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MEMRISTIVE BEHAVIOR OF PLASMA TREATED TIO_2 THIN FILMS

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ABSTRACT

This paper reports the fabrication method and the essential electrical and physical characteristics of a memristive device using titania as an active layer. Two layers of titania thin film were grown by the RF-magnetron sputtering technique onto silicon substrates. The surface of the first titania layer was treated by argon plasma to produce oxygen vacancies which are important for the memristive behavior. The plasma-treated sample was compared with an as-deposited (without plasma treatment) sample to investigate the effect of the plasma treatment. Current–voltage (I-V) curves of the samples were measured by sweeping the voltage from 0V to -5V, -5V to 5V then back to 0V. It was proven that the sample with plasma treatment exhibits better memristive behavior than the sample without plasma treatment. This is due to the reduction of oxygen vacancies during the plasma treatment, whereby the as-deposited sample and the treated sample have 60.59 wt% and 60.03 wt% respectively and the thickness of the sample reduces from 95.8 nm to 85.3 nm.

***Keywords**:* Memristive behavior; memristor; titania; RF magnetron sputtering; switching mechanism.

INTRODUCTION

The memristor is known as the missing fourth fundamental passive circuit element which was first hypothesized in 1971 (Chua, 1971). A memristor is an element that has a relation between the charge and flux ($d\varphi=Mdq$) (Chua, 1971; Williams, 2008) and this relation is evidently missing from the basic fundamental circuit element which contains the resistor (relating voltage and current), capacitor (relating charge and voltage), and inductor (relating flux and current). Hence the memristor completes the four fundamental passive circuit elements, as shown in Figure 1. The first memristor physical device was experimentally demonstrated by Stanley Williams and his team at Hewlett-Packard Laboratories (HP Lab) in 2008 (Strukov et al., 2008), and they successfully constructed their nano-scale cross bar array that relates to Leon Chua's theory (Williams, 2008). The name "memristor" was coined by Leon Chua as a short form of "memory resistor", because it has the capability to remember its previous resistance state. It is a two-terminal device in which the resistance depends on the magnitude and polarity of the voltage applied to it and the length of time that the voltage is applied (Chua, 1971; Strukov et al., 2008).

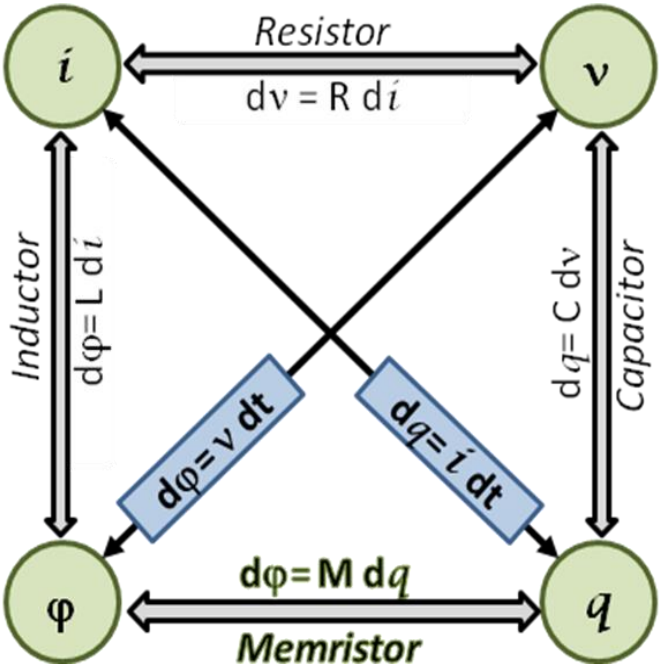

Figure 1. Leon Chua's symmetrical argument showing that a memristor completes the four fundamental passive circuit elements (Chua, 1971).

When the voltage is turned off, the memristor remembers its most recent resistance until the next time it is turned on (Williams, 2008). The memristive behavior in the device occurs due to the charge displacement in the active layer (Prodromakis et al., 2010a, 2010b; Chua, 1971) where the charge that originates from the oxygen vacancies in the active layer controls the conductivity and switching behavior of the device (Chua & Kang, 1976; Gergel-Hackett et al., 2011). The active layer of the memristor generally consists of one or two layers of thin films using numerous materials such as organic monolayer (Blackstock et al., 2006; Stewart et al., 2004), amorphous silicon (Sacchetto et al., 2010; Haykel Ben Jamaa et al., 2009), ferroelectric material (Kaneko et al., 2010), and titania (Duraisamy et al., 2012; Aznilinda et al., 2012). Out of all these materials, titania has the potential to produce good memristive behavior (Strukov et al., 2008; Williams, 2008; Miller et al., 2010; Yang et al., 2008) and is widely used as the active layer in the memristive device. Memristive devices have been successfully fabricated using a number of techniques such as sol gel (Gergel-Hackett et al., 2011) thermal oxidation (Li et al., 2010), electron beam evaporation (Miller et al., 2010), and sputter deposition (Prodromakis et al., 2010a). The memristive behavior can be identified at a nanometer scale of the active layer (Strukov et al., 2008; Won et al., 2009) and also at a micrometer scale of the active layer (Muhammad et al., 2013). To control the thickness of the thin film to be at either nano scale or micro scale, the radio frequency (RF) magnetron sputtering technique offers a controllable system where the deposited thin films can be optimized by the setting in the system's parameters (Nair et al., 2011; Singh & Kaur, 2010). In this work, the RF (radio frequency) magnetron sputtering method is used to deposit the titania active layer. The plasma treatment process that can be carried out (Aznilinda et al., 2012; Su et al., 2010, Berman & Krim, 2012; Kim et al., 2011; Oya & Kusano, 2009) in the sputtering chamber is used to create oxygen vacancies which are known to be the main carrier in memristive devices (Strukov et al., 2008) at the active layer. The effect of plasma treatment on the memristive behavior of the devices fabricated on silicon substrates is being studied.

METHODOLOGY

The silicon substrates used in this work are 1 x 1 cm silicon substrates. The substrates were cleaned by the standard cleaning method by dipping the substrates into 1% HF with 10% deionized (DI) water for 5 minutes and then rinsed with DI water to remove organic and inorganic contamination. The substrates were then blown dry under nitrogen gas. Clean substrates were coated with 60 nm thick platinum as its bottom electrode. The deposition of the titania was executed using RF magnetron sputtering in an environment condition at an ambient argon and oxygen ratio of 50:1 at a working pressure of 5 x 10^{-3} Torr using a 99.99% titania target. The RF magnetron sputtering system equipped with a load-lock chamber was vacuumed to a background pressure less than 5.0 x 10^{-6} Torr in order to minimize the residual gas components before the deposition was started. To ensure that the target surface is free from contamination, a pre-sputter cycle was first performed upfront. The first layer of titania thin film was grown by the RF magnetron sputtering at a sputtering power of 300W for 5 minutes, with a substrate temperature of 200°C, and the substrate was biased at 20V. A surface treatment was then performed on the first layer before the deposition of the second layer of titania. The surface treatment was executed by exposing the first titania layer to plasma for 10 minutes. The second layer of titania was then deposited for 2 minutes. An as-deposited sample was also fabricated with 2 layers of titania without the plasma treatment. This whole process was carried out in the sputtering chamber in a one-flow process without exposing the sample to the room ambient. The memristive behavior was measured using a Keithly current–voltage (I-V) measurement system with the voltage loop from 0V to -5V, -5V to 5V then back to 0V. The cross-section image, thicknesses and the composition of the thin film were measured using a field emission scanning electron microscope (FESEM, JEOL JSM 7600F) with EDS (energy dispersive X-ray spectroscopy). The surface roughness of the samples was characterized using atomic force microscopy (AFM, XE-100 Park System) in the non-contact mode.

RESULTS AND DISCUSSION

Figure 2 shows the memristive behavior which was characterized from 0V to -5V, -5V to 5V then back to 0V of the (a) as-deposited and (b) 10 min plasma-treated samples. Figure 2(a) illustrates that the sample exhibits conductivity only at the negative voltage. This may indicate that a small amount of oxygen vacancies exist in between the two layers of titania that are deposited together, so that when a negative bias is applied, the small amount of oxygen vacancies are attracted to the top layer and cause them to spread, creating a conductive layer at the titania region. When positive bias is applied, it repels the oxygen vacancies, creating an insulative layer at the top, hence giving a nonconductive region. These are illustrated in Figure 3(a), which explains the behavior of the sample in Figure 2(a) that shows conductivity only in the negative voltage region.

The I–V measurement of the sample with 10 minutes plasma treatment shown in Figure 2(b) exhibits a switching loop at positive and negative voltage regions although the loops are quite noisy. The switching behavior shown at both positive and negative voltage regions might be due to the plasma-treated sample having more oxygen vacancies at the interface, resulting from the longer exposure to plasma. Longer plasma treatment contributes to a higher concentration of mobile positive ions in the layer (Williams, 2008). However, the interface between the plasma-treated layer and the upper layer might be poor because the plasma-treated thin film surface can be expected to be rough due to the bombardment of highly energetic particles during the plasma treatment (Berman & Krim, 2012; Cvelbar et al., 2003; Aznilinda et al., 2012; Kim et al., 2011).

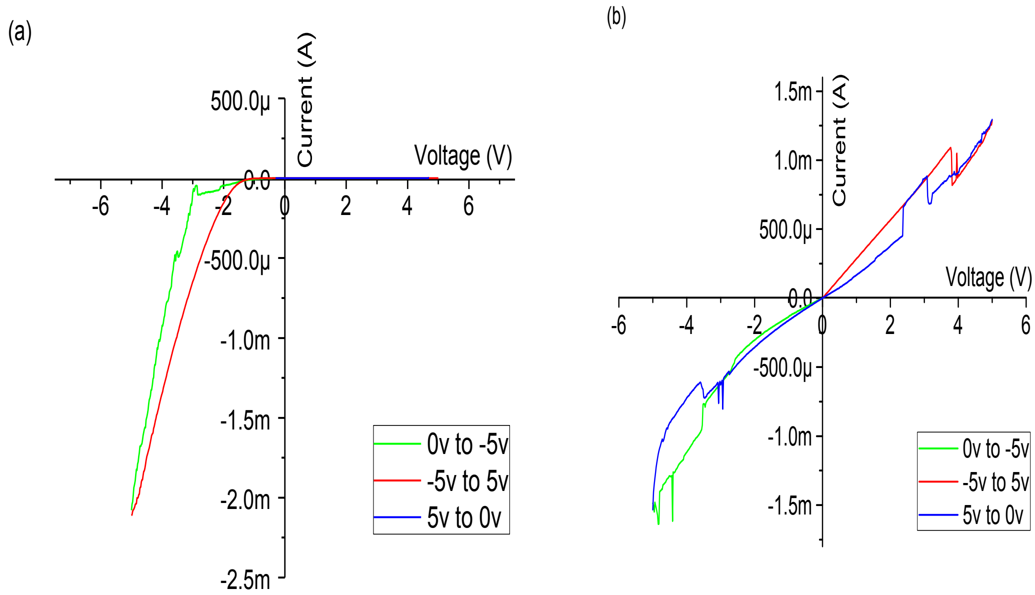

Figure 2. Memristive switching curves experiential from the current-voltage (I-V) measurement system which was measured from the voltage loop 0V→-5V→5V→ 0V 5V→5V→ -5V: (a) as deposited sample (b) 10 min plasma treatment.

Referring to Figure 3(b) on the sample with 10 min plasma treatment, when a negative bias is applied, similar behavior transpires as in the as-deposited sample. But in this sample, due to a higher concentration of oxygen vacancies, the conductive region is wider, enabling more current to flow (10^{-3} Ampere, compared to the as-deposited sample's 10^{-4} Ampere). When the applied bias is 0V, the positive ions repel and go to the initial state. When positive bias is applied, with a higher concentration of mobile positive ions, the charges repel and spread out towards the bottom of the device, creating a conductive layer that allows a current flow in the region. This results in having switching loops in both voltage regions.

The particles and cross-section of the sample were also analyzed to observe any significant difference between them. Figure 4 a(i) and b(ii) show the FESEM images of the cross-section and surface morphology for the as-deposited sample and the sample with 10 minutes plasma treatment. We observed a columnar structure in the sample with 10 min plasma treatment. The columnar structure gives a smoother path for electrons to move along due to the lower resistance existing in this structure compared to the agglomerated nanostructure. This could be one of the reasons that contribute to a better flow of current, thus giving a better memristive behavior. However there are no significant differences in the surface morphology, as seen in Figure 4 a(ii) and b(ii).

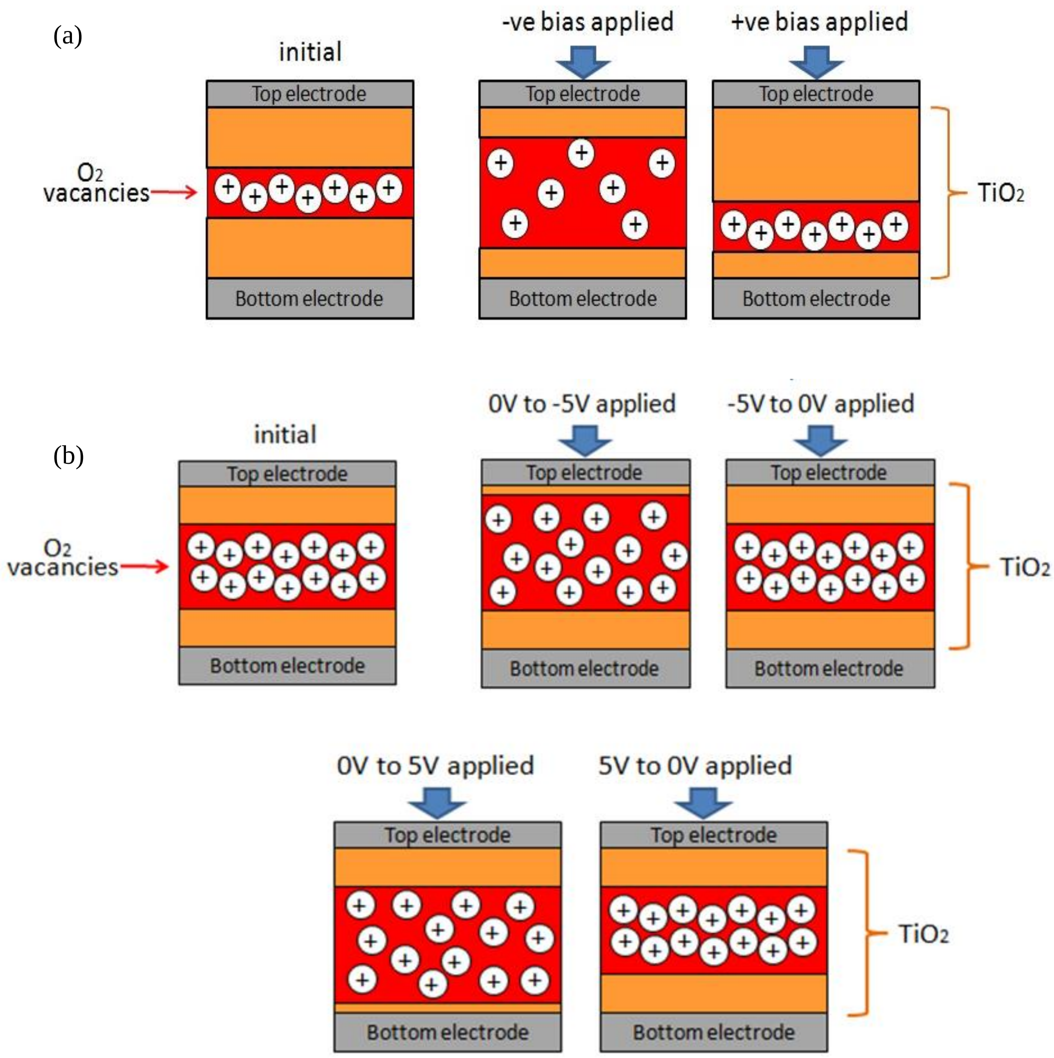

Figure 3. Schematic diagram of possible ionic (oxygen vacancies) movement for (a) as-deposited sample, and (b) sample with 10 min plasma treatment. The thickness of the titania active layer is drawn excessively thickly for a clearer view and is thus not to scale.

Table 1. TiO_2 thin film thickness after being exposed to plasma treatment.

Sample	Thickness of layer 1 (nm)	Thickness of layer 2 (nm)	Oxygen concentration in layer 1 (weight %)
As-deposited sample	95.8	34.2	60.59
10 min plasma treatment	85.3	54.4	60.03

Table 1 shows the thickness of each layer by observing the FESEM cross-section images. It can be observed that the thickness of the first titania layer exposed to plasma treatment is less than the as-deposited sample. Thinner film is reported to be able to exhibit better memristive behavior (Strukov et al., 2008). An analysis of the oxygen vacancies was done using the EDS system to observe the oxygen concentration. From the EDS data summarized in Table 1, it is observed that the oxygen concentration in the sample with 10 minutes plasma treatment is less than the as-deposited sample, with 60.03 wt% and 60.59 wt% respectively. This shows the removal of oxygen atoms on the first layer during the plasma treatment. With the removal of oxygen atoms, it provides more oxygen vacancies and creates a TiO_{2-x} layer which results in more mobile positive ions.

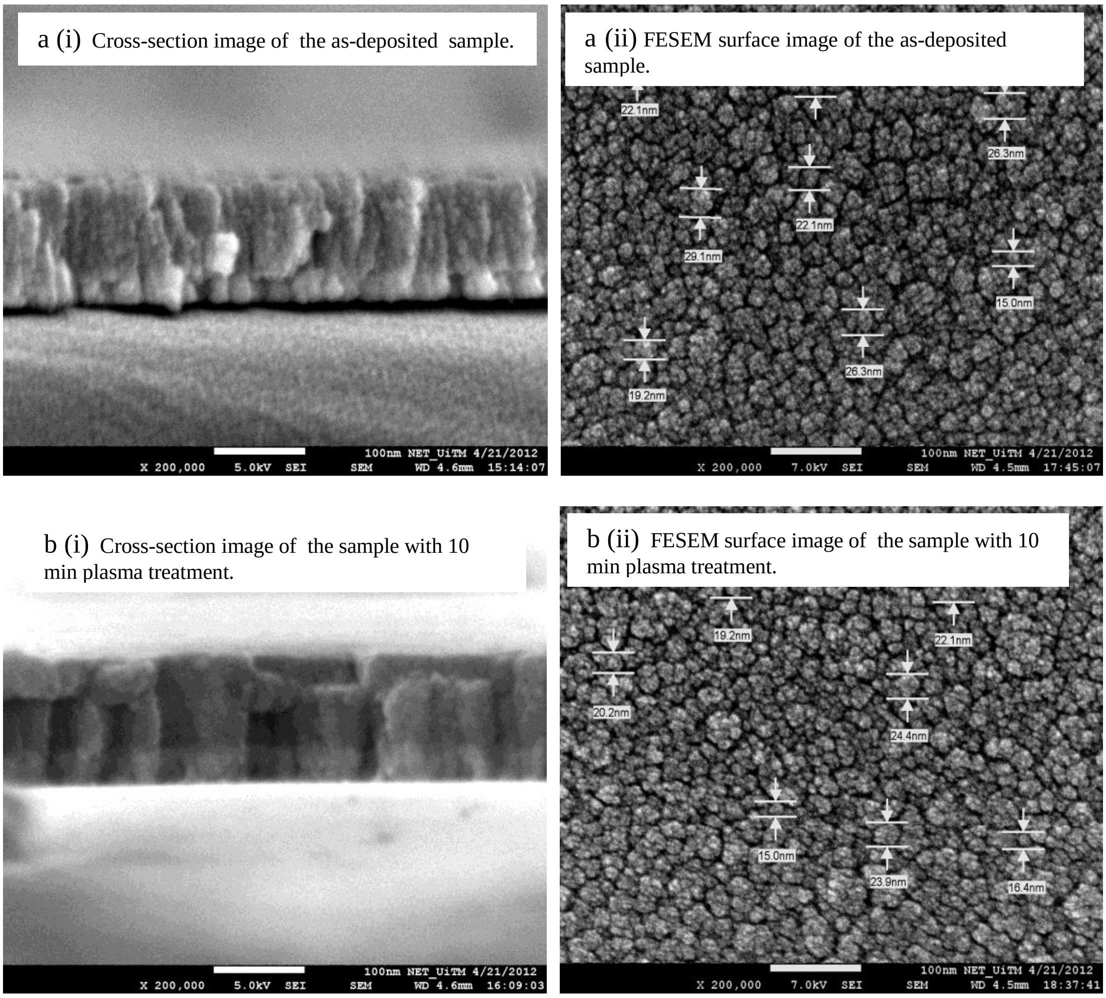

Figure 4. (a) As-deposited sample, (b) Sample with 10 min plasma treatment.

The evolution of the 3D-surface topography images of the titania thin film was observed by AFM and illustrated in Figure 5 as a function of plasma treatment time together with its surface roughness. The titania thin film surfaces that were exposed to plasma have higher surface roughness, which may be due to the removal of particles during the plasma treatment. This proves that particles are being removed from the titania surface during the plasma treatment, and the particles being removed are the oxygen particles, as confirmed by the EDS data shown in Table 1.

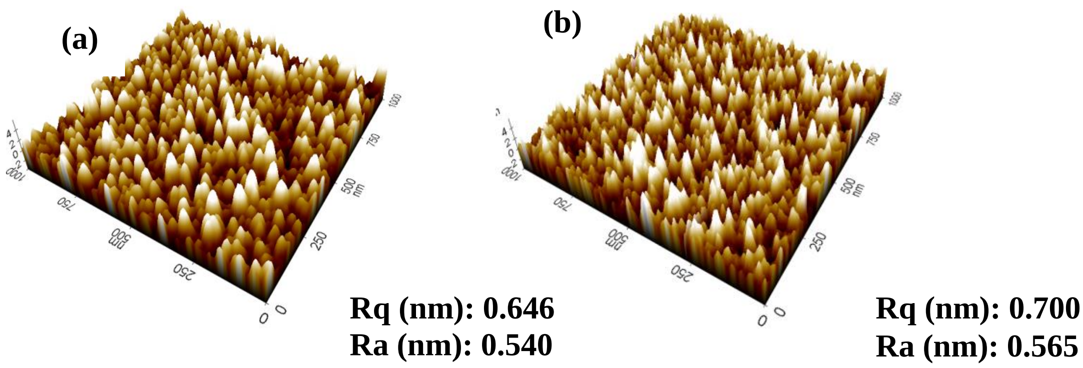

Figure 5. The 3-dimensional AFM image and surface roughness of the titania thin film exposed to plasma treatment: (a) as-deposited sample; (b) sample with 10 min plasma treatment.

CONCLUSION

In this study, the fabrication of a memristive device with two layers of titania on a silicon substrate has been successfully illustrated. The active layer was created by considering a surface treatment method which is the plasma treatment used to remove an amount of oxygen in order to increase the carrier. As a result, more oxygen vacancies appear at the interface, creating a TiO_{2-x} layer, so resulting in more mobile positive ions. From the experiment and data presented, it can be concluded that plasma treatment does contribute in the exhibition of memristive hysteresis behavior.

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