Conversion from unipolar to bipolar resistance switching by inserting Ta_2O_5 layer in Pt/TaO_x/Pt cells

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We observed unipolar resistance switching in Pt/TaO_x/Pt cells. We could make the cell have the bipolar resistance switching by inserting a stoichiometric Ta_2O_5 layer between Pt and TaO_x layers. Bipolar resistance switching in Pt/Ta_2O_5/TaO_x/Pt cells occurred reliably without applying an external compliance current. With increase in the Ta_2O_5 layer thickness, the current value at the low-resistance state became decreased but the forming voltage became increased. We could explain these intriguing phenomena using the interface-modified random circuit breaker network model. © *2011 American Institute of Physics*. [doi:10.1063/1.3587809]

Resistance switching (RS) refers to reversible changes between two metastable states induced by an external voltage. This intriguing physical phenomenon has recently attracted much attention due to application potentials in nonvolatile memory devices, called resistance random access memory (RRAM).[1–7] In this rapidly expanding field, even simple aspects of RS effects have not been well understood. In addition, most works have focused on experimental observations without a comparison with detailed theoretical predictions. Thus, a fundamental understanding of the underlying physics of RS effects is still far from being completed.

RS effects can be classified into two types based on electric polarity dependence, i.e., dependence on the sign (positive or negative) of the applied voltage.[3,4] In unipolar RS (URS), current–voltage ($I-V$) curves are quite symmetric with respect to the applied bias voltage. Thus, only one kind of polarity is sufficient for URS operation. On the other hand, in bipolar RS (BRS), $I-V$ curves are highly asymmetric, and both polarities are required for BRS operation. Recently, attention in this field has shifted to bipolar RRAM because BRS has several important advantages for device applications, including lower current and smaller switching-voltage fluctuation.[2,3,6]

Here, we report that URS observed in Pt/TaO_x/Pt cells can change to BRS by inserting a stoichiometric Ta_2O_5 layer between the top Pt electrode and TaO_x layers. We also investigate how the characteristics of BRS in Pt/Ta_2O_5/TaO_x/Pt cells can be varied depending on the Ta_2O_5 and TaO_x layer thicknesses. We explain these systematic changes using percolation models.

We fabricated two types of samples, Pt/TaO_x/Pt and Pt/Ta_2O_5/TaO_x/Pt cells, using reactive RF magnetron sputtering. We deposited the TaO_x thin films on Pt-coated Si substrates at 3% oxygen partial pressure and a substrate temperature of 400 °C.[7] For electrical measurements, we prepared 40-nm-thick, 30×30 μm^2 Pt top electrodes using photolithography. A cross-sectional transmission electron microscopy (TEM) image, displayed in Fig. 1(a), shows that the Pt/TaO_x/Pt cells do not have any other layer between Pt and TaO_x. To grow an additional Ta_2O_5 layer between the TaO_x film and the top electrode, we used a plasma-oxidation technique. Before putting the Pt top electrode, we exposed TaO_x films to argon and 10% oxygen plasma at 500 °C. X-ray photoemission spectroscopy studies confirmed the formation of Ta_2O_5 layers.[7] The TEM image in Fig. 1(b) shows the formation of an additional Ta_2O_5 layer just below the top Pt electrode.

We measured the $I-V$ curves using an Agilent HP 4155C semiconductor parameter analyzer. Figure 1(c) shows that URS occurred in the Pt/TaO_x/Pt cell. Its $I-V$ curves are symmetric with respect to the polarity of the bias voltages. For simplicity, we have shown the negative-voltage side only. When we applied a voltage of −6 V on the pristine sample, current flow increased suddenly, and the Pt/TaO_x/Pt cell entered a low-resistance state (LRS). This forming process is known to originate from the soft dielectric breakdown process.[8] When we applied a voltage of −1 V subsequently, the LRS changed to a high-resistance state (HRS). This pro-

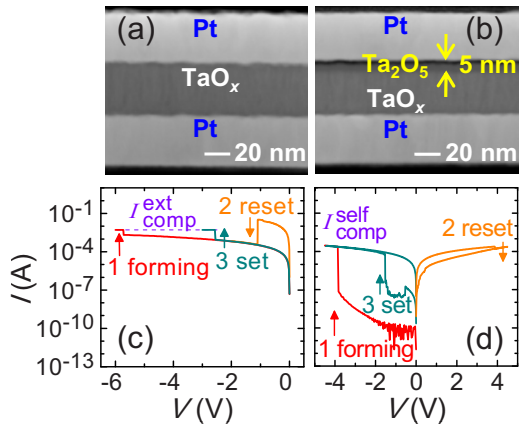

FIG. 1. (Color online) Cross-sectional TEM images of (a) a Pt/TaO_x/Pt cell and (b) a Pt/Ta_2O_5/TaO_x/Pt cell. Current–voltage ($I-V$) curves of (c) URS in Pt/TaO_x/Pt cells and (d) BRS in Pt/Ta_2O_5/TaO_x/Pt cells.

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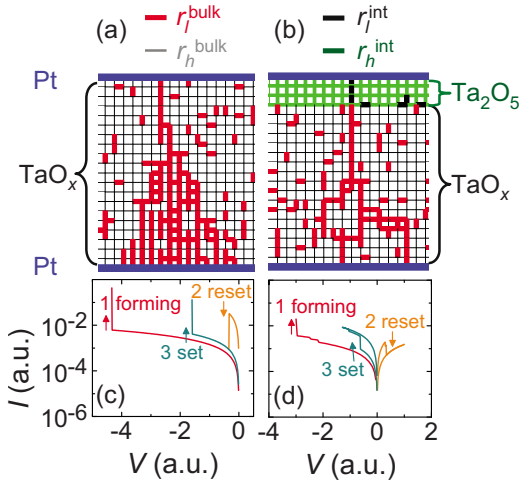

FIG. 2. (Color online) Schematic displays of the circuit breaker networks in (a) the RCB network model and (b) the interface-modified RCB network model. Low-resistance r_l^{bulk} and high-resistance r_h^{bulk} in the bulk region, corresponding to TaO_x, are marked by thin gray and thick red bonds, respectively. We inserted low r_l^{int} and high r_h^{int} resistance near the interfacial region, corresponding to Ta_2O_5, as indicated by the thick green and black bonds, respectively. The computer simulations, based on (a) and (b), display $I-V$ curves which are characteristics of (c) URS and (d) BRS, respectively.

cess is referred to as reset process. When we applied another voltage of −2 V, the HRS changed to an LRS. This set process always requires higher voltage than the reset process.[1,3–5] To prevent permanent damage during the forming and set processes, the current flow should be limited by an external circuit. The limiting value of the current flow is called the compliance current (I_{comp}^{ext}).[9]

We were able to change the RS type from URS to BRS by inserting a Ta_2O_5 layer to form $Pt/Ta_2O_5/TaO_x/Pt$ cells. Figure 1(d) shows that BRS occurred in the $Pt/Ta_2O_5/TaO_x/Pt$ cells; the $I-V$ curves were not symmetric with respect to the bias voltage polarity. The forming process occurred near −4 V. The resulting LRS changed subsequently to a HRS only when a positive voltage was applied. This reset process occurred near +4 V. The HRS changed back to an LRS when a negative voltage was applied. The set process occurred near −2 V.

Recently, we introduced a new percolation model, called the random circuit breaker (RCB) network model, to explain URS.[1] We approximated the switching medium as a network composed of circuit breakers with bistable resistance states, i.e., LRS (r_l^{bulk}) and HRS $r_h^{bulk}(\gg r_l^{bulk})$, which are marked by thick red and thin gray bonds in Fig. 2(a), respectively. With a couple of polarity-independent switching rules between r_l^{bulk} and r_h^{bulk}, we could explain most experimental observations in URS, including wide distributions of set and reset voltages,[1] scaling behaviors,[10] and large $1/f$ noise.[11]

More recently, we generalized the RCB network model to explain both URS and BRS in one scheme.[12] As schematically displayed in Fig. 2(b), we introduced an additional interfacial layer near one of the electrodes. This model is called the interface-modified RCB network model. We assumed that the interfacial layer has different bistable insulating states, i.e., LRS r_l^{int} and HRS $r_h^{int}(>r_l^{int}>r_l^{bulk})$, as indicated by the thick black and green bonds in Fig. 2(b), respectively. By introducing polarity-dependent switching rules between r_l^{int} and r_h^{int}, we could explain many aspects of BRS, including the forming process.[12] Details of this percolation model and associated simulation videos were published elsewhere.[12]

Here, we made computer simulations based on the RCB network models to explain the type change from URS to BRS. Without the interfacial layer, as in the case of $Pt/TaO_x/Pt$ cells, a percolating cluster of circuit breakers with r_l^{bulk} will form just after the forming process, as shown in Fig. 2(a). As shown in Fig. 2(c), further simulations confirmed that URS should occur in this case. Figures 2(b) and 2(d) show $Pt/Ta_2O_5/TaO_x/Pt$ cells, in which an interfacial layer was inserted near one of the electrodes. It is important to note that, just after the forming process, a percolating cluster of circuit breakers with r_l^{bulk} existed in the bulk region, as displayed in Fig. 2(b). It was serially connected to circuit breakers with r_l^{int} in the interfacial region. Figure 2(d) shows that BRS occurred due to polarity-dependent switching properties of the circuit breakers in the interfacial layer.

To validate the percolation models, we examined the $I-V$ curves in detail. Interestingly, we found that I_{comp}^{ext} was not required during forming and set processes of the $Pt/Ta_2O_5/TaO_x/Pt$ cells. It was quite surprising since it was required to limit the current flow in most earlier works on BRS as well as URS.[3,4,9] Without compliance current during both forming and set processes, the current flow increased suddenly and uncontrollably, causing potentially permanent damage to the samples. However, in our $Pt/Ta_2O_5/TaO_x/Pt$ cells, the current did not increase uncontrollably even without setting the compliance current level externally. As shown in Fig. 1(d), increase in the current flow became stopped by the LRS curve, i.e., due to its resistance value. We refer to this current value as self-compliance current (I_{comp}^{self}).

We investigated the variation in $I-V$ characteristics based on Ta_2O_5 and TaO_x layer thicknesses in $Pt/Ta_2O_5/TaO_x/Pt$ cells. When TaO_x layer thickness, d_{TaOx}, was fixed, the I_{comp}^{self} value increased with decreasing Ta_2O_5 layer thickness, d_{Ta2O5}. Namely, with $d_{TaOx}\approx 20$ nm, $I_{comp}^{self}\approx 50$ μA for $d_{Ta2O5}\approx 10$ nm [Fig. 3(a)], and $I_{comp}^{self}\approx 250$ μA for $d_{Ta2O5}\approx 5$ nm [Fig. 3(b)]. Figures 3(a) and 3(b) also show that the current levels of both the LRS and HRS increased slightly with decreasing d_{Ta2O5}. On the other hand, when d_{Ta2O5} was

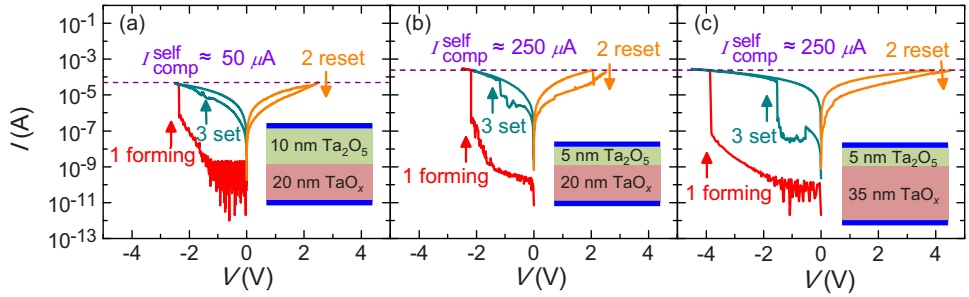

FIG. 3. (Color online) $I-V$ curves of $Pt/Ta_2O_5/TaO_x/Pt$ cells with various Ta_2O_5 and TaO_x layer thicknesses. (a) $d_{Ta2O5}\approx 10$ nm, $d_{TaOx}\approx 20$ nm, (b) $d_{Ta2O5}\approx 5$ nm, $d_{TaOx}\approx 20$ nm, and (c) $d_{Ta2O5}\approx 5$ nm, $d_{TaOx}\approx 35$ nm. I_{comp}^{self} increases with decreasing d_{Ta2O5}, and the forming voltage increases with increasing d_{TaOx}.

fixed, the I_{comp}^{self} value was nearly independent of d_{TaOx}, as shown in Figs. 3(b) and 3(c). Instead, the BRS forming voltage increased with d_{TaOx}. Namely, with $d_{Ta2O5} \approx 5$ nm, forming occurred near -2.5 V for $d_{TaOx} \approx 20$ nm [Fig. 3(b)] and -4 V for $d_{TaOx} \approx 35$ nm [Fig. 3(c)], as indicated by the red forming lines.

The interface-modified RCB network model can explain the changes in $I-V$ characteristics of $Pt/Ta_2O_5/TaO_x/Pt$ cells. (1) As shown in Fig. 2(b), the LRS conduction should occur through a nearly percolating cluster of circuit breakers with r_l^{bulk} in the bulk region serially connected to circuit breakers with r_l^{int} in the interfacial region. And the resistance of the Ta_2O_5 layer was much larger (by orders of magnitude) than that of the TaO_x layer.[2] So the diverging current flow in the bulk region during the forming or set processes was limited by the large resistance of the Ta_2O_5 layer, resulting in I_{comp}^{self}. (2) Due to the serial connection, the Ta_2O_5/TaO_x double layer can be considered an effective voltage divider. Most of the external voltage should have been applied to the Ta_2O_5 layer, and I_{comp}^{self} would depend on its resistance value. When d_{TaOx} was fixed, I_{comp}^{self} should have increased with decreasing d_{Ta2O5}. On the other hand, when d_{Ta2O5} was fixed, I_{comp}^{self} was nearly independent of d_{TaOx}. (3) During the forming process, a nearly percolating cluster of highly conducting filaments was created in the TaO_x layer, as shown in Fig. 2(b). When d_{Ta2O5} was fixed, a higher external bias voltage was required to induce soft dielectric breakdown in a sample with thicker d_{TaOx}.

There are a few important points which we want to address. (1) Application of our percolation models is not limited by specific materials. For example, there have been many papers on URS in polycrystalline $Pt/TiO_x/Pt$ cells.[5] Consistent with our suggestion, Yang *et al.*[13] recently reported BRS in polycrystalline $Pt/TiO_2/TiO_x/Pt$ cells. (2) For BRS, the forming voltage decreased with decreasing TaO_x thickness in our $Pt/Ta_2O_5/TaO_x/Pt$ cells. Yang *et al.*[13] also reported that the forming process disappeared as the thickness of the TiO_x layer decreased in $Pt/TiO_2/TiO_x/Pt$ cells. For some highly insulating TaO_x films, BRS was also reported without the forming process.[2] In such cases, the binary oxide films might play the role of interfacial layer without the bulk region. (3) Many workers attributed the microscopic origin of the BRS to oxygen vacancy movements.[2–4] The excellent agreements between our experimental data and theoretic predictions suggest that collective connectivity changes in the low-resistance r_l^{int} in our interface-modified RCB network model might mimic the oxygen vacancy movements.[10] Further investigations are highly desirable.

In summary, we observed that RS type changed from unipolar to bipolar in $Pt/TaO_x/Pt$ cells by inserting a Ta_2O_5 layer between the Pt electrode and the TaO_x layer. We found that the bipolar RS characteristics became strongly affected by the TaO_x layer as well as the Ta_2O_5 layers. Our percolation model could explain the effects of the TaO_x and Ta_2O_5 layers.

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[1] 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. (Weinheim, Ger.) **20**, 1154 (2008).
[2] J. J. Yang, M.-X. Zhang, J. P. Strachan, F. Miao, M. D. Pickett, R. D. Kelley, G. Medeiros-Ribeiro, and R. S. Williams, Appl. Phys. Lett. **97**, 232102 (2010).
[3] R. Waser, R. Dittmann, G. Staikov, and K. Szot, Adv. Mater. (Weinheim, Ger.) **21**, 2632 (2009).
[4] A. Sawa, Mater. Today **11**, 28 (2008).
[5] D.-H. Kwon, K. M. Kim, J. H. Jang, J. M. Jeon, M. H. Lee, G. H. Kim, X.-S. Li, G.-S. Park, B. Lee, S. Han, M. Kim, and C. S. Hwang, Nat. Nanotechnol. **5**, 148 (2010).
[6] J. Borghetti, G. S. Snider, P. J. Kuekes, J. J. Yang, D. R. Stewart, and R. S. Williams, Nature (London) **464**, 873 (2010).
[7] J. H. Hur, M.-J. Lee, C. B. Lee, Y.-B. Kim, and C.-J. Kim, Phys. Rev. B **82**, 155321 (2010).
[8] J. J. O'Dwyer, *The Theory of Electrical Conduction and Breakdown in Solid Dielectrics* (Clarendon, Oxford, 1973).
[9] K. Kinoshita, K. Tsunoda, Y. Sato, H. Noshiro, S. Yagaki, M. Aoki, and Y. Sugiyama, Appl. Phys. Lett. **93**, 033506 (2008).
[10] J. S. Lee, S. B. Lee, S. H. Chang, L. G. Gao, B. S. Kang, M.-J. Lee, C. J. Kim, T. W. Noh, and B. Kahng, Phys. Rev. Lett. **105**, 205701 (2010).
[11] S. B. Lee, S. Park, J. S. Lee, S. C. Chae, S. H. Chang, M. H. Jung, Y. Jo, B. Kahng, B. S. Kang, M.-J. Lee, and T. W. Noh, Appl. Phys. Lett. **95**, 122112 (2009).
[12] S. B. Lee, J. S. Lee, S. H. Chang, H. K. Yoo, B. S. Kang, B. Kahng, M.-J. Lee, C. J. Kim, and T. W. Noh, Appl. Phys. Lett. **98**, 033502 (2011).
[13] J. J. Yang, F. Miao, M. D. Pickett, D. A. A. Ohlberg, D. R. Stewart, C. N. Lau, and R. S. Williams, Nanotechnology **20**, 215201 (2009).