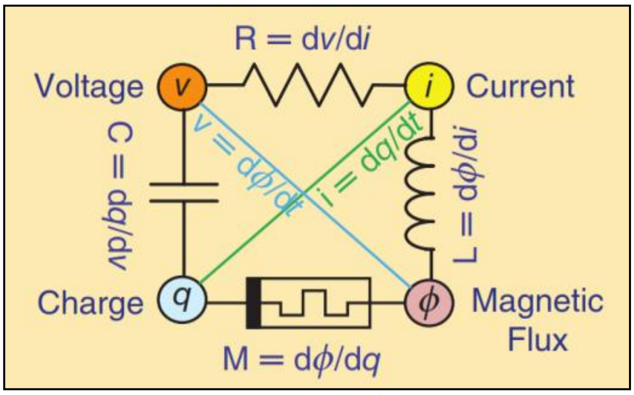


Fig. 1. Direct relationship between all the fundamentals basic circuit elements including the memristor [9]

II. METHODOLOGY

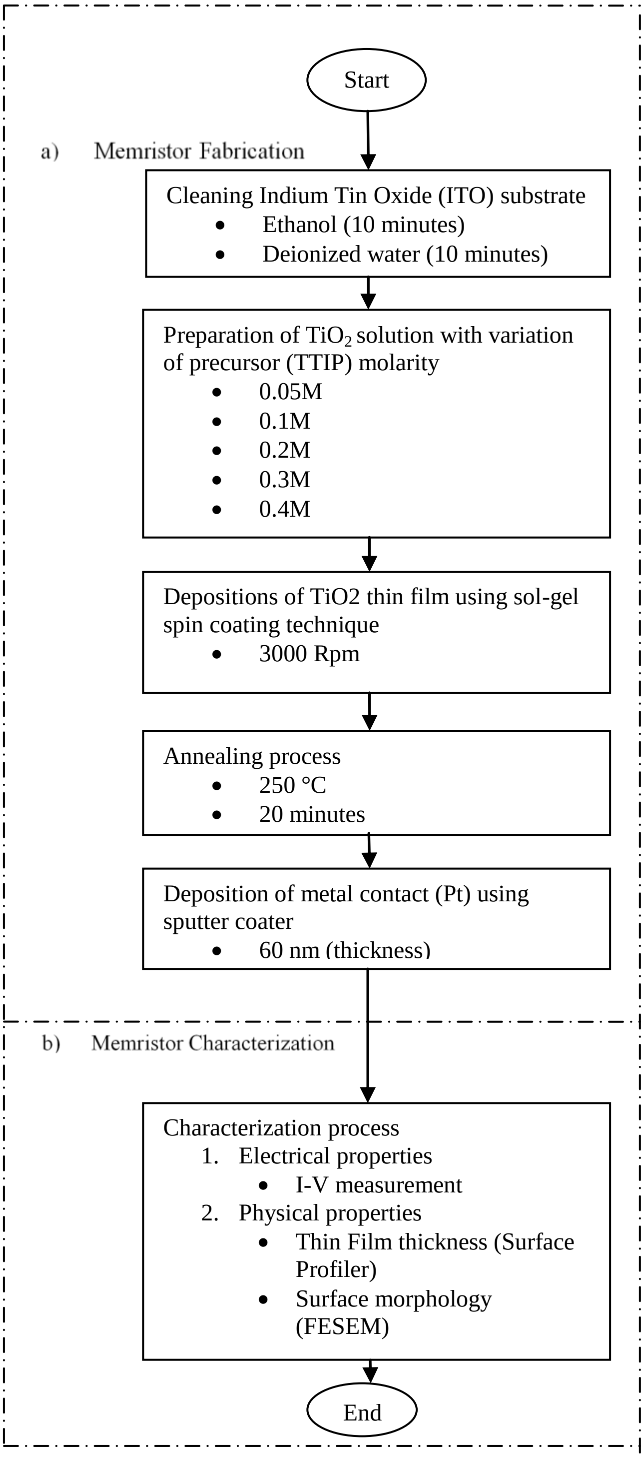


Fig. 2. Summarization flow chart of this work

A. *Memristor Fabrication*

The ITO substrate which acts as a bottom electrode for the device was cleaned using methanol and deionized water for 10 minutes each. Then, the ITO substrate was blown by nitrogen gas in order to dry it up. In order to fabricate memristors with different precursor molarity, there are several chemical substances involved to produce TiO_2 solution, which are titanium (IV) isopropoxide (TTIP), glacial acetic acid (GAA), absolute ethanol, Triton X-100 and deionized water. There are two stages of mixing the chemical substances, which the first stage is mixing titanium (IV) isopropoxide, half amount of ethanol absolute and glacial acetic acid as solution A. The other half amount of the ethanol absolute was mixed together with Triton X-100 and deionized water as solution B. After that, both of the solution was stirred for 60 minutes. After 60 minutes, both solution A and solution B were mixed together and stirred again for another 60 minutes and become TiO_2 sol-gel. Then, the solution was deposited onto the ITO substrate by using spin coating method. The spin speed used for this work is 3000 rpm and spin for 60 seconds. During this process, 10 drops of TiO_2 sol-gel were dropped onto the spinning ITO substrate. Next, the TiO_2 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.

B. *Memristor Characterization*

The current voltage (IV) measurement for each sample was performed by the two point probe method using Keithley 4200 semiconductor characterization system connected to a probe station at room temperature. To determine the memristive behaviour, I-V measurement was done by applying electric potential to the top electrode as shown in Fig. 3. Positive voltage sweep (0V to 5V, 5V to -5V and -5V back to 0V) was applied to the sample during this measurement. From the result, resistance (R_{OFF}/R_{ON}) ratio can be obtained as shown in Fig. 4.

The surface morphology of the samples were observed by using Field Emission Scanning Electrode Microscope (FESEM, JEOL JSM 7600F) and the thickness of the TiO_2 thin film was measured by using Surface Profiler (VEECO DEKTAK 750 Profile System). The thickness measurement was taken at 5 different points on the sample and the average thickness was recorded.

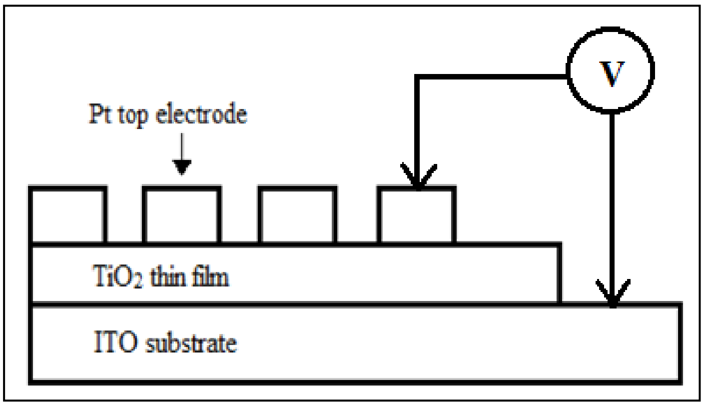


Fig. 3. Schematic diagram of I-V measurement for a TiO_2 memristor device

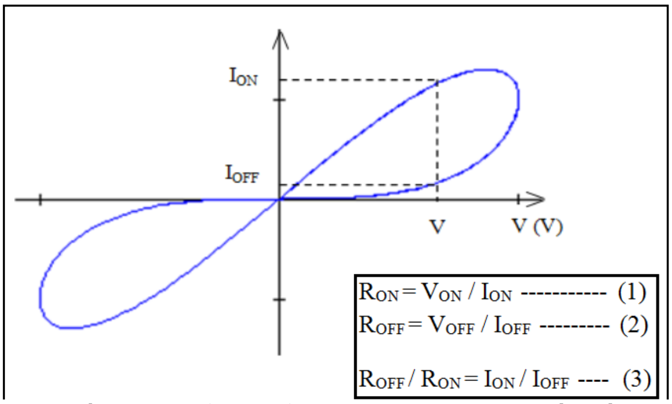


Fig. 4. The resistance (R_{OFF}/R_{ON}) ratio measurement at a particular voltage

III. Result And Discussion

A. Memristive behaviour

Fig. 5 shows the current-voltage (I-V) measurement for 5 samples which have different precursor molarity for 0.05M, 0.1M, 0.2M, 0.3M, and 0.4M, respectively.

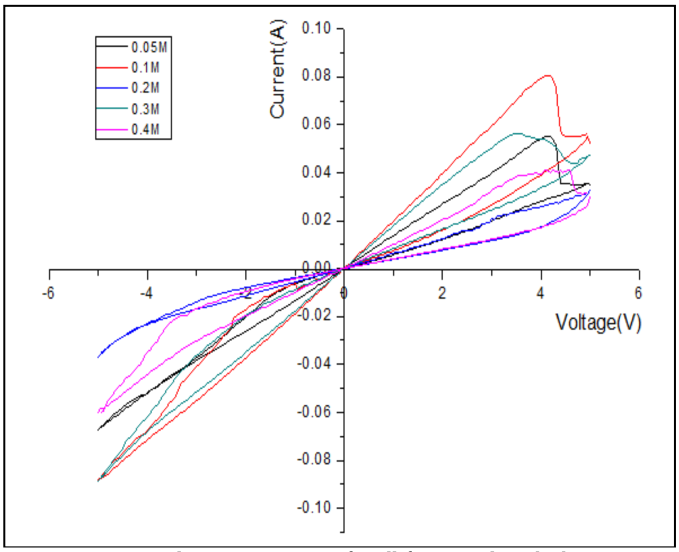


Fig. 5. Current-voltage measurement for all five samples which respect to the different precursor molarity for 0.05M, 0.1m, 0.2M, 0.3M, and 0.4M

From Fig. 5, all samples show the bias-dependant switching characteristic which look alike a bow-tie shape that match the electrical behaviour reported for memristor [2], [4]. The switching loop of all the samples is taken after the third measurement to ensure the best switching loop was obtained. The method of measurement taken in order to obtain the current voltage (IV) measurement was done by applying positive voltage sweep (0V to 5V, 5V to -5V and -5V back to 0V) to the sample. From the result, it was observed that all the samples which have a variation of precursor molarity have almost similar resistance (R_{OFF}/R_{ON}) ratio ranging from 1.80 to 2.29 as shown in Table 1. Samples 0.4M gave the highest resistance ratio, while samples 0.2M gave the lowest resistance ratio. The resistance ratio was taken at the point of maximum current at low resistance state of the switching loop as also shown in Table 1. Fig. 6 shows the graph of the thickness of titania thin film versus precursor molarity. What can be observed is that thin film of the samples with high precursor molarity is thicker than the samples with low precursor molarity as reported [16].

It has been reported that the resistance ratio is higher at thinner film thickness [3], [17]. 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 [18]. 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	Resistance ratio, (R_{OFF}/R_{ON})	Maximum current, I_{max} at LRS
0.05M	1.96	0.054A
0.1M	2.03	0.079A
0.2M	1.80	0.023A
0.3M	2.00	0.056A
0.4M	2.29	0.040A

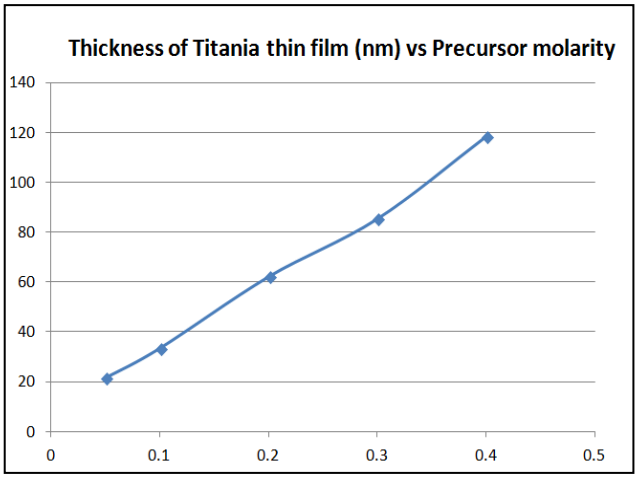
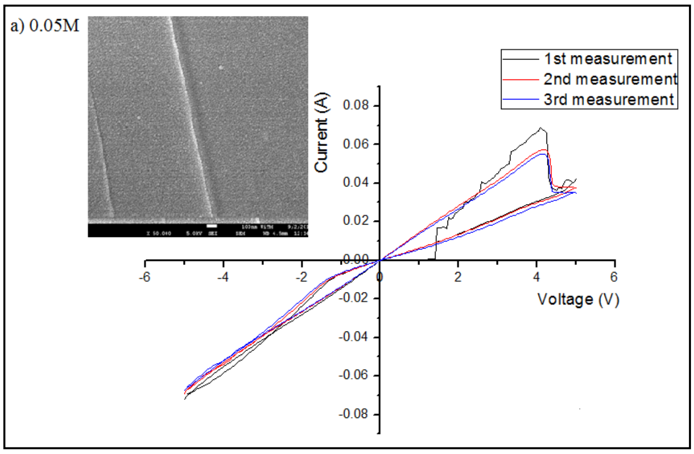
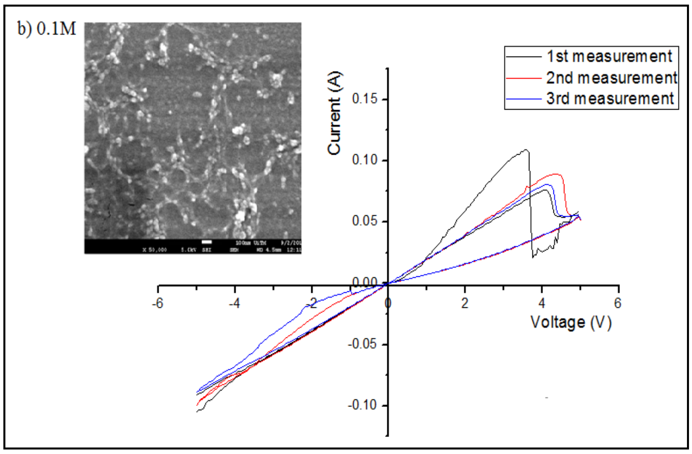


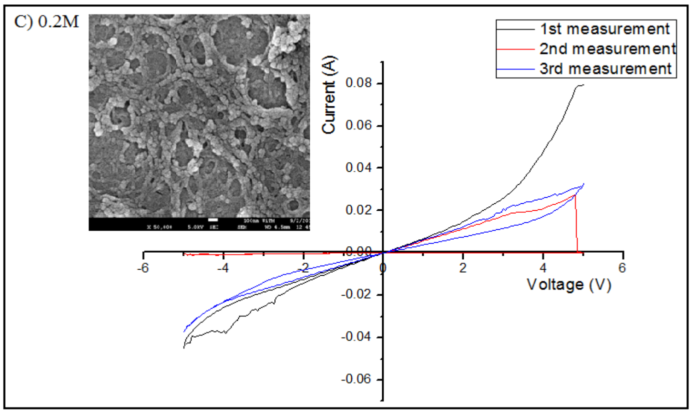
Fig. 6. Graph of thickness of the Titania thin film versus the precursor molarity

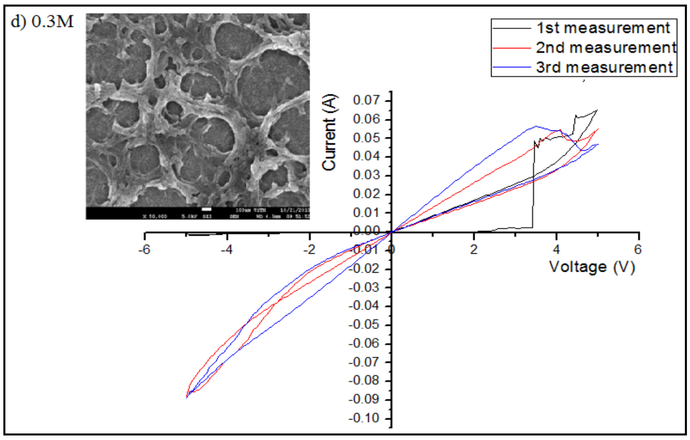
B. Device Performances

Fig. 7 (a) to (e) shows the current-voltage (I-V) measurements which were taken three times for each of 5 samples that have different precursor molarity and the inset shows the FESEM image of the surface morphology of each sample. The current voltage (IV) measurement was taken three times in order to get the best switching by applying positive voltage sweep as mentioned earlier. Apart from that, the SEM image of surface morphology was obtained from every sample by applying fixed magnification of 500K.









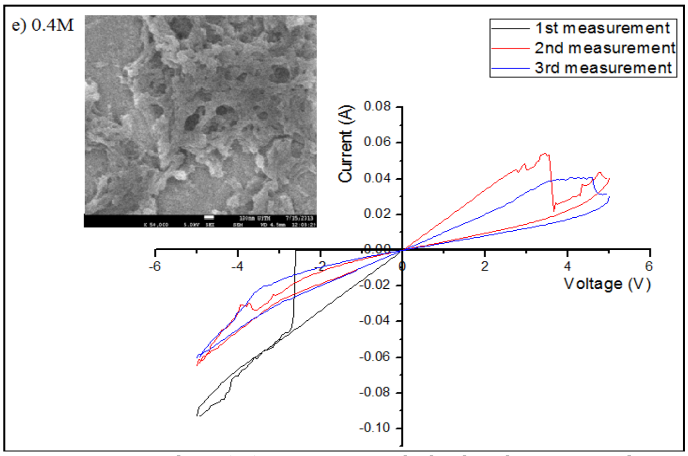


Fig. 7. Current voltage (IV) measurement which taken three times and inset FESEM image of surface morphology for each samples with respect to different precursor molarity

From Fig. 7, it was observed that the best and stable switching loop for sample 0.05M and 0.1M was produced during second measurement. However, for sample 0.2M, 0.3M, and 0.4M, the stable switching loop only able be obtained during third measurement. Then, from the FESEM images of the surface morphology of the each sample, it was observed that, samples 0.05M gave the smoothest surface morphology, while samples with precursor molarity of 0.4M, the grains that seen on the surface morphology are dense with agglomerate particles. Besides, the higher the precursor molarity, the thickness of TiO_2 thin film will be increased as mentioned earlier. Thus, we hypothesize that the thicker the TiO_2 thin film, the surface became more agglomerate, and then the more time was taken to the memristor achieving the stable and best switching loop. We assumed, since the switching loop of the memristor is dealing with the movement of ion which is the O_2 vacancies, so, in the agglomerate surface of the thin film, the movement of ion will be not smooth and disturbed by the agglomerate particles and required longer time to achieve the stable switching loop.

One conclusion can be made for this work. In order to fabricate memristor with optimized performance, the memristor with less of precursor molarity is better due to the best and stable switching loop were able to be obtained in a short time interval compared to the memristor with high precursor molarity.

IV. CONCLUSION

We have successfully deposited TiO_2 thin film by applying sol-gel spin coating method. The TiO_2 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 required lesser time to obtain the best and stable switching loop compared to the sample with high precursor molarity.

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