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Single- and bi-layer memristive devices with tunable properties using TiO_x switching layers deposited by reactive sputtering

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The authors systematically studied reactive sputtering deposition of TiO_x thin films using a mixture of Ar and O_2 gases under different ratios of O_2 flow. As directly revealed by X-ray photoelectron spectroscopy, the deposition changed from a metallic Ti target mode to an oxide target mode when the O_2 flow ratio was beyond 40%, resulting in TiO_x thin films with different chemical compositions. Consequently, metal/oxide/metal devices with a single TiO_x layer exhibited a broad spectrum of electrical characteristics such as Ohmic, rectifying, and memristive behavior. The reactive sputtering deposited TiO_x thin films were also used in a bilayer memristive device structure, and a transition from bipolar to unipolar switching behavior was observed for devices based on thin films prepared with different oxygen flow. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871709>]

In 2008, resistive switching devices based on TiO_x were first linked to memristors or more generally memristive devices that were postulated by Chua four decades ago.¹ Due to the reported advantages such as low power consumption (<100 fJ),² high switching speed (<1 ns),³ high on/off ratio ($\sim 10^3$),⁴ and great scalability (sub-8 nm),⁵ the TiO_x -based memristive devices have been demonstrated to be promising for bio-inspired computing,⁶ reconfigurable switches,⁷ and implication logic.⁸ Such memristive devices possess a common metal/insulator/metal (MIM) structure: a TiO_x functional layer is sandwiched by two metal electrodes. The properties of the TiO_x switching layer and the oxide/electrode interfaces are critical to the device performances,⁴ which in turn can be controlled by the thin film preparation process. A number of fabrication techniques have been used to prepare TiO_x thin films, for instance, sputtering deposition,⁴ electron-beam evaporation,⁹ sol-gel methods,¹⁰ chemical vapor deposition (CVD),¹¹ and atomic layer deposition (ALD).¹² Among these, ALD has demonstrated the best thin film quality with precise control over the thickness and the chemical composition.¹³ While sputtering deposition technique, which uses energetic ions to bombard the target and eject material clusters away through momentum exchange, is a popular choice to prepare uniform and dense TiO_x thin films, due to its cost efficiency.^{4,14} However, sputtering from a ceramic TiO_2 target limits the flexibility in tuning the composition of the sputtered thin film and hence not able to tailor the properties of memristive devices.

On the other hand, a reactive sputtering process, in which compound thin films are prepared by sputtering metal targets in an active gas atmosphere, offers thin films with a wider range of chemical compositions. Reactive sputtering of Ti target was early studied by Abe and Yamashina,¹⁵ and a drop of the thin film deposition rate was observed. It was attributed to a transition from metallic target mode to the oxide target mode, but no physical characterization was deployed to prove the hypothesis. Similar claim was made by others,^{16,17} also simply based on the deposition rate

change. To the end of device behavior, Lee *et al.* reported unipolar resistive switching in reactive sputtered TiO_x based single layer devices.¹⁸ On the other hand, Bousoulas *et al.* recently demonstrated bipolar resistive switching behavior with single layer reactive sputtered TiO_x ¹⁹ by inserting a thin Ti layer directly between the top electrode (TE) and the oxide layer. This Ti layer reacted with the TiO_x and effectively formed an oxygen deficient layer underneath, as proposed by Yang *et al.*²⁰ Nonetheless, the correlation between the switching polarity/properties and the reactive sputtering deposition of the oxide thin films has not been studied yet.

In this Letter, we report on our systematic study on direct current (DC) reactive sputtering deposition for TiO_x thin films by bombarding a Ti target with a mixture of Ar and O_2 . We directly confirmed the metallic to oxide target mode change with higher O_2 flow ratio by using X-ray photoelectron spectroscopy (XPS) characterization on the target. We deposited thin TiO_x films with different chemical compositions by varying the O_2 flow ratio, and made single oxide layer memristive devices that exhibited a wide spectrum of electrical behavior including Ohmic, rectifying, and resistive switching. Finally, we demonstrated that double layer memristive devices based on the reactive sputtered thin TiO_x films can be engineered into either unipolar or bipolar, depending on the preparation condition of the films. We further attributed the difference in the switching behavior to the different oxygen vacancy profiles created by the reactive sputtering process in the thin oxide films.

In this work, a 2-in.-diameter titanium target (purity 99.5%) was used in an AJA Orion 8 sputtering system. Throughout this study, the combined flow rate of Ar and O_2 was kept at 14.56 SCCM, and the DC power was set to 400 W, while the O_2 flow ratio was varied from 0% to 50%. The surface chemistry of the target and the sputtered films was characterized by XPS (PHI quantum 2000), and the morphology of the sputtered films was examined under a transmission electron microscope (TEM) (JEOL JEM-2000FX).

All memristive devices were fabricated on clean Si substrates with 100 nm thermally grown oxide. The bottom electrode (BE) was shared for all devices on the same wafer, and

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the TEs were isolated metal disks of 50 μm diameter. Both the BEs and TEs were deposited in an electron beam evaporator, and a metal shadow mask was employed during the deposition of the TEs. Both single switching layer and bilayer devices were made in this work, and their geometries (from bottom to top) were 5 nm Ti/10 nm Pt//~20 nm TiO_x //20 nm Pt and 2 nm Cr/20 nm Pt//~30 nm TiO_x //20 nm TiO_2 //20 nm Pt, respectively. All the TiO_x layers were deposited through the reactive sputtering process while the top TiO_2 layer in the bilayer devices was deposited by RF-sputtering from a ceramic TiO_2 target, all at room temperature. Current-voltage (IV) characterization of the fabricated devices was conducted using a Keithley 4200 semiconductor parameter analyzer. During the measurements, the BE was grounded while the TEs were biased.

The oxygen flow ratio during the sputtering process determined if the deposition is in metal or oxide target mode (Fig. 1). With pure Ar, Ti was sputtered and the deposition rate (R_{Ti}) was 0.17 nm/s. However, when 3% O_2 flow ratio was introduced, the deposition rate (R_{TiO_x}) jumped to 0.22 nm/s. This can be understood by the fact that the sputtered Ti clusters were oxidized during the travel to the substrate. However, increasing the O_2 flow ratio to 7% did not change the thin film deposition rate significantly and the rate (0.22 nm/s) stabilized till 35%. This is believed to be resulted from the balance between two processes, the oxidation of the sputtered Ti and the ion bombardment of the target that competed for the oxygen ions. More interestingly, an abrupt decrease in the deposition rate occurred at a critical O_2 flow ratio of 40% (0.015 nm/s), turning the deposition from a metallic target mode to an oxide target mode.^{16,17} In this mode, the surface of the metal target was first oxidized and thin films were deposited by sputtering the surface oxide, which had a much lower sputtering yield than that for a metal target under DC sputtering condition.

The O_2 flow ratio dictated deposition modes was further confirmed by the surface characterization of the target. Figs. 2(a) and 2(b) show the pictures of the same target that has worked at the metallic and the oxide modes, respectively. At the metallic mode (O_2 flow ratio of 35%), the target was

FIG. 1. Oxygen flow ratio dependence of the deposition mode. The deposition changed from a metallic target mode into an oxide target mode when the oxygen flow ratio is 40% or higher. The deposition rate of TiO_x at the metallic stabilizes at around 0.22 nm/s while that at the oxide target mode is 0.015 nm/s. The blue and purple colors in the chart represent the plasma color at the metallic and oxide target modes, respectively.

FIG. 2. Photos of the same target working at (a) the metallic mode (35% O_2 flow ratio) and (b) the oxide mode (O_2 flow ratio of 45%). (c) XPS results for the Ti 2p levels on the target surface at different modes. The intensity unit is arbitrary.

bright with evident metallic luster. However, when worked at the oxide mode (45% O_2 flow ratio), it became colorful due to the oxidation at the surface. The non-uniformity in the color should be attributed to the non-uniform plasma density during the deposition due to the uneven target surface profile. XPS spectra (Fig. 2(c)) of the target show that metallic Ti states (2p1/2 at 460.2 eV and 2p3/2 at 454.22 eV) dominated the Ti 2p core level when the target was used at the metal mode. However, if it worked at the oxide mode, the characteristic peaks of the Ti^{4+} state (2p3/2 at 458.77 eV) were dominant, which verifies that the surface has been oxidized.

Sputtered films under different O_2 flow ratios had different chemical compositions. Fig. 3(a) shows the Ti 2p XPS spectra inside films that were deposited with O_2 flow ratios ranging from 3% to 50%. With an O_2 flow ratio of 3%, the Ti was only slightly oxidized. The dominant 2p3/2 (2p1/2) peak at 454.78 eV (460.82 eV) indicated the existence of Ti^{2+} state. When the O_2 flow ratio was increased to 7%, except for the Ti^{2+} states, characteristic peaks corresponding to the Ti^{4+} state appeared (2p3/2 peak at 458.82 eV and 2p1/2 peak at 464.04 eV). With 15% and 25% O_2 flow ratios, the characteristic 2p3/2 peaks of Ti^{4+} became more evident, while the characteristic Ti^{2+} peaks gradually disappeared, indicating further oxidation of Ti. Finally, for the film deposited with an O_2 flow ratio of as high as 50%, peaks of the Ti^{4+} state dominated. The XPS data suggested that the thin films were oxygen deficient when the target worked at the metallic mode, while those deposited at the oxide mode were more stoichiometric. Further, the deposited TiO_x thin film under 50% O_2 flow ratio was amorphous, as revealed by the TEM image and electron diffraction pattern (Figs. 3(b) and 3(c)). The thin films deposited with reactive sputtering were of high quality. Our preliminary work using microwave impedance microscopy (MIM)²¹ analyses for TiO_x films

FIG. 3. Material characterization of the deposited TiO_x thin films. (a) XPS analyses on films prepared with different O_2 flow ratios. The dominant peaks change from Ti^{2+} to Ti^{4+} with the oxygen flow ratio during sputtering. The intensity unit is arbitrary. (b) TEM image and (c) electron diffraction pattern of the film deposited with an O_2 flow ratio of 50%, suggesting it is amorphous.

deposited with 15%, 25%, and 35% oxygen flow ratios has confirmed that no pinholes beyond the MIM detection resolution (10 nm) were found within a $3\ \mu\text{m}$ by $3\ \mu\text{m}$ area for all these films.

The electrical behavior of single layer devices made from the films deposited under different O_2 flow ratios was dramatically different. A transition from a linear to non-linear and finally to memristive behavior was observed (Fig. 4). With films prepared at low O_2 flow ratios (3% and 7%), the devices exhibited linear IV behavior, suggesting the existence of Ohmic contacts at the oxide/electrode interfaces. For devices made from thin films deposited at higher oxygen flow rates (15%, 25%, and 35%), the I-V curves became more and more non-linear. Interestingly, devices based on the film deposited at the oxide target mode ($>40\%$ O_2 flow ratio) showed resistive switching phenomenon (hysteresis IV curves) that were not found in films prepared at the metallic target mode. For example, Fig. 4(b) displays the typical forming and subsequent 10 switching cycles from the device based on films sputtered with 50% O_2 flow ratio. After electroforming at $-1.5\ \text{V}$, the devices could be repeatedly RESET to the high resistance state (HRS) at around $1.3\ \text{V}$ and be SET back to the low resistance state (LRS) at

FIG. 4. Electrical behavior for single layer devices made from TiO_x prepared with different oxygen flow ratios. (a) I-V curves from single layer devices based on films prepared with O_2 flow ratios varied from 3% to 35%. A transition from linear to non-linear behavior is observed. Insets show the geometry and a scanning electron microscopy (SEM) picture of our typical device in this study. (b) Typical I-V curves of the forming step and subsequent 10 switching cycles from a single layer device based on the film deposited with 50% O_2 flow ratio. Bipolar resistive switching behavior is observed in this device. The black arrows indicate the switching directions.

about $-0.6\ \text{V}$. The ON- and OFF-state resistances read at $-0.1\ \text{V}$ were 648 ± 171 and $230\,200 \pm 57\,412\ \Omega$, respectively. The variation in ON and OFF resistance can be further improved by inserting one more transition oxide layer as demonstrated earlier.²² These operating parameters were similar to those for a single layer device fabricated with a TiO_2 film sputtered from a ceramic target, confirming the stoichiometry of the thin film deposited at the oxide target mode. The transition from Ohmic to rectifying and to memristive behavior is attributed to the evolution of oxygen vacancy concentration at different deposition conditions. At low O_2 flow ratios, the thin films were more oxygen deficient, which means the concentration of conductive oxygen vacancies was high enough to enable Ohmic contacts between the oxide and the Pt electrodes. However, gradually increasing the O_2 ratio resulted in a decreased concentration of oxygen vacancies in the thin film and energy barriers at the oxide/Pt interfaces, leading to non-linear IV behavior. Further increase in the oxygen flow ratio depleted the oxygen vacancies in the thin film. After a forming step with a negative voltage sweep, conducting filaments consisting of oxygen vacancies can be formed from the bottom towards the

top electrodes.²³ Subsequently, the devices can be switched ON and OFF due to the oxide/TE interface modulation through the migration of oxygen vacancies.

Although the TiO_x films deposited at the metallic target mode are not able to be directly used as switching materials, they can be applied into a popular bilayer device structure to engineer the electrical performance of memristive devices. Fig. 5(a) inset shows the structure of a bilayer device with a top layer (TiO_2) sputtered from a stoichiometric ceramic

target and a bottom layer (TiO_x) deposited with reactive sputtering from a Ti target at the metallic mode. Depending on the deposition condition (particularly the oxygen ratio) of this layer, the device behavior changed from bipolar to unipolar switching. With a low O_2 flow ratio (7%, for example), the bilayer device exhibited typical bipolar resistive switching behavior (Fig. 5(a)), with a forming voltage of -5 V and SET and RESET voltages of -1 and 0.75 V, respectively. For the endurance measurement, $1\ \mu\text{s}$ pulses (-1.8 V for SET and 1.6 V RESET operation) were used to switch the device ON or OFF and device resistance was measured at 100 mV between switching events. Figure 5(b) shows the endurance performance of a bilayer device with a geometry shown in the inset of Fig. 5(a). Although the ON/OFF ratio decreased, the device was still switchable after 10^4 cycles. The endurance data are comparable with previous reported results, and it is believed that the complex stable phases in Ti-O system were responsible for its poorer endurance when compared with Ta oxide system.²⁴ When the O_2 flow ratio was increased to higher than 15% for the bottom TiO_x layer (25%, for example), the bilayer device was unipolar (Fig. 5(c)). The device was formed at -6.6 V and had a SET voltage of -3.25 V (or 2.9 V) and a RESET voltage of -1.4 V (or 1.7 V). The change from bipolar to unipolar switching behavior was again due to the concentration of the oxygen vacancies in the bottom oxide layer. With a lower oxygen flow ratio, the produced bottom TiO_x layer contained large amount of oxygen vacancies, contributing to an Ohmic contact at the BE/ TiO_x interface and a strongly asymmetric oxygen-rich/oxygen-deficient structure in the bilayer structure that has a well-defined bipolar switching polarity.¹² On the other hand, when the bottom TiO_x layer was prepared with higher oxygen flow, the BE/ TiO_x interface was no longer Ohmic (as shown in Fig. 4(a)). With two rectifying oxide/metal interfaces, the switching was likely due to Joule heating that led to unipolar behavior, as has been observed recently in the TaO_x system.²⁵

In summary, we have studied the reactive sputtering deposition of TiO_x thin films under different O_2 flow ratios. The target changed from a metallic mode to an oxide mode when the O_2 flow ratio was increased beyond a certain value. Consequently, the chemical composition of the deposited TiO_x thin films was different as revealed by XPS analyses. Single layer devices made from these thin films exhibited different electrical characteristics, changing from Ohmic to rectifying to memristive behavior with the increase of oxygen flow. Furthermore, we applied the reactive sputtering deposited TiO_x thin film in a bilayer memristive device structure and discovered a bipolar to unipolar transition with increase of oxygen flow during thin film preparation. The current observation suggested a simple approach to engineer memristive device behavior through tuning the chemical composition of the switching layer(s).

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FIG. 5. Electrical behavior for double layer memristive devices with TiO_x as the base layers. (a) Typical bipolar resistive switching I-V curve from the bi-layer device with the base layer prepared under an O_2 flow ratio of 7%. (b) Endurance data tested using $1\ \mu\text{s}$ duration pulses for device in (a). (c) Typical unipolar resistive switching I-V curve from the bi-layer device using the base layer prepared with 25% O_2 flow ratio. The black arrows indicate the switching directions. The insets illustrate the schematic of the bi-layer structure in this study.

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