Multilevel unipolar resistance switching in TiO_2 thin films

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We report on multilevel switching behavior in the unipolar resistance switching of TiO_2 thin films. Multiple metastable states were observed during the reset process by measuring *I*–*V* curves. As observed using a conducting atomic force microscope, the multilevel resistance switching was accompanied by decreases in area and in the conductance of the top surface conducting regions. These experimental observations at both the macroscopic and microscopic levels could be explained by using the "random circuit breaker network" model, which is a dynamic bond percolation model.

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Resistance switching (RS) of metal oxides has attracted considerable attention due to its potential applications in nonvolatile memory elements. Multilevel switching is one of the important experimental features that could be applied to future multi-bit memory operations. Multilevel resistance switching has often been reported for bipolar RS materials, such as Cr:$SrZrO_3$, Cr:$SrTiO_3$, and $Pr_{0.7}Ca_{0.3}MnO_3$ thin films.[1-3] An explanation of the multilevel RS using a phenomenological model in which the multilevel switching occurs via charge injection on switching media is given in Ref. 4. However, the basic mechanisms for bipolar RS and its multilevel switching are still controversial.[5]

Compared to bipolar RS, unipolar RS has several advantages in practical memory applications due to its much larger resistance ratio of two metastable states.[6] Understandings on multilevel switching should be more important in unipolar RS. However, both experimental and theoretical reports on multilevel RS in unipolar RS are quite rare. We only know reports on multilevel RS behaviors in NiO films,[7,8] which were used to obtain several states with different resistance values, not to investigate nature of multilevel switching.

In this letter, we report multilevel unipolar RS of Pt/TiO_2/Pt capacitors. By carefully controlling the external bias, we obtained multilevel RS in macroscopic *I–V* measurements. Using a conducting atomic force microscope (AFM), we also observed microscopic changes in the conductance distribution on the TiO_2 surface; during multilevel RS, both the conducting area and the current flow per unit area decrease. Based on the recently proposed random circuit breaker (RCB) network model,[9] we simulated these multilevel resistance switching behaviors. Our simulations could explain both the macroscopic and microscopic experimental data, confirming that multilevel switching in the unipolar RS materials should occur through a percolative rupturing process.

We prepared TiO_2 thin films by thermally oxidizing 40-nm-thick metal Ti thin films that had been evaporated onto Pt/TiO_x/SiO_2/Si (100) substrates; detailed growth conditions have been published elsewhere.[9] After obtaining the TiO_2 films, we used e-beam evaporation with a 46 × 46 μm^2 shadow mask to deposit Pt top electrodes. *I–V* sweep measurements were performed using the Pt top electrodes in a voltage-driven mode with a semiconductor parameter analyzer (Agilent 4155c; Agilent Technologies, Santa Clara, CA). Direct microscopic studies of the bare TiO_2 surfaces, which were open between the Pt top electrodes, were also performed using a conducting AFM (SPA-400; SII Nanotechnology, Chiba, Japan).

Figure 1(a) shows that multilevel RS can occur in a Pt/TiO_2/Pt capacitor. The TiO_2 film experiences the set process, a change from the high resistance state (HRS) to the low resistance state (LRS), at around 1.5 V. It also experiences a reset process, a change from the LRS to the HRS, at a little over 0.43 V. Details of unipolar RS operations can be found elsewhere.[9] Note that by controlling the applied voltage carefully around 0.43 V in the LRS, we could change the resistance of the TiO_2 film to a value between that of the LRS and HRS. This new state was metastable; it could maintain its resistance value until a new external bias was applied with a value near the reset voltage. We could also obtain several metastable resistance states during the reset process, as shown in Fig. 1(a).

We investigated microscopic conductance changes on the bare TiO_2 surfaces using the conducting AFM.[10] The unipolar RS is well known to originate from the forming and rupturing of conducting filamentary channels.[9] The LRS state was emulated by scanning the bare TiO_2 surface while applying a 10 V bias to the conducting AFM tip, thereby creating the conducting filamentary channels.[9] After this forming process, the surface resistance was mapped by scanning with a 0.1 V bias and measuring the conducting current. As shown in Fig. 2(a), we observed some regions with high conducting current, indicating that highly conducting filamentary channels are formed in the LRS. To create a metastable state between the LRS and HRS, we scanned the same TiO_2 area with a bias of 2.5 V, and then mapped the surface conductance. We repeated these measurements; the results are shown in Fig. 2(b)–(d), which show that the conducting channel area decreased during the multilevel RS process.

We also obtained line profiles of the current flowing along line “A” shown in Fig. 2(e). Since the conductance mappings were obtained from the same TiO_2 surface area, changes in the line profiles indicate local conductance changes in the conducting channels. Note that the current density flowing into the local region also decreases during the multilevel RS process.

Two important experimental facts must be stressed. First, the conducting AFM studies were made on the bare TiO_2 surface, while the *I–V* measurements were performed with top Pt electrodes. Second, the effective tip-size limited the resolution of the conducting AFM to approximately 5 nm. Due to convolution effects,[11] it is not clear whether the bright area in Fig. 2(a) originated from one conducting filament with a large diameter or from many conducting filaments of much smaller diameters. Therefore, we must exercise caution in comparing the conducting AFM results to those from the *I–V* measurements.

To better understand the multilevel RS, we performed computer simulations using the RCB network model,[12] which has been applied to explain numerous issues related to unipolar RS, including scaling behaviors and predictability of RESET voltages,[13,14] coexistence with threshold RS,[12] and occurrence of abnormal RS behaviors.[15] This dynamic bond percolation model can describe the formation and rupture of the conducting filaments in terms of the ON and OFF operations of circuit breakers; ON describes a dielectric breakdown whereby the voltage applied to a circuit breaker becomes larger than a threshold value, and OFF describes the recovery of the insulating state by Joule heating whereby the temperature of the circuit breaker reaches a certain value. The simulations were carried out using a 90×30 circuit breaker lattice under the periodic boundary condition. By varying the initial ON and OFF states, we could obtain multilevel RS *I–V* sweeps. Figure 1(b) shows an *I–V* simulation with three intermediate metastable states, marked as P1–P3 between LRS (i.e., P0) and HRS (i.e., P4), which indicates that the RCB network model can explain multilevel RS.

Figure 3(a) shows snapshots of a small portion of the RCB network for the P1-P4 states, where a percolating channel becomes developed in LRS. The thick and thin lines of the networks represent ON (i.e., conducting) and OFF (i.e., insulating) circuit breaker states, respectively. The thick red lines in the network denote the circuit breakers with higher temperatures due to Joule heating. Turning off the hottest circuit breaker in the network changes the configuration of the conducting channels.[16] Figure 3(a) shows its subsequent collapse during multilevel RS.

In Fig. 3(a), the colored areas of the top electrode show the regions in which it touches the conducting paths inside the sample. To explain the conducting AFM data, we calculated the conductance at the top surface of the RCB network for the given snapshot without the top electrode. We then evaluated the current flow at a given point on the top surface by assuming a given applied external voltage on that spot. Figure 3(b) shows the line current profiles calculated along the top surface. Note that these profiles are quite similar to the experimental AFM data shown in Fig. 2(e). As the multilevel RS proceeds, both the area and the current flow of the conducting regions on the top surface decrease.

In summary, we investigated the multilevel resistance switching in TiO_2 films. From the *I*–*V* measurements, we observed intermediate metastable states during reset of the unipolar resistance switching. Compared to conducting AFM studies, we found that both the conducting area and the current flow per unit area decreased during the multilevel RS. These changes at the macroscopic and microscopic levels were explained using the RCB network model. Considering the nature of the percolation process, it would not be easy to control arbitrarily the multi-states of resistance in devices with the capacitor geometry.

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References

1. A. Beck, J. G. Bednorz, C. Gerber, C. Rossel and D. Widmer, Appl. Phys. Lett. **77**, 139 (2000).
2. Y. Watanabe, J. G. Bednorz, A. Bietsch, C. Gerber, D. Widmer, A. Beck and S. J. Wind, Appl. Phys. Lett. **78**, 3738 (2001).
3. A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, Y. Y. Xue and C. W. Chu, Appl. Phys. Lett. **83**, 957 (2003).
4. M. J. Rozenberg, I. H. Inoue and M. J. Sanchez, Phys. Rev. Lett. **92**, 178302 (2004).
5. R. Waser and M. Aono, Nat. Mater. **6**, 833 (2007).
6. S.-E. Ahn, M. J. Lee, Y. Park, B. S. Kang, C. B. Lee, K. H. Kim, S. Seo, D. S. Suh, D. C. Kim, J. Hur, W. Xianyu, G. Stefanovich, H. Yin, I. K. Yoo, J. H. Lee, J. B. Park, I. G. Baek and B. H. Park, Adv. Mater. **20**, 924 (2008).
7. D. C. Kim, S. Seo, S. E. Ahn, D. S. Suh, M. J. Lee, B. H. Park, I. K. Yoo, I. G. Baek, H. J. Kim, E. K. Yim, J. E. Lee, S. O. Park, H. S. Kim, U. I. Chung, J. T. Moon and B. I. Ryu, Appl. Phys. Lett. **88**, 202102 (2006).
8. S. B. Lee, S. C. Chae, S. H. Chang, J. S. Lee, S. Park, Y. Jo, S. Seo, B. Kahng and T. W. Noh, Appl. Phys. Lett. **93**, 252102 (2008).
9. S. C. Chae, J. S. Lee, S. Kim, S. B. Lee, S. H. Chang, C. Liu, B. Kahng, H. Shin, D.-W. Kim, C. U. Jung, S. Seo, M.-J. Lee and T. W. Noh, Adv. Mater. **20**, 1154 (2008).
10. J.-B. Yun, S. Kim, S. Seo, M.-J. Lee, D. C. Kim, S.-E. Ahn, Y. Park, J. Kim and H. Shin, Phy. Stat. Solidi (RRL) **1**, 280 (2007).
11. B. J. Choi, D. S. Jeong, S. K. Kim, C. Rohde, S. Choi, J. H. Oh, H. J. Kim, C. S. Hwang, K. Szot, R. Waser, B. Reichenberg and S. Tiedke, J. Appl. Phys. **98**, 033715 (2005).
12. S. H. Chang, J. S. Lee, S. C. Chae, S. B. Lee, C. Liu, B. Kahng, D. W. Kim and T. W.

Noh, Phys. Rev. Lett. **102**, 026801 (2009).

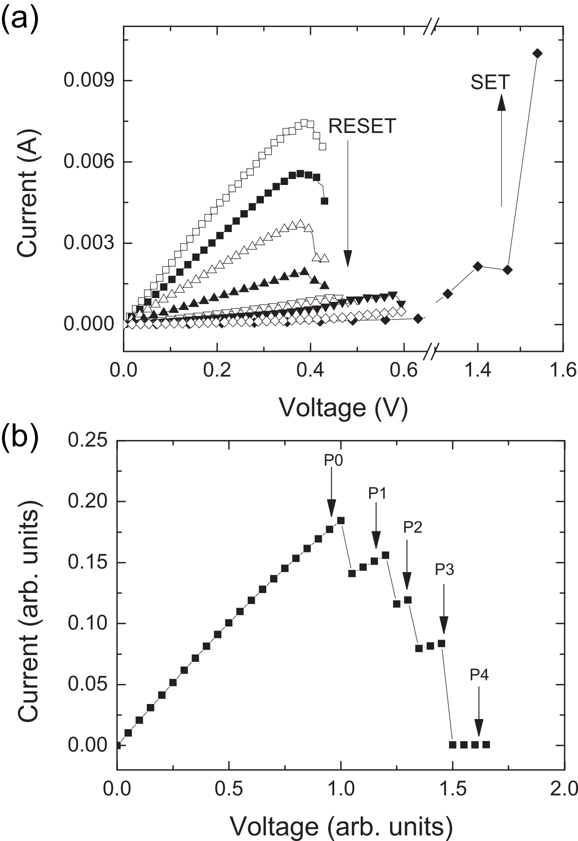
13. S. B. Lee, S. C. Chae, S. H. Chang, J. S. Lee, S. Seo, B. Kahng and T. W. Noh, Appl. Phys. Lett. **93** (21), 212105 (2008).
14. S. B. Lee, S. C. Chae, S. H. Chang and T. W. Noh, Appl. Phys. Lett. **94**, 173503 (2009).
15. C. Liu, S. C. Chae, J. S. Lee, S. H. Chang, S. B. Lee, D. W. Kim, C. U. Jung, S. Seo, S. E. Ahn, B. Kahng and T. W. Noh, J. Phys. D **42**, 015506 (2009).
16. L. de Arcangelis, S. Redner and H. J. Herrmann, J. Phys.(Paris) Lett **46**, 585 (1985).

Figure captions

FIG. 1. Multilevel reset switching behaviors in unipolar resistance switching. (a) Experimental *I*–*V* sweeps for a $Pt/TiO_2/Pt$ capacitor. Successive voltage sweeps of up to 0.43 V yielded multilevel resistance switching with various intermediate states. (b) Simulation results based on the random circuit breaker (RCB) network model. Note that the simulations can explain the existence of several metastable states during the reset process.

FIG. 2. (Color online) Microscopic conductance changes of the TiO_2 surface during the multilevel reset switching process obtained through AFM studies. (a)–(d) Successive conductance mapping images obtained by scanning the same TiO_2 area with a bias of 2.5 V. (b) Line current profiles along the “A.” In repeat scans, both the conducting area and the amount of the current flow per unit area decrease.

FIG. 3. (Color online) Simulation results for multilevel reset switching using the RCB network model. (a) Snapshots of the conducting paths at the metastable stages denoted by P1, P2, P3, and P4 in Fig. 1. The thick and thin network lines indicate ON (i.e., conducting) and OFF (i.e., insulating) circuit breaker states, respectively. The colored areas in the top electrode show the regions in which it contacts the conducting paths inside the sample. (b) Line current profiles along the top surfaces for various resistance states (P1–P4).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Current (A)
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0.003
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0.009
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0.2
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0.6
1.4
1.6
(b)
Current (arb. units)
Voltage (arb. units)
P0
P1
P2
P3
P4
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0.10
0.15
0.20
0.25
0.0
0.5
1.0
1.5
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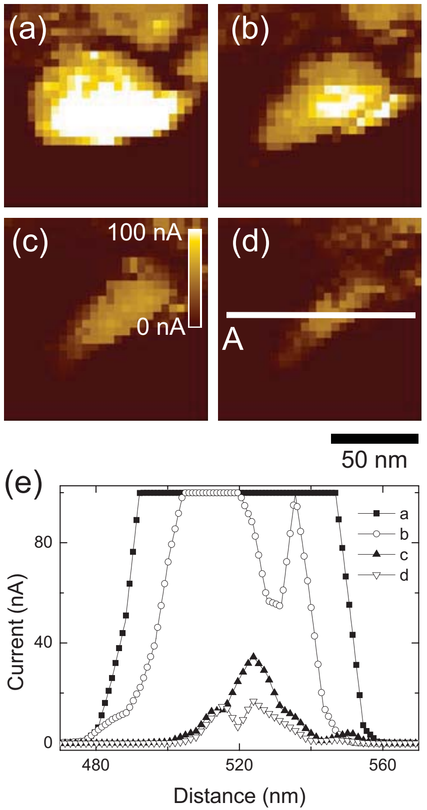
(a)
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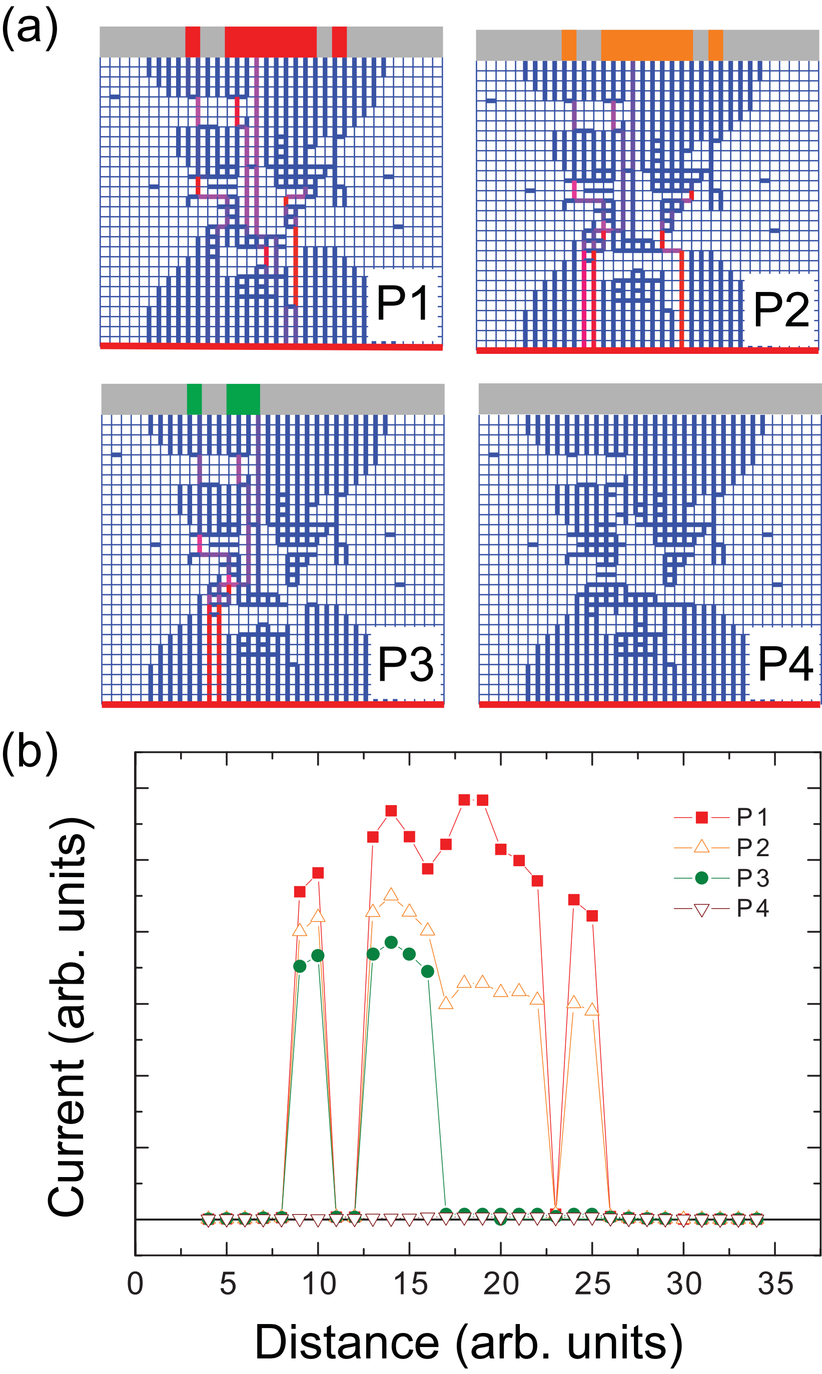
(a)
P1
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Current (arb. units)
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0
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