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The influence of copper top electrodes on the resistive switching effect in TiO$_2$ thin films studied by conductive atomic force microscopy

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Titanium dioxide thin films (30 nm) are deposited on platinized substrates by atomic layer deposition and locally studied by conductive atomic force microscopy showing repetitive bipolar resistive switching. Experiments using macroscopic copper top electrodes, which are electroformed, bipolar switched, and removed again from the TiO$_2$–Pt stack, prove the formation of local conductive filaments with bipolar switching properties. The localized filaments can be switched repetitively with a resistance ratio of 30. Our findings underline that Cu diffusion and the formation of filaments are the major mechanism for the resistive switching in Cu/TiO$_2$/Pt cells. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3167810]

Resistance random access memory (ReRAM) has been intensively studied due to its great potential of nonvolatility, low power consumption, high scalability, multibit storage, and CMOS compatibility.[1] A large variety of materials have been reported for their resistive switching behavior, e.g., chalcogenides such as Ag$_2$S [2] and Ge$_x$Se$_{1-x}$,[3] Cu$_2$S,[4] transitions metal oxides, such as NiO,[5] TiO$_2$,[6,7] WO$_3$,[8] Cr-doped SrZrO$_3$,[9,10] SrTiO$_3$,[11,12] and even SiO$_2$.[13–15] Resistive switching materials are characterized by the fact that the resistance can be toggled between a low resistance state (LRS or "ON") and a high resistance state (HRS or "OFF") by applying a suitable electrical voltage to the metal-insulator-metal (MIM) configuration. The currently most discussed switching mechanism is the formation and rupture of filaments between the top and bottom electrodes. This effect is either bipolar, where one polarity is used to switch in the LRS and the opposite polarity to switch back into the HRS or the effect is unipolar, which means the SET and the RESET process takes place at different amplitudes of the same polarity (positive or negative). The nature and composition of such conductive paths are still under discussion, but can be classified into two categories, if the switching effect is of bipolar nature. First, anion migration in transition metal oxides deposited between two inert metal electrodes (e.g., Pt) and second cation migration (e.g., Cu, Ag) in chalcogenides, WO$_3$, and SiO$_2$ thin films.[1] In our previous work we observed unipolar as well as bipolar resistive switching in TiO$_2$ thin films deposited with atomic layer deposition (ALD) in combination with Cu electrodes.[16] We now implement conductive atomic force microscopy (CAFM), where an AFM tip serves as top electrode, as a powerful technique to study the local conductivity, as shown by Szot *et al.*[11] who reported on single conductive spots with diameters down to 1 nm in SrTiO$_3$ single crystals.

This article aims at the study of filamentary switching behavior formed under a Cu top electrode by means of scanning probe microscopy. Thin films of 30 nm TiO$_2$ were deposited directly on Pt(100 nm)/TiO$_2$/SiO$_2$/Si substrates by ALD at 240 °C using titanium tetra-iso-propoxide,

Ti[OCH$_2$(CH$_3$)$_2$]$_4$, dissolved in ethylcyclohexane as precursor and water as oxidant. The detailed process parameters are described by Watanabe *et al.*[16] X-ray photoelectron spectroscopy analysis revealed a stoichiometry of titanium to oxygen of nearly 1:2 and transmission electron microscopy (TEM) studies showed a nanocrystalline structure (not shown here). Copper top electrodes of 500 μm in diameter and 100 nm thickness were deposited by evaporation and lift-off technique.

First, the cell was electroformed by applying a positive potential to the Cu top electrode and set to the LRS. Figure 1 illustrates typical $I(V)$ sweeps done with an Agilent B1500A. The transition from the HRS to the LRS takes place at about +0.8 V whereby the current was limited to 300 μA in order to prevent destruction. For the RESET a negative potential of −1.5 V was applied.

The CAFM measurements on samples without top electrode were conducted at 10^{-5} mbar, at room temperature with a JEOL JSPM-4210A using a Pt coated tip, which is grounded. A sketch of the CAFM measurement setup is shown in Fig. 2(a). A topography scan of the surface (500 × 500 nm^2) is shown in Fig. 2(b). The roughness was measured to 0.423 nm (rms). Applying the Pt tip on an arbitrary location of the surface, the current-voltage characteristic of such a symmetric Pt/TiO$_2$/Pt system [Fig. 2(a)] showed very small resistive switching. The current measured in HRS and
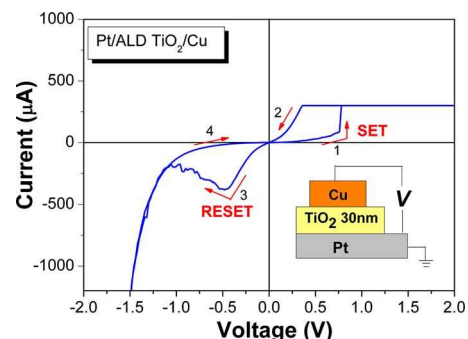

FIG. 1. (Color online) Typical switching characteristics of a Cu/TiO$_2$/Pt cell.

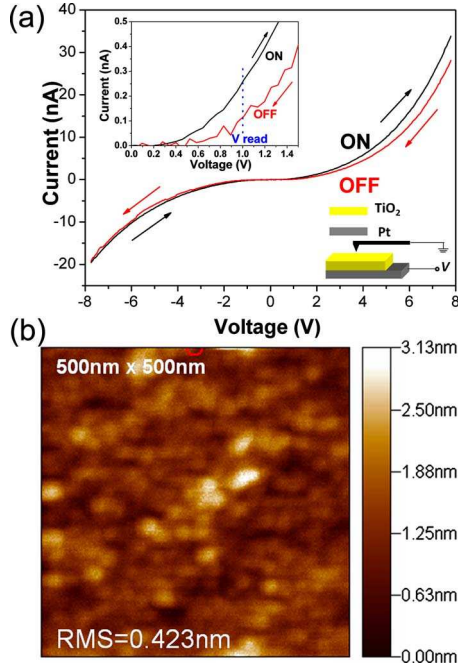a)Electronic mail: c.kuegeler@fz-juelich.de.

FIG. 2. (Color online) (a) Local current-voltage conductive AFM measurement on a pristine Pt/TiO_2 (30 nm) surface. The inset shows the measurement setup and the current-voltage characteristic between 0 and 1.5 V. (b) The topography of the studied area (500×500 nm^2) exhibit a roughness of 0.423 nm.

LRS at 1 V were only 120 pA and 264 pA, respectively. Figure 3 illustrates the electrical data of the CAFM experiments, where first a 500×500 nm^2 large square was scanned with $V_{read} = 1$ V showing no significant conduction [Fig. 3(a)]. Scanning the center region of 200×200 nm^2 with -7 V decreases the resistance of the TiO_2, which is proven by a subsequent read scan [Fig. 3(b)]. Better conductive regions (light area) with a grain boundary structure are observed without a noticeable change in the surface topography. Scanning the center region with $+7$ V changes the material back to the HRS [Fig. 3(c)]. The local transition
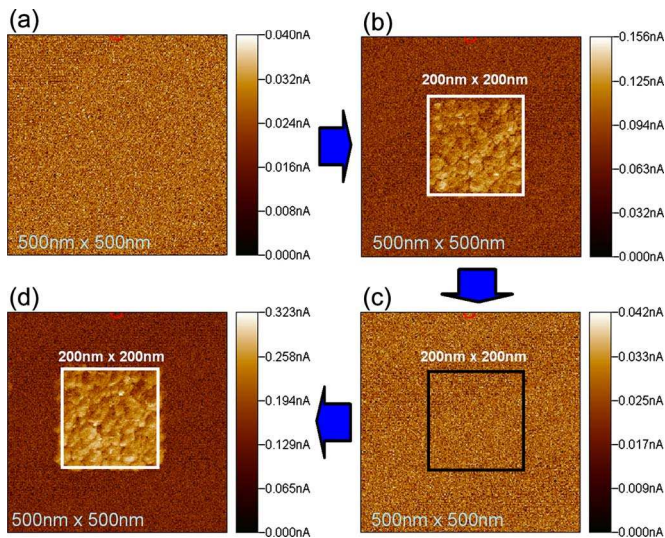

FIG. 3. (Color online) CAFM measurement on an as-deposited ALD TiO_2 film. The current images with $V_{read} = +1$ V are always in the same area (500×500 nm^2) after subsequent SET and RESET operations in the center area (200×200 nm^2). [(a)–(d)] indicate subsequent OFF-ON-OFF-ON states after the SET or RESET operation.
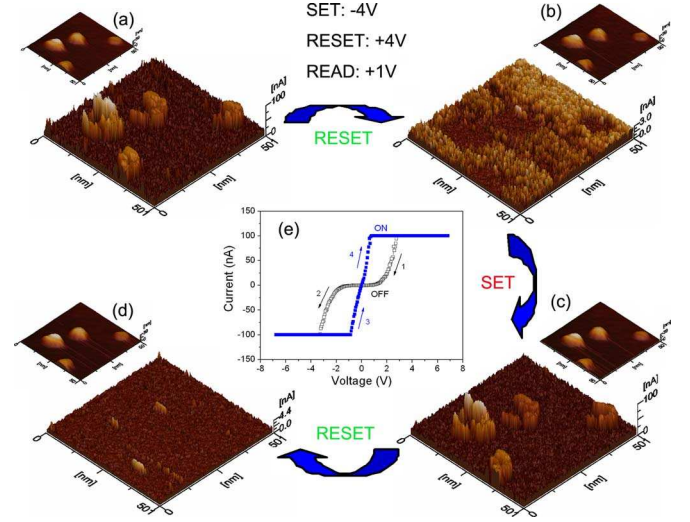

FIG. 4. (Color online) CAFM measurement in an area where first a Cu top electrode was deposited then switched to the LRS and finally etched away again. The sequential read out cycles after SET or RESET show the reversible resistive switching (a) LRS, (b) HRS, (c) LRS, and (d) HRS. The small figures show the corresponding topography. (e) $I(V)$ hysterics of a single filament by using the AFM tip as top electrode. SET from -7 to $+7$ V (blue), RESET from $+7$ to -7 V (current compliance=100 nA).

between the two resistances can be repeated several times [Fig. 3(d)] with a resistance ratio larger than 5, at total currents of several hundred picoampere at LRS.

The second set of CAFM experiments concentrates on the influence of Cu top electrodes on the switching mechanism. After switching a $Cu/TiO_2/Pt$ stack into LRS the top electrode was removed by wet etching in 0.1 mol $FeCl_3$ (90 s). Time of Flight Secondary Ion Mass Spectrometry analysis proved that already after Cu deposition and electroforming a certain amount of Cu migrated into the TiO_2. A CAFM scan of 500×500 nm^2 revealed hillocks with a diameter up to 100 nm and a height up to 40 nm randomly distributed. Moreover, these spots were always conductive and could be repetitively switched from LRS to HRS and vice versa [Figs. 4(a)–4(d)]. The small pictures show the corresponding topography. The large pictures depict current images recorded with $V_{read} = +1$ V as "read out" of the resistance in area. Between each read out cycle the whole area was scanned with $V = \pm 4$ V for SET and RESET scanning. The conductive spots always appear at the same positions [compare Figs. 4(a) and 4(c)] without any change in the topography. By moving the AFM tip to one of the better conductive locations, the shape of continuous $I(V)$ sweeps [Fig. 4(e)] were comparable to those observed on cells with Cu top electrodes (Fig. 1). The experiments support the idea that the formation of filaments is responsible for the resistive switching effect in $Cu/TiO_2/Pt$ cells. However, the required switching voltage to SET into LRS (2 V) under CAFM is larger than observed on macroscopic pads (<1 V). This is attributed to the formation of an adsorbate layer between the Pt tip and the TiO_2 layer, which causes an additional potential drop.[17,18] Compared with the $I(V)$ characteristics of pristine TiO_2 [Fig. 2(a)], a clearly more pronounced switching effect a higher resistance ratio was observed. This indicates a significant contribution of Cu diffusion to the resistive switching effect in the $Cu/TiO_2/Pt$ MIM structures.

In conclusion, titanium dioxide thin films were prepared by ALD on Pt electrodes and the electrical properties were analyzed by CAFM measurements. From the results we conclude that probably two mechanisms are involved in resistance switching if copper is incorporated. A minor part is caused by the inherent conduction due to oxygen vacancies of the TiO_2 film. The majority is attributed to the diffusion of copper and the formation of conductive filaments. This is proved by CAFM measurements, which reveal bipolar resistive switching with a HRS/LRS ratio of about 30.

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