Fabrication And Memristive Behavior Characterization Of Titania Thin Films Deposited By Reactive Sputtering

Muhamad Uzair Bin Shamsul

Faculty Of Electrical Engineering, Universiti Teknologi Mara (UiTM), 40450, Shah Alam, Selangor.

Email: muh6239851@gmail.com

***Abstract*— This paper presents the memristive behavior of sputtered titanium dioxide (TiO_2) thin films on ITO substrate. TiO_2 thin films were deposited on ITO substrate reactive sputtering method while varying the oxygen flow rate (O_2/ (O_2 + Ar) x100) from 10, 20 to 30%. TiO_2 film with 40 nm thickness was deposited between Pt and ITO substrate to form a metal-insulator-metal (MIM) structure, which is the fundamental structure of a memristive device. Current voltage measurements (I-V) of the samples were taken within the range of -5 V and 5 V. The electroforming of the I-V measurement was done by applying positive bias from 0V to 10V. It was found that the memristive behavior was less noisy after the electroforming process compared to before the electroforming and the sample deposited with 20% oxygen flow rate gave the best memristive behavior.**

***Index Terms*— Titanium dioxide; memristor; physical vapour deposition;**

I. INTRODUCTION

In 1971, Leon Chua theorized the existence of what was believed to be the fourth fundamental passive circuit element, memristor. Memristor is an element that has the relation between charge and flux (dφ=Mdq)[1] and this relation is evidently missing from the basic fundamental circuit element which contains the resistor, capacitor, and inductor.

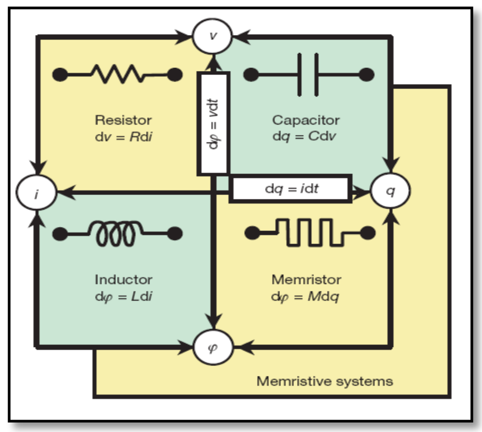


Figure 1. The four fundamental two-terminal circuit elements [2]

Figure 1 above shows that the resistor relates voltage and current (dv=R.di), capacitor relates charge and voltage (dq=C.dv), and inductor relates flux and current (dφ=L.di), thus the relation between charge and flux proposed to be a memristor[3]. The memristor completes the four fundamental passive circuit elements. Stanley Williams and team at Hewlett-Packard Laboratories (HP Lab) in 2008 have experimented the first memristor[3] and was successfully found and structured in their nanoscale cross bar array that relates to Leon Chua's theory[1].

Memristor is generally made from a metal-insulator-metal (MIM) sandwich with the insulator usually consisting of a thin film of TiO_2[4]. Memristor consists of two layers, one is mainly conductive layer due to oxygen vacancies and the remaining is an insulative layer. On the upper layer of TiO_2 usually contain oxygen vacancies.

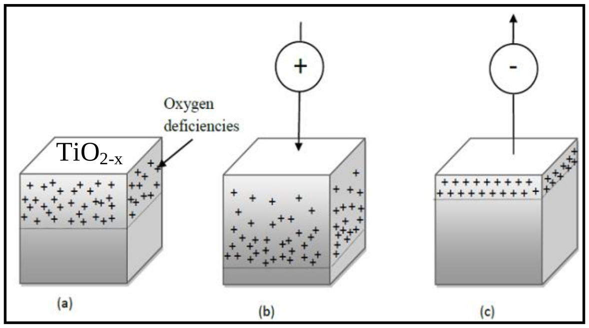


Figure 2. Behavior of HP memristor when positive and negative voltage is applied [2].

From Figure 2, we can see that when positive voltage is applied, positive charge oxygen vacancies in the TiO_{2-x} repelled and they are moving the undoped TiO_2 layer. These results in boundary between the two materials move and cause the percentage of the conducting TiO_{2-x} layer increase and increase the conductivity of the whole memristor. When negative voltage is applied, positive charge of oxygen vacancies are being pulled out of TiO_2 layer and increase the amount of insulating, this increase the resistivity of the whole device. When there is no voltage applied, the oxygen vacancies do not move. The boundary between two layers are static. This is how the memristor 'remembers' the voltage last applied.

From Figure 2, Fig (a) shows the condition of TiO_2 when one side is doped (contains oxygen vacancies), and the other side is undoped (perfect stoichiometry of TiO2). Fig (b) shows the condition when positive voltage is applied. The positive oxygen vacancies is push towards the undoped TiO_2, reducing the percentage of insulating TiO_2 and decrease the resistivity in the device. In Fig (c), when negative voltage is applied the positive O_2 vacancies is attracted to the TiO_{2-x} layer thus increase the percentage of the TiO_2 insulating. This results as increasing the device resistivity[2]. This shows that the oxygen vacancies play an important role in the memristive behavior. In this work, the effect of oxygen content in the TiO_2 film to the memristive behavior is studied.

Among other deposition techniques that have been used in fabricating memristive devices are sol gel [6, 7], electron beam evaporation [8], thermal oxidation [9], chemical vapour deposition (CVD) [10], atomic layer deposition (ALD) [11], and sputter deposition [12,13,14]. ALD gave better memristive characteristics than others, but ALD is much expensive and not applicable to large area scale. In this work, reactive sputtering method is used to fabricate the memristive device while varying the oxygen flow rate during the deposition resulting in TiO_2 thin films with variation of oxygen content.

The device is considered to be a memristive device if its current-voltage (I-V) characteristic exhibits the hysteresis loop as shown in Figure 3, where Leon chua's original graph of the hypothetical memristor's behavior shown at left and the graph of Stanley Williams's experimental results is at right.

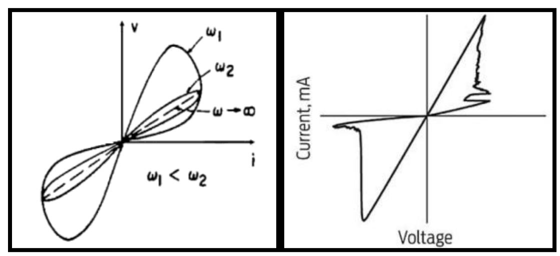


Figure 3. Current-voltage (I-V) characteristic curve (a) Leon Chua's original graph of the hypothetical memristor's behavior [1]. (b) Stanley Williams's experimental result [2]

Our previous work [17], showed that the methods of the memristive behavior characterization is crucial to obtain a good memristive behavior. For example, starting the voltage sweep during I-V characterization with a positive voltage will result in a different switching loop compared to the measurement starting with a negative voltage. And it was reported that applying a high voltage to the sample (electroforming) before the I-V measurement will drive the device to the conducting state [2]. Thus, in this work, besides investigating on the effect of oxygen content to the memristive behavior, we also studied the effect of the characterization method on the memristive behavior.

II. METHODOLOGY

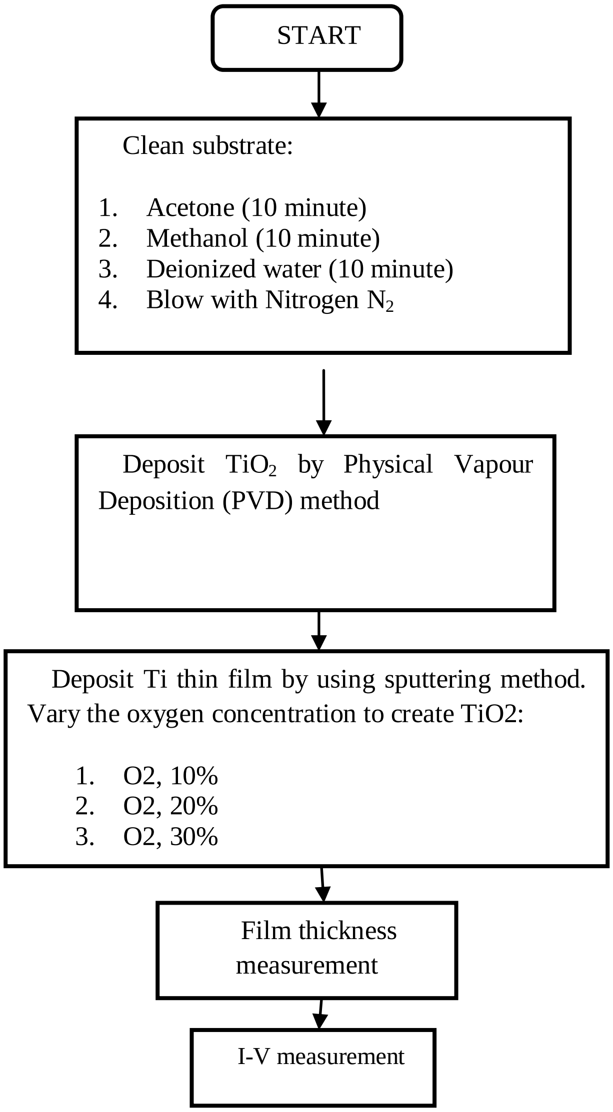


Fig. 4.Summarization flow chart of this work

A. *DEPOSITION OF TiO_2 USING SPUTTERING METHOD*

The TiO_2 target will be pre-sputtered before the deposition. This is to make sure that the target is free from any impurity. Pre-sputter is done about 15 to 30 second. TiO_2 thin film will be deposited on ITO as an active layer for the memristor.

TiO_2 thin films were grown on conductive ITO-coated glass as the substrate and also the bottom electrode with different O_2 flow rate of 10%, 20%, and 30%. To complete the MIM configuration, platinum (Pt) is deposited on the TiO2 layer as the top electrode.

B. *I-V CHARACTERIZATION*

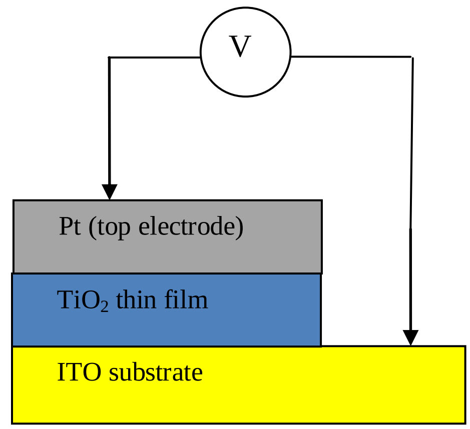


Fig. 5. Schematic diagram of I-V measurement for a memristor device structure with ITO and Pt used as bottom and top electrode.

I-V measurement will be handling in this process to measure the characteristic of the memristive device. The stylus of the I-V measurement will be place at bottom and top electrode respectively.

To test the memristive behavior, current voltage measurements (IV measurement) of samples were taken while simultaneously measuring the current with the range of 0V to 5V, 5V to -5V, and -5V to 0V (positive loop). After that the measurement was taken for the range of 0V to -5V, -5V to 5V, and 5V to 0V (negative loop). The measurement was done as shown in Fig.5 For electroforming, a 10 V was applied to the sample. The memristive behavior or memristence can be quantified by the R_{ON}/R_{OFF} ratio. The ratio was calculated by taking maximum and minimum current at a particular voltage giving the biggest switching loop for both positive and negative bias direction which is shown in Figure 6. Equation (1) shows the R_{ON}/R_{OFF} ratio calculation.

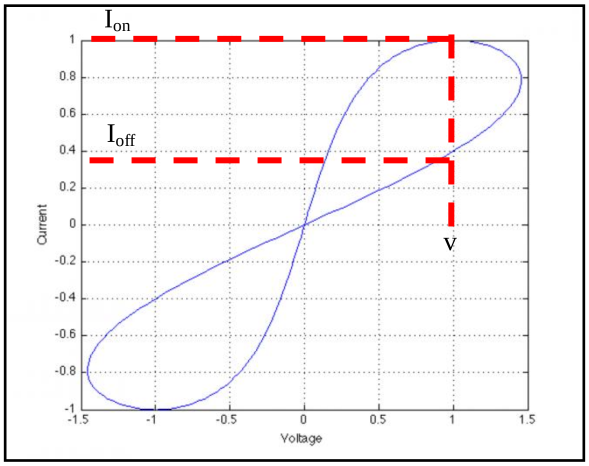


Fig. 6. The R_{ON}/R_{OFF} ratio measurement of the sample at a particular voltage.

$$\mathbf{R_{ON} = V / I_{ON}}$$
$$\mathbf{R_{OFF} = V / I_{OFF}} \quad (1)$$

III. RESULTS AND DISCUSSION

A. FILM THICKNESS

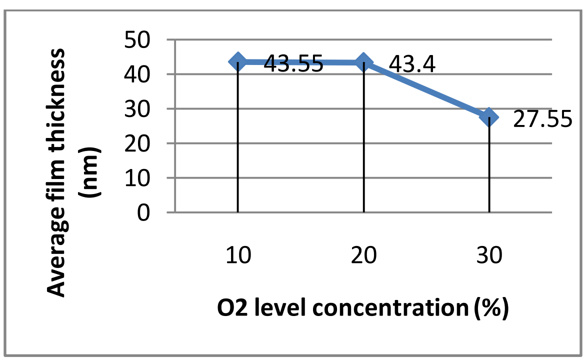


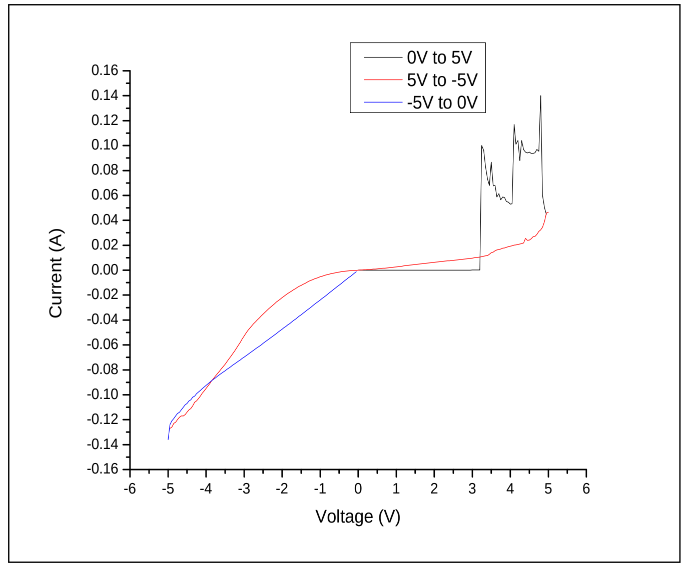
Figure 7. Film thickness of surface profiler for sputtered titania thin film for 10%, 20%, and 30% of O_2 flow rate level in nanometer

Figure 7 shows the thickness of sputtered titania thin film in nanoscale. It can be observed that sample with 30% of O_2 flow rate thickness is lower than 10% and 20%. It can be assumed that oxygen partial pressures during the deposition could affect the film structure and composition, thus the thickness decrease when the oxygen flow rate increase [16].

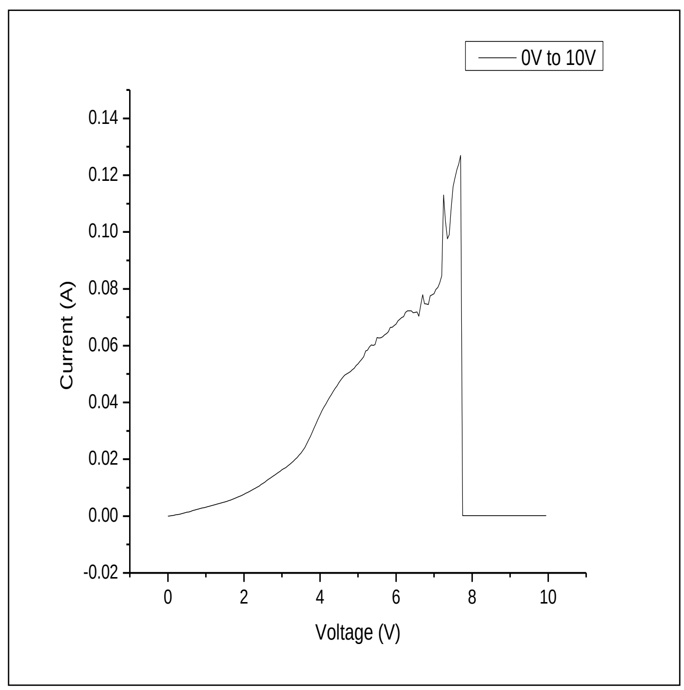
B. MEMRISTIVE BEHAVIOR CHARACTERIZATION

1) Effect of Electroforming

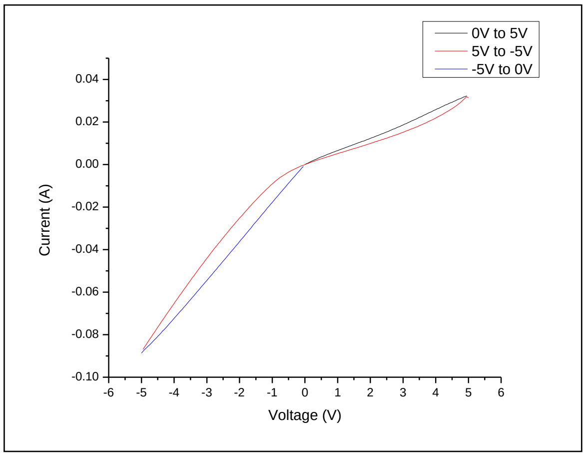
a) Before electroforming



b) 10V electroforming



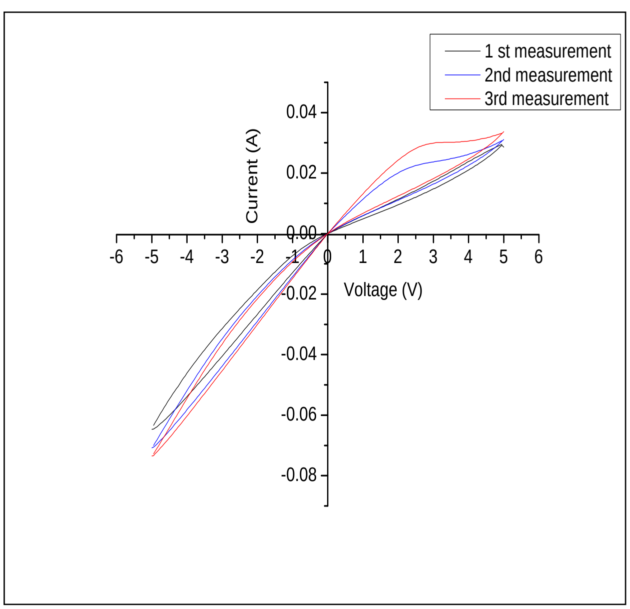
c) After electroforming



Figures 8 (a), (b) and (c) show I-V characteristics of the virgin sample (without electroforming), I-V during the electroforming, and that of the same sample after the electroforming. It can be seen that the I-V characteristic after the electroforming give a better behavior. Before the electroforming, the switching loop shows more noise compare with after the electroforming. This is because when a voltage stress is applied on the device, oxygen ion migrates to the anode and oxygen deficiencies (cation) move to the cathode. The O_2 ion will be stored in TiO_{2-x} or be oxidized near the anode, and O_2 gas bubbles were formed. After the electroforming, O_2 deficiencies assemble at cathode and form a conducting path [5].

2) Direction of bias voltage

a) Positive loop



b) Negative loop

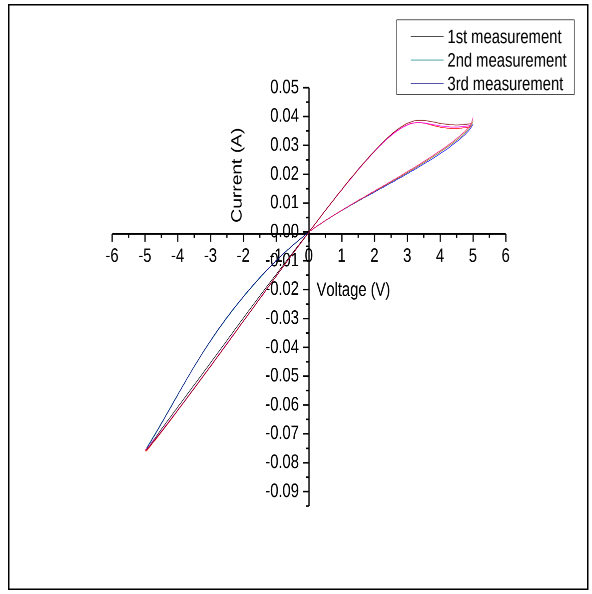


Fig. 9. Direction of bias voltage from current-voltage (I-V) measurement system (a) positive switching loop 0V to 5V, 5V to -5V and -5V to 0V (b) negative switching loop 0V to -5V, -5V to 5V, and 5V to 0V.

Fig. 9 (a) and (b) shows the I-V measurement system with positive direction of bias voltage ranging 0V to 5V, 5V to -5V and -5V to 0V, and negative direction of bias voltage ranging from 0V to -5V, -5V to 5V, and 5V to 0V. From the observation, the negative direction of bias voltage gave a more stable switching behavior and it gave much bigger switching loop at both positive and negative loop. The difference in the memristive behavior due to the bias direction may result from the characteristic of TiO_2 thin film which was explained in Section I. Introduction in which, the current carriers are positive ions. Different from electrons, the ions will remain at the last position before bias is removed, or for virgin sample, the initial position of the oxygen vacancies. Thus, the initial position of the ionic carriers before bias is being applied is crucial in the formation of the switching loop.

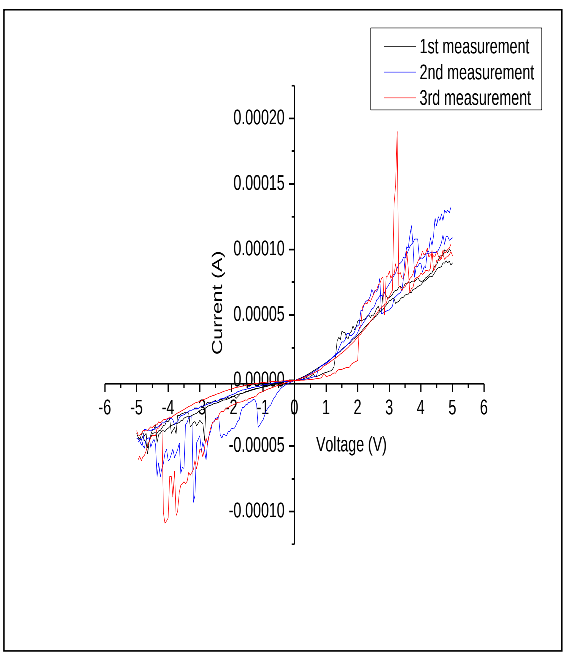
3) Effect of oxygen content

Figures 10 (a) (b) and (c), show the memristive behavior of the samples deposited with 10%, 20%, and 30% oxygen flow rate.

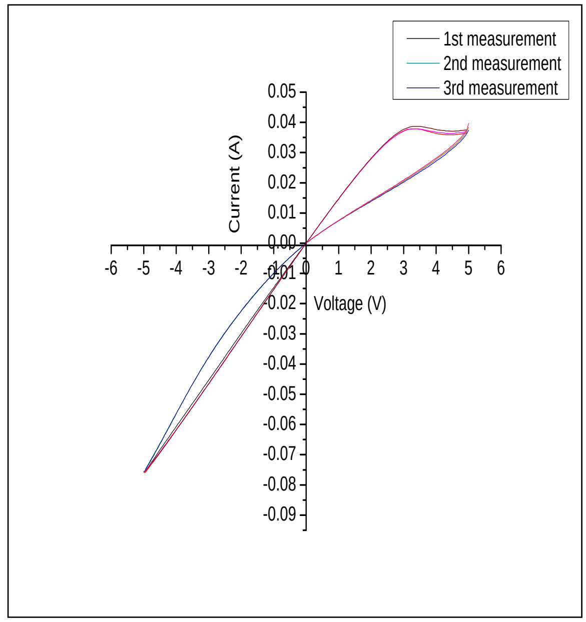
It can be seen that the switching loops of the sample deposited with 10% oxygen flow rate are very noisy while the switching loops of the samples deposited with 20 and 30% oxygen flow are better. Lower oxygen flow rate during the deposition will result in lower oxygen content in the film, which means more oxygen vacancies (mobile positive ions). However, comparing the samples of 10% and 20% oxygen flow rate, the result is contradicting. This may due to other factors such as crystallinity, surface morphology or others that need further investigation. While comparing 20% and 30%, it can be seen that the switching loop for 20% is better than 30% especially at negative region. This can be explained by considering the fact that the sample deposited with 20% oxygen flow rate has more oxygen vacancies compared to that of 30%, thus better memristive behavior.

To check the reliability of the device, 3 measurements were taken on the same sample. It can be seen that the repeatability of the measurements for samples 20 and 30% oxygen flow is relatively good.

a) 10% : negative loop



b) 20% : negative loop



c) 30% : negative loop

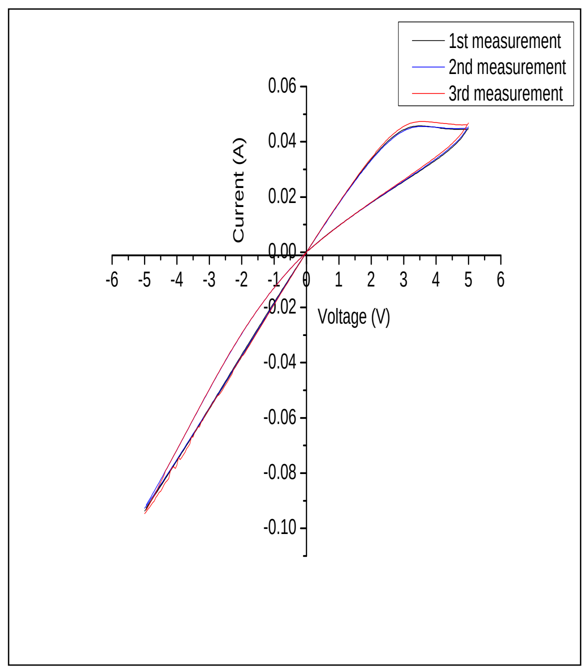


Fig. 10. Current-voltage measurement for sample deposited at different oxygen flow rate of (a)10%: negative loop (b)20%: negative loop (c)30%:negative loop .

C. R_{ON} AND R_{OFF} RATIO

Table 1 shows the R_{ON}/R_{OFF} ratios of the samples calculated for the best memristive behavior (largest loop). It can be seen that the ratio for the sample deposited using 20% oxygen flow rate gives the highest ratio compared to others. For memory device application, the larger ratio is better to differentiate the state of the memory.

Oxygen flow rate (%)	Voltage at maximum Ron/Roff ratio (V)	Ron/Roff ratio
10	-2.7	0.3
20	**3.0**	**1.82**
30	3.0	1.7

Table 1. Calculation of Ron/Roff ratio at maximum current for oxygen flow rate of 10%, 20%, and 30% at negative switching loop.

IV. CONCLUSIONS AND FUTURE RECOMMENDATIONS

From the result, the thickness of the films decreases when the oxygen flow rate increases. The electroforming give better memristive behavior with less noise compare to sample without electroforming due to more positive voltage is applied the more conductive the device becomes. From table 1 results, sample with 20% oxygen flow rate exhibit better memristive characteristic due to highest Ron/Roff ratio compare to sample with 10% and 30% oxygen flow rate.

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