Bipolar resistive switching on TiO2/Au by conducting Atomic Force Microscopy

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Abstract

In this work we present a Conducting Atomic Force Microscopy (CAFM) study of TiO_2 thin films that display bipolar resistive switching behavior. Samples were synthesized by reactive sputtering after a lithography process to obtain the bottom Au electrodes on a SiO_2/Si substrate. Pt and Pt-Ir coated tips were used for CAFM measurements. We compare these results with I-V characteristics of the same device with Al top electrodes in a crossbar pattern. We demonstrate the existence of two stable resistive states and the bipolar nature of the switching through current-voltage CAFM measurements, discussing the possible transport and switching mechanisms.

The development of innovative materials and devices based on new phenomena is required in order to continue the pace of miniaturization, speed and power consumption necessary for current Random Access Memory technologies [1]. Non-volatile memories based on the phenomenon of Resistive Switching are a possible candidate for this application. Resistive Switching (RS) is a physical phenomenon in which a dielectric suddenly changes its resistance under the action of a strong electric field or current. The change of resistance is non-volatile and reversible. It is usually studied in capacitor-like structures, where a voltage or current is applied to an oxide insulator sandwiched between two metallic electrodes. Many oxides exhibit this phenomenon; in particular TiO_2 has been a very popular choice for RS devices since memory – resistor (memristor) capabilities were demonstrated [2,3].

In this work we present a comparison between CAFM and device performance of RS measurements based in TiO_2 thin films. We demonstrate the existence of two stable resistive states and the bipolar nature of the switching. We discuss the forming and switching mechanisms based on the creation and relocation of oxygen vacancies in the film along nanofilaments that connect regions close to the electrodes [4,5].

1. Experimental

Amorphous TiO_2 films were deposited on 1 μm-SiO_2/Si substrate by DC reactive sputtering, at 300 W under 7.5 mTorr of Ar and O_2 with a 3/1 flow ratio, respectively. Previous to the titania deposition, Au/Cr bottom electrodes were defined by UV lithography and deposited by DC sputtering, where the 20 nm Cr layer ensures the adherence of the 60 nm Au layer over silicon dioxide.

After the TiO_2, Al top electrodes were deposited in the same way as the Au ones, creating crossbar devices of different lateral sizes, ranging between 5 and 50 μm (see Figure 1(a)). The TiO_2 film thickness was controlled by the time deposition, and confirmed by optical profilometry and Atomic Force Microscopy (AFM) topography. In this work we studied films with 54 nm and 17 nm thickness (named as T54 and T17 respectively).

CAFM experiments were performed in a MFP-3D Asylum AFM in air at room temperature, using Pt coated silicon tips over the exposed TiO_2 surface over the Au bottom electrode, which was contacted to a DC potential and the conducting tip was grounded. Thus, the Pt AFM tip becomes a nanoscale top electrode at each spot where the current-voltage (I-V) curves were performed. Samples were cleaned with ethanol and acetone and heated to 200 °C before the experiments. The Au/TiO_2/Al crossbar devices were also studied performing I-V cycles using a Source Measuring Unit (SMU) Keithley SCS-4200 connected to a Probe Station Wentworth Pegasus S200 within a faraday box, also operating in air at room temperature (see Figure 1 (a)). An optical image of a sample, during CAFM scan, and the scheme of the electric circuit for the samples are shown in Figure 1(a) and its inset respectively.

2. Results and discussion

Both in the CAFM as in the crossbar devices measurements, a previous forming process is necessary to observe the RS hysteresis. For the crossbar cells with Al top electrodes (Al/TiO$_2$/Au devices), T54 was formed successfully with positive bias (~15 V) (see Inset of Figure 1 (b)), while a negative bias forming produced no repeatable behavior.
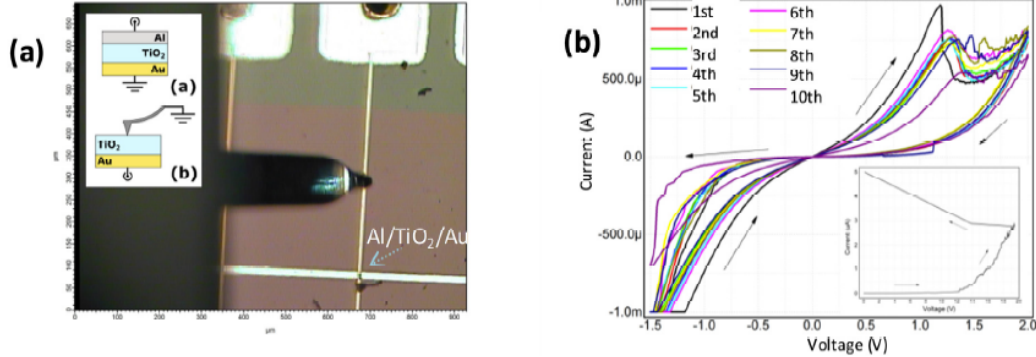

Figure 1: (a) Optical image of the CAFM tip over the TiO$_2$/Au pads during measurements. Bottom electrode Au paths are visible through the transparent TiO$_2$ layer. An Al/TiO2/Au cell is also present. Inset: electrical connection used for IV measurements in the crossbar array (a) and CAFM measurements of Pt-tip devices (b). (b) Typical IV curves for the T54 Al/TiO$_2$/Au crossbar in 10x10μm^2 electrodes. Inset: forming curve for T54 Al/TiO$_2$/Au.

However, it was not possible to form the T17 sample for neither positive nor negative bias. An irreversible breakdown was obtained as soon as current started flowing, or they were found in low resistive (LR) state, and it was not possible to reset them. This effect would be related to the low thickness and high roughness of the film, providing several regions where electrical breakdown would be easier to occur. For the CAFM measurements, the forming consisted on a negative bias sweep from 0 V to -8 V for T54 and from 0 V to -5 V for T17, depending of the thickness (Insets of Figures 2(a) and 2(b)).

After the initial electroforming process on pristine samples, we performed I-V curves to study the devices. Figures 1(b) and 2 show typical I-V curves for these samples. In all cases we can observe traces of hysteresis.

Figure 1(b) shows typical I-V curves for the T54 crossbar device after the forming process (the inset Figure 1(b)). Sweeps were performed between -1.5 V and 2 V, showing a high resistive (HR) state at the beginning of the negative branch and turning into a LR state before reaching -1.5 V, keeping the LR state at the positive branch, up to ~1.2 V, where switches again to the HR state.

The CAFM voltage sweeps were performed between -4 V and +4 V, with 4 mV steps, (-6 V and 6 V, with 6 mV steps) for T17 (T54). Initially, the sample exhibits a high electrical resistance until a threshold negative voltage is reached (V$_{SET}$), becoming more conductive after V$_{SET}$. This change is reversed after completing the cycle for positive voltage. The V$_{SET}$ is (-3.0 ± 0.1) V for T17 and (-5.3 ± 0.2) V for T54. This process does not scale down with the film thickness, so it would not be only determined by the breakdown electric field of an homogeneous material, suggesting there must be other parameters involved as heterogeneous regions and the voltage pulse rise time influence during forming. Unlike the T54 crossbar device curves, which are crossing and quite symmetric, the CAFM curves exhibit the strong rectifying properties.

For CAFM measurements, repeatability and stability were higher in T17 than in T54. At all of the sites where the I-V curves were performed, showed the same switching pattern and the same successful forming procedure. On the other hand, the Pt-tip contact for T54 showed a lower performance with some sites not being able to produce I-V curves with hysteresis, and having to change the forming strategy to obtain the same results in different sites. For this sample, some conduction starts to appear for positive bias after several cycles. In contrast, the T54 crossbars measurements resulted in a much better performance.

It is worthy to note the differences observed in the electric transport behavior between CAFM measurements and the ones made on T54 crossbars devices, respectively the rectifying characteristics against the symmetry in the I-V curves. This would be originated in the metal-oxide interface, Al/TiO$_2$ and Pt(AFM tip)/TiO$_2$, at the top electrode.

Oxygen vacancies in TiO$_2$ act as n-type dopants, rendering the TiO$_2$ more conductive in the region where it has been locally reduced [6-8]. It is a well-known fact that TiO$_2$ can lose oxygen relatively easy, resulting in the formation of oxygen vacancies both in bulk and at the surface [5,9]. When a positive voltage is applied (over the bottom electrode) for the first time, oxygen vacancies distributed in the bulk move toward the Al/TiO$_2$ interface to gather together eventually forming a conductive path composed of TiO$_{2-x}$ that percolates through the entire width of the sample. On the other hand, if negative voltage is applied initially, oxygen vacancies are attracted to the bottom electrode and oxygen ions are rejected rendering the TiO$_2$ more insulating [4]. Therefore the forming procedure could be also critical for the electric transport behavior during the RS regime.
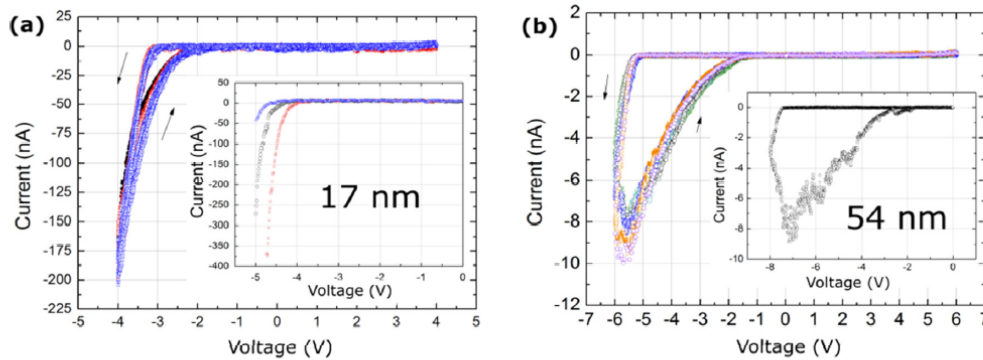
Figure 2: Typical I-V curves of CAFM measurements for (a) T17 and (b) T54. Insets (a) and (b): The respective forming curves for CAFM measurements of T17 and T54.

For CAFM results, after the forming process is completed, the reproducibility of the I-V during the voltage cycling (see Figure 2 (a) and (b)) reveals the existence of two resistive states possibly associated to the formation and rupture of the conductive path formed during the initial steps. It is interesting to see that given the strong rectification produced by the junction, which can be seen from Figures 2 (a) and (b), when the junction is reverse biased, the main voltage drop takes place in the junction and very little in the bulk. For this reason it would be necessary to reach higher voltages to induce the breakdown for the forming to occur in the case of positive bias. In the case of the crossbar devices the applied electric fields could induce the migration of oxygen vacancies increasing or decreasing the thickness of an aluminum oxide layer which would allow to "tune" the Schottky barrier at both interfaces [10].

4. Conclusions

In this work we have explored the RS response of TiO_2 thin film devices using two approaches, first Conducting tip Atomic Force Microscopy using Pt tips and second by means of a source measure unit contacted through micrometer sized Al electrodes. We were able to investigate the switching capabilities of the devices and speculate on the possible forming and switching mechanism of the samples, depending on the metal and size of the top electrode for different thicknesses of the TiO_2 film. The CAFM measurements for T17 showed a very repeatable behavior that clearly contrasted with the T17 crossbar devices results, suggesting that it would be possible to improve the devices performance and sort out the appearance of defects related with the thickness of the films by reducing the electrode size. Within this scenario, it seems promising to conduct further measurements to investigate endurance, different forming strategies, pulsed I-V sweeps, and accumulation.

Acknowledgements

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