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Coexistence of Bipolar and Unipolar Resistive Switching Behaviors in a Pt/TiO_2/Pt Stack

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Bipolar resistive switching (BRS) as well as unipolar resistive switching (URS) behaviors in Pt/27 nm thick TiO_2/Pt stacks were investigated. Depending on the current compliance during the electroforming process, either BRS or URS was observed. With a lower current compliance (<0.1 mA) during electroforming, asymmetric current-voltage curves showing BRS were observed in the voltage range -1.6 to $+1.1$ V, while with a higher current compliance (1–10 mA) URS behavior was observed. Furthermore, the permanent transition from BRS to URS was investigated by applying a voltage with a higher current compliance (~ 3 mA).

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The resistive switching behavior of transition metal oxide (TMO) materials is a very attractive subject of scientific and technical research. TMOs, including TiO_2 and NiO, show bistable resistive switching behavior, i.e., reversible switching between a high-resistance state (HRS) and a low-resistance state (LRS) achieved by the applied voltage.[1-3] This resistive switching is classified into unipolar resistive switching (URS) because the switching behavior hardly depends on the polarity of the applied voltage, so that both the SET switching (HRS→LRS) and the RESET switching (LRS → HRS) occur regardless of the polarity of the applied voltage. The URS of TMOs can be potentially applied in resistive switching random access memory (ReRAM) devices due to its high off/on ratio and the low inherent scaling problem compared to capacitance-based RAMs.[4] However, a high current flow of a few tens of mA, is necessary for the RESET switching of the URS, thus hindering the scaling down of devices. In addition, the RESET current is not proportional to the stack area; for instance, the scaling down of a cell size from 100 to 0.01 μm^2 results in a decrease of the RESET current less than one order of magnitude.[5] Therefore, fabricating a resistor stack with a smaller area does not guarantee a low enough RESET current for the scaling down of devices. It is therefore very important for the application for resistive switching RAM to search for solutions able to reduce the RESET current.

Bipolar resistive switching (BRS), showing a dependence of the resistive switching on the polarity of the applied voltage, has been reported in perovskite-type oxides including $SrZrO_3$,[6] $Pb(Zr_x,Ti_{1-x})O_3$,[7] and $Pr_{0.7}Ca_{0.3}MnO_3$.[8] Another very interesting aspect of the BRS is that the RESET switching takes place with a current of several hundred microamperes or even less.

In this paper, we report on the switching behavior of polycrystalline, sputter grown TiO_2 thin films between Pt electrodes. This stack shows BRS as well as URS relying on current compliance during electroforming, which is an interesting aspect because the binary TMOs and the perovskite-type oxides have been considered to show only URS and BRS, respectively. Furthermore, we report the activation of the BRS behavior with increasing applied voltages as well as currents and the transition from the BRS mode to the URS mode.

A 27 nm thick blanket TiO_2 thin film was deposited on a platinized Si-wafer at room temperature by reactive sputtering. The details of the TiO_2 film have been reported elsewhere.[9] For resistive switching measurements, circle-shaped Pt top electrodes (TE) with a radius of 100 μm were formed on the blanket TiO_2 film by dc sputtering using a lift-off process. The resistance of the as produced Pt/TiO_2/Pt stack is in the gigaohm range at 1 V showing good insulating properties. Electroforming, a necessary initial process for URS as well as BRS, was carried out by applying a positive voltage of about 5 V on the TE with setting a proper current compliance critical to prevent permanent dielectric breakdown of the as produced stack. The current compliance during the electroforming decides on the resistive switching mode. Namely, setting a high current compliance (>1 mA) leads to URS and setting a low compliance (<0.1 mA) leads to BRS. However, in the compliance range of 0.1–1 mA it is hard to define a dominant resistive switching mode because both URS and BRS can be activated. The current-voltage (*I-V*) measurements were carried out using an HP4155A at room temperature with a proper current compliance.

The *I-V* curves of TiO_2 undergoing BRS are shown in Fig. 1a, measured with a current compliance of 1 mA and electroformed beforehand by applying a positive voltage on the TE with a current compliance of 100 μA. Switching between HRS and LRS can be observed within the current range (-1 to 1 mA) proving the large reduction of the switching current compared to the URS mode.[2,9] By decreasing the applied voltage from a starting voltage of 1.1 V, the current decreases along the path denoted by (A) suggesting that the SET switching takes place by applying the starting voltage. After passing the origin point, the current increases negatively along the path (B). Around -1 V, the RESET switching starts with a gradual increase of resistance in the *I-V* curve until the current compliance (1 mA) is reached at about 1.6 V. This is different from the URS mode of TiO_2 for which the RESET switching is accompanied by a steep negative differential resistance phenomenon. Increasing the applied voltage to positive values (paths C and D) the SET switching takes place again around 1 V in the path (D). Both HRS and LRS are stable at a read-out voltage of 0.3 V, for which the resistance ratio of HRS to LRS is about 5 as can be seen in Fig. 1b. Note that the resistance values of the LRS with respect to the number of cycles are less scattered than those of the HRS in Fig. 1b. Figure 1a shows that the *I-V* curve in the LRS is almost symmetric as long as the applied voltage is less than the RESET switching voltage and the current level is quite high even in the HRS compared to the as-

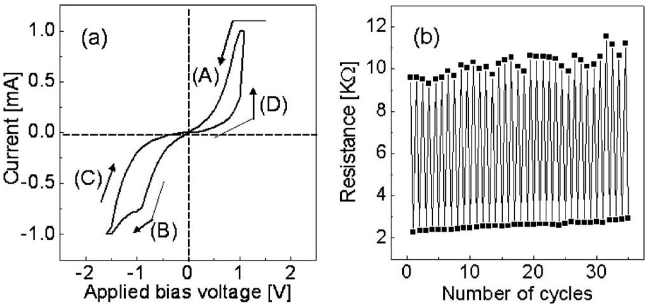

Figure 1. (a) *I-V* curve of a Pt/TiO_2/Pt stack with a current compliance of 1 mA showing asymmetric switching in the BRS mode. (b) The resistances in the HRS and LRS at a read-out voltage of 0.3 V as a function of the number of cycles.

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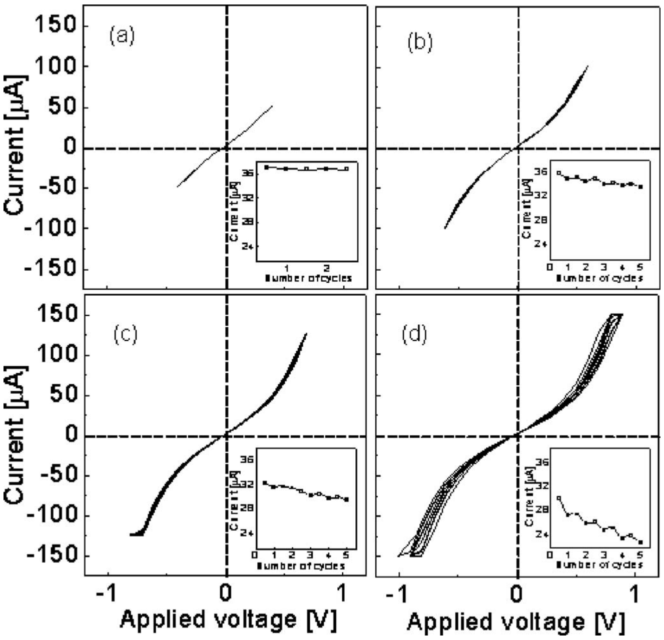

Figure 2. *I-V* curves measured with increasing current compliance of (a) 50, (b) 100, (c) 125, and (d) 150 μA. The insets show current values read-out at 0.3 V as a function of the number of cycles, the open squares are from the decreasing voltage sweeps and the full squares from the increasing voltage sweeps.

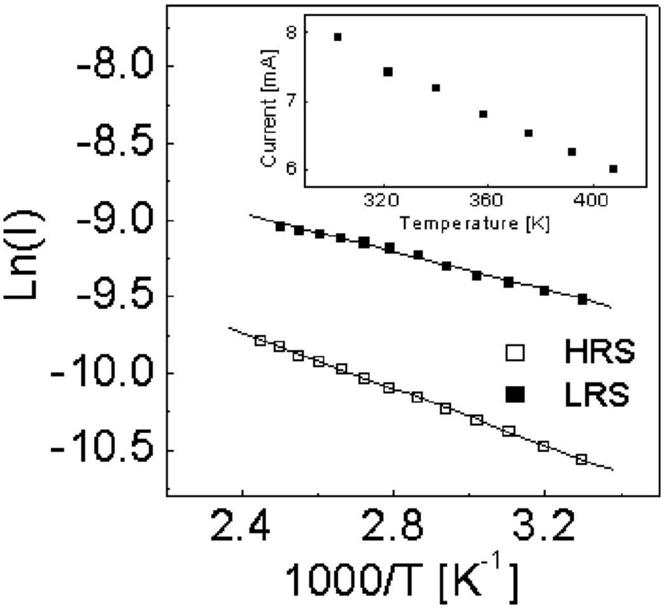

Figure 3. Measured temperature dependence of the currents at 0.1 V in the BRS mode. The open and full squares denote the HRS and LRS, respectively. The inset is the temperature dependency of the current in the LRS of the URS mode at 0.1 V.

produced Pt/TiO_2/Pt stack, i.e., before electroforming, suggesting that the *I-V* behavior is controlled by a different, newly formed conduction paths in the TiO_2 insulating matrix as frequently suggested for the URS mode in the literature.[2,9]

Even after the electroforming with a current compliance of 100 μA current higher than the electroforming current should be applied to activate the BRS. Figures 2a-d show *I-V* curves measured after electroforming with various current compliances (50, 100, 125, and 150 μA, respectively) before the activation of the BRS. With increasing current compliance, that is, approaching an applied voltage of 1 V corresponding to the SET and RESET switching voltages shown in Fig. 1a, hysteretic *I-V* behavior as well as a change from linear to nonlinear *I-V* behavior becomes prominent. That means that a certain minimum current ($\cong 1$ mA) must be provided for the activation of the BRS mode. This is unlike the URS mode for which switching to the LRS immediately takes place after the electroforming regardless of the provided current after the electroforming.

Figure 3 shows the temperature dependence of the currents in the BRS mode in an Arrhenius plot suggesting thermally activated conduction behavior in both HRS and LRS with activation energies of 79 and 54 meV, respectively. Ti interstitial (Ti_i) ions can serve as quadruple shallow donors and are fully ionized at room temperature. Ti_i is energetically favorable in a TiO_2 matrix because of its non-close packed crystal structure having many vacant octahedral sites.[10] Recent results on defect formation energy calculations in anatase TiO_2 have shown that the Ti_i formation energy is very low or even negative, implying that the formation is spontaneous.[11] In addition, band calculations on TiO_2 containing Ti interstitials have shown that the corresponding electrons are localized in the vicinity of their interstitials, a behavior characterized as large polaron and described as band conduction with a lowering of the conduction band minimum. Assuming a spatial distribution of these Ti_i in filament-like regions connecting TE and BE, the electronic transport in the conduction band along these channels might be a possible mechanism in TiO_2. Then, the measured activation energies for the conduction in both HRS and LRS may be associated with the activation energies of the mobilities in each state. On the other hand, small polaron conduction, a hopping mechanism, may be another possible mechanism. However, the activation energy of electron hopping in TiO_{2-x} is 0.4 eV, much greater than the experimental values.[12]

The nature of the BRS must be different from that of the URS in the sense that switching in the URS does not depend on the polarity. The URS possibly results from the fuse and antifuse of conduction paths, e.g., due to Joule heat having no polarity. A possible mechanism for the BRS mode may be an electrochemical reaction taking place in the vicinity of the interface (Pt/TiO_2). Kinoshita et al.[13] recently reported experimental identifications of the role of the anode in resistive switching. The authors showed the Pt sputtering effect on the resistance states of NiO programmed by positive or negative voltage, concluding that resistive switching takes place close to the anode. Therefore, it is suggested that electrochemical reactions in both forward and reverse directions, namely cathodic and anodic reactions relying on the polarity of the applied voltage, are involved in the BRS mechanism. The details will be reported elsewhere.[14]

Increasing current compliance gives rise to the transition from the BRS to the URS as demonstrated in Fig. 4. Several continuous voltage sweeps from +3 to −3 V (R → L) and back to +3 V (L → R) were applied with setting a current compliance of 3 mA. Finally, the transition resulted in a linear *I-V* behavior corresponding to the LRS of the URS. After this transition, stable URS behavior is observed in the *I-V* curves as shown in Fig. 5a. The ratio of HRS to LRS is higher than 1000 [see Fig. 5b]. Comparison of Fig. 1a and Fig. 5a shows that the resistance values of both resistance states of the BRS mode are in between those of the URS mode, i.e., the HRS and the LRS of the URS mode show higher and lower resistance values than the HRS and the LRS of the BRS mode, respectively. Furthermore, the temperature dependence of the current in the LRS of the URS shown in the inset of Fig. 3 shows metallic conduction behavior unlike that of the BRS, suggesting that the transition from the BRS to the URS is accompanied by the transition of the conduction behavior, i.e., from the thermally activated behavior to the metallic conduction behavior. For the case of the HRS of the URS, the temperature dependence of the current shows huge scattering. The RESET current of the URS is in the range of 30–50 mA, much higher than that of the BRS (<1 mA). Current compliance during

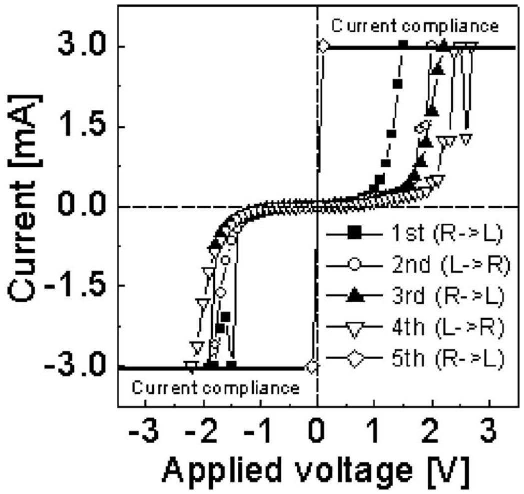

Figure 4. Transition from BRS to URS by applying voltage sweeps with a current compliance of 3 mA. R → L and L → R indicate the voltage sweeps from +3 to −3 V and from −3 to +3 V, respectively.

the SET switching was set to be 1 mA, which is lower than the compliance current for the transition to the URS mode (3 mA) implying that the HRS of the URS is very easily switched to the LRS of the URS even with a low current compliance instead of being changed to be the BRS mode. Therefore, it can be concluded that once the URS mode is activated, the reverse transition, i.e., from the URS to the BRS, is hardly observable.

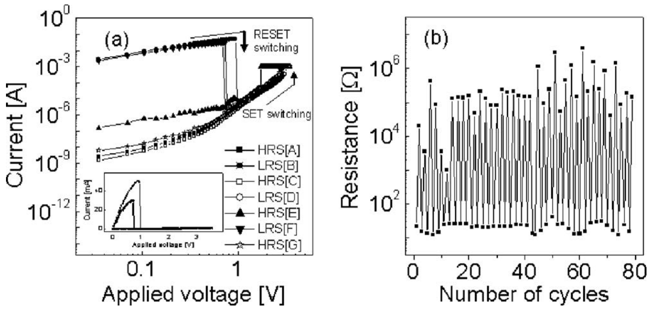

Figure 5. (a) *I-V* curves in the URS mode using a logarithmic scale; the inset shows the same curves using a linear scale. (b) The resistances of HRS and LRS at a read-out voltage of 0.3 V vs the number of cycles.

In summary, stable BRS was observed in Pt/TiO_2/Pt stacks with a current compliance of 1 mA, which is much less than the current compliance value necessary for the URS. The BRS relies on the polarity of the electroforming voltage, suggesting that the switching is related to some polarity dependent property. A model assuming electrochemical redox reactions occurring in the vicinity of the interface between TiO_2 and the anode was suggested to account for this experimental observation. Furthermore, applying a voltage with high current compliance (≥3 mA) triggered the transition from BRS to stable URS.

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