Occurrence of Both Unipolar Memory and Threshold Resistance Switching in a NiO Film

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(Received 29 March 2008; published 12 January 2009)

We observed two types of reversible resistance switching (RS) effects in a NiO film: memory RS at low temperature and threshold RS at high temperature. We were able to control the type of RS effects by thermal cycling. These phenomena were explained using a new dynamic percolation model that can describe the rupture and formation of conducting filaments. We showed that the RS effects are governed by the thermal stability of the filaments, which arise from competition between Joule heating and thermal dissipation. This work provides us understandings on basic mechanism of the RS effects and their interrelation.

DOI: 10.1103/PhysRevLett.102.026801 PACS numbers: 73.40.Rw, 71.30.+h, 77.80.Fm

The semiconductor industry has long searched for a state-of-the-art nonvolatile memory device that can retain its data even when the power is interrupted [1]. A new concept called resistance random access memory, in which resistance can be repeatedly switched between a high and a low value by an applied electric field, has recently attracted a great deal of scientific and technological interest [1,2]. This reversible resistance switching (RS) effect has been observed in many insulating systems, including binary oxides [3], complex perovskite oxides [4–6], sulfides [7], and organics [8]. To explain the intriguing effect, numerous theoretical models have been proposed. However, most of these models leave unanswered questions [2,9]. Despite its fundamental importance, our understanding of the underlying physics of the RS effect is still poor.

Because of very diverse experimental findings, there has been a great deal of confusion and many controversies in this rapidly expanding field. Even simple aspects of the RS effect, such as electric polarity dependence [2], vary from sample to sample. For example, for most perovskite oxides, current-voltage (I-V) curves are highly asymmetric about the applied bias V [5,6], while they are symmetric for many binary oxides [3,10]. These different responses of RS effects under opposite polarity suggest that they might be classified into some different possible phenomena. In this Letter, we focus on unipolar RS effects, in which I-V curves are symmetric.

There are two types of unipolar RS effects: memory RS [10–15] and threshold RS [3,16], the characteristic I-V curves of which are shown in Figs. 1(a) and 1(b), respectively. The memory RS effect has two reversible transitions. At a certain voltage, there is a change from a low resistance state (LRS) to a high resistance state (HRS). A change from a HRS to a LRS occurs at higher voltages. The latter resistance change is sometimes accompanied by complete dielectric breakdown. To prevent such permanent damage, the current flowing in the sample should be kept below so-called the current compliance I_{comp}. As both LRS and HRS are stable at $V = 0$, they can be used in a nonvolatile memory devices. However, as shown in Fig. 1(b), the threshold RS effect has only one stable resistance state with no external bias applied. To date, there have been no experiments observing the memory and threshold RS effects in the same sample. In most cases, these unipolar RS effects have been treated as independent phenomena.

Here, we report the occurrence of both memory RS and threshold RS in one sample, a simple binary NiO film. We were able to control the type of unipolar RS by thermal cycling, suggesting that these RS phenomena were interrelated. Based on these intriguing experimental findings, we attributed both of these unipolar RS effects to the same origin, i.e., the rupture and formation of conducting filaments. Finally, we developed a unified percolation model that could explain in detail the behavior of both memory and threshold RS effects in terms of the thermal stability of LRS.

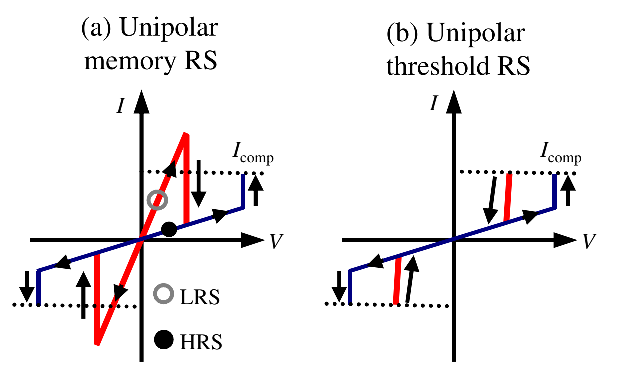

FIG. 1 (color online). Schematic diagrams of current-voltage (I-V) curves for two resistance switching (RS) phenomena: (a) unipolar memory RS and (b) unipolar threshold RS. Unipolar memory RS can have two resistance states without applied V: a low resistance state (LRS) and a high resistance state (HRS). The dashed lines on the RS represent a setting limit of current flow, i.e., the compliance current I_{comp}.

We prepared a $Pt/Ti/SiO_2/Si$ substrate with a Pt bottom electrode layer of 30 nm. We then deposited a Ni film using e-beam evaporation, and oxidized it into a NiO layer at 450 °C in ambient air for 1 h. The resultant NiO film was approximately 60 nm thick. We followed this by evaporating a Au(30 nm)/Pt(10 nm) top electrode layer to make a series of Pt/NiO/Pt capacitors. The sample was mounted to a gold-coated plate and put into a cryostat. The RS characteristics of these Pt/NiO/Pt capacitors were examined by measuring I-V curves at temperatures (T) between 80 and 300 K. The experimental error for sample temperature was found to be less than two degrees. Further details of the sample preparation methods and I-V measurements are presented elsewhere [13].

At low T, our NiO film showed a typical memory RS. Figure 2(a) shows the NiO film I-V curves at 118 K. Under an applied external bias V of about 6.2 V, the pristine sample changed its resistance state, marked on the graph as "forming." It then entered the LRS. When we started to increase V from 0 V again, it suddenly changed to a HRS at $V \approx 2.0$ V, marked as "reset." This HRS was stable even without external bias, and changed to a LRS again at $V \approx 4.5$ V, marked as "set." For both the forming and set processes, I_{comp} was restricted to 10 mA.

We could control the RS type of our NiO film by changing T. When we increased T to 300 K, the I-V curve was typical of threshold RS, as shown in Fig. 2(b); cooling the sample to 80 K, caused the reappearance of memory RS, Fig. 2(c); and increasing T to 300 K, resulted in threshold RS again, Fig. 2(d). These thermal cycles were repeated several times, and we also observed the same cycling effects in eight other samples. These results show that both memory and threshold RS can be obtained from one sample by repeated thermal cycling, indicating that these two RS are closely connected to each other by thermal effects.

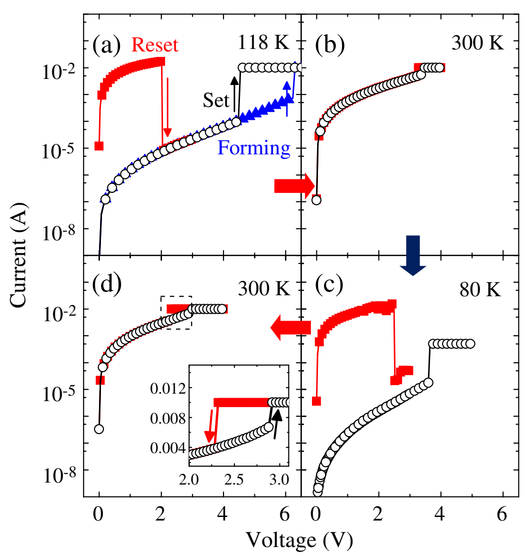

FIG. 2 (color online). Temperature (T)-dependent changes of RS type in a NiO film. (a), (b), (c), and (d) show the I-V curves measured at 118, 300, 80, and 300 K, respectively. Note that memory and threshold RS behaviors are reversible during repeated thermal cycling. The inset in Fig. 2(d) shows the details on a linear y scale for the resistance changes, marked with the dashed area.

The detailed behaviors of threshold RS, shown in the inset of Fig. 2(d), suggest how we can relate these two types of RS effects. The state with the lower resistance, generated by applying V, does not seem to be stable without an external bias, so it returns to the original higher resistance state with a decrease in V. We propose that this instability of the lower resistance state is the main difference between observed memory and threshold RS.

To obtain further insight, we plotted the T-dependent values of the conductance, $G(V = 0.2\ \text{V})$, of the NiO film at $V \approx 0.2$ V. Figure 3 shows the average values of $G(V = 0.2\ \text{V})$, measured on several NiO capacitors for various values of T. In memory RS, the LRS $G(V = 0.2\ \text{V})$ is weakly dependent on T and shows metallic behavior. On the other hand, the HRS $G(V = 0.2\ \text{V})$ shows insulating behavior and follows $G \sim \exp(-\phi/k_BT)$, with an activation energy of $\phi = 75.8$ meV. This T dependence is consistent with earlier observations for memory RS [14]. Note that the G values for the stable state in threshold RS fall approximately on the same $G \sim \exp(-\phi/k_BT)$ curve as for the HRS in memory RS. If we assume that the corresponding LRS becomes unstable in threshold RS, i.e., at higher T, we can explain both RS effects of our NiO film using a simple unified picture.

Recently, we observed the existence of conducting filamentary paths in samples with memory RS and suggested a new type of bond percolation model, called the "random circuit breaker (RCB) network model" [15]. We postulated that the rupture and formation of such conducting filaments could be represented by the connection between on and

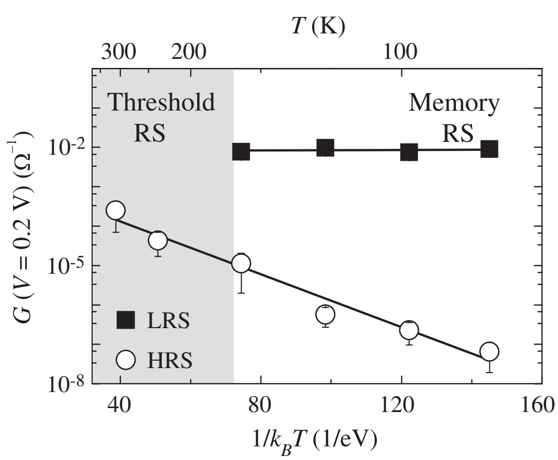

FIG. 3. T-dependent conductance G values at a bias voltage of 0.2 V for the NiO film. There are bistable states for $T \leqq 156$ K, i.e., the region with memory RS. However, there is only one stable state for $T \geqq 225$ K, i.e., the region with threshold RS.

off state of circuit breakers. We then treated the transport in our thin films as a bond percolation problem [17] with an $M \times N$ lattice network composed of circuit breakers, as shown in Fig. 4(a). Each circuit breaker is in either an on or off state, with corresponding resistance values r_l and r_h [$r_h \gg r_l$]. The thick solid (red) and thin dotted (blue) lines in Fig. 4(a) represent on and off states, respectively.

In the original RCB network model, the switchability of the bond resistance value was assumed to depend only on the bias voltage, Δv, applied to each circuit breaker. As shown in Fig. 4(b), the on state changes into the off state when $\Delta v > v_{\rm off}$, and the off state returns to the on state when $\Delta v > v_{\rm on}$ [$v_{\rm on} > v_{\rm off}$]. Note that Δv depends on the distribution of the on or off states of the circuit breakers, the initial values of which are chosen randomly as a given fraction in the simulations. By increasing V, more bonds are turned on. When a percolating cluster of on-state circuit breakers is formed through the RCB network, the sample will be in a LRS. Then, when such a cluster becomes broken by turning off one or several circuit breakers, it will be in a HRS. Our simulations on the two-dimensional square lattice successfully explained most of the experimental observations of memory RS [15].

To explain the T-dependent RS type change in our NiO film, we extended the RCB network model by assuming that the turning-off process could be affected by a bond's local temperature $T_{\rm loc}$ change. There are two competing

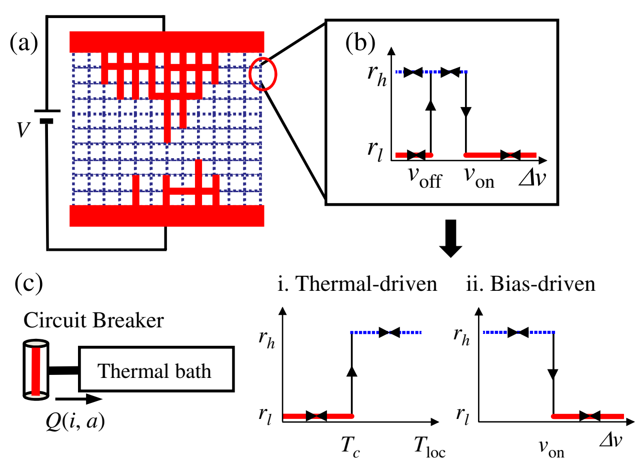

FIG. 4 (color online). (a) Schematic diagram of a random circuit breaker (RCB) network composed of circuit breakers. The thick solid (red) and thin dotted (blue) line represent the on and off states, respectively. (b) The switching rules for turning on and off operations in the original RCB network model [15]. Note that both switching rules are governed by electric fields. (c) The newly assigned switching rules in this Letter. The heat Q of each circuit breaker is assumed to be dissipated to a thermal bath of temperature T_b. When its local temperature $T_{\rm loc}$ becomes higher than a threshold temperature T_c, it will change its resistance from r_l to r_h (a thermal-driven process). On the other hand, if the applied bias becomes larger than $v_{\rm on}$, the state with r_h will change to r_l, independent of $T_{\rm loc}$.

thermal effects that determine $T_{\rm loc}$: i.e., the Joule heating effect and thermal dissipation raise and lower $T_{\rm loc}$, respectively. Note that the current flow in the RCB network is highly inhomogeneous [17]. As $r_h \gg r_l$, most of the current will flow through the largest cluster of on-state bonds. According to the percolation theory [18], just above the percolation threshold, most of the current will flow in a single bond, called the "hottest bond." Therefore, the $T_{\rm loc}$ change will become the most significant for the hottest bond. In the modified RCB network model, we assumed that the circuit breaker changes its resistance from r_l to r_h when $T_{\rm loc}$ becomes higher than a threshold value, denoted T_c, as shown in Fig. 4(c).

In our simulations, we used a 50×20 two-dimensional square lattice. We started our simulations with a pristine state, where 0.5% of the circuit breakers were chosen randomly to be in an on state and $T_{\rm loc}$ for all bonds initially equaled the thermal bath temperature T_b. We increased V in steps from zero, assuming that the external bias at each step was applied for a fixed time duration t_d, corresponding to an experimental measurement time.

As thermal response is generally much slower than the electrical response, we assumed the Δv distribution should be adjusted instantaneously [11]. At $t = 0$, the Δv distribution was evaluated by solving Laplace's equation. If Δv of at least one off-state bond satisfied the bias-driven switching condition of $\Delta v > v_{\rm on}$, we changed r_h to r_l, reevaluated the Δv distribution, and rechecked the switching condition. This process was iterated until a stable Δv distribution was reached. When the electrical response became stable, we considered the changes in thermal response. To evaluate $T_{\rm loc}$, we made the simple approximation that the heat for each bond was dissipated to a thermal bath of T_b, as shown in Fig. 4(c) [19]. As the Joule heating effect due to the flow of current i and the thermal dissipation process compete, we calculated the time-dependent $T_{\rm loc}$ of each bond using

$$c \frac{dT_{\rm loc}}{dt} = ri^2 - a(T_{\rm loc} - T_b), \qquad (1)$$

where c, r, and a are the heat capacitance, resistance, and thermal conductance of each bond, respectively. If $T_{\rm loc}$ of an on-state circuit breaker reached T_c when $t < t_d$, the thermal-driven switching condition was met. Therefore, we changed r_l to r_h and recalculated a stable Δv distribution. If t reached t_d without switching, we increased V by ΔV ($\Delta V = 0.05$ V) and repeated the whole procedure of calculating the Δv distribution and subsequent $T_{\rm loc}$ changes.

Simulations for an I-V curve were repeated by increasing V until the current flowing through the network started to increase very rapidly and reached $I_{\rm comp}$. This corresponded to either the forming or the set operation. When this occurred, we set V to zero immediately, and then calculated the time-dependent changes of $T_{\rm loc}$ and contin-

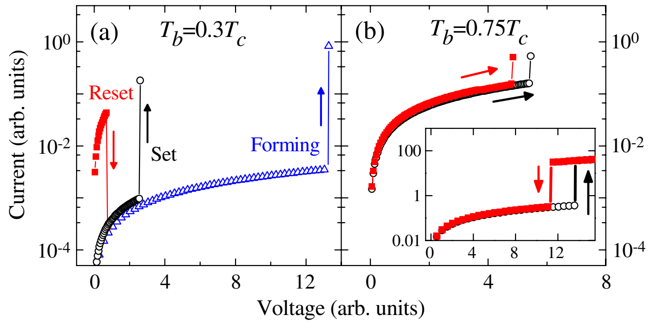

FIG. 5 (color online). Simulation results for I-V curves for the cases of T_b/T_c values of (a) 0.3 and (b) 0.75. The former and latter correspond to memory and threshold RS, respectively. The inset in (b) shows the simulation result when V is decreased gradually after reaching the formed state.

ued to update the on or off states using the thermal-driven switching condition. Once a stable state was reached, we started to increase V from zero again to obtain the next I-V curve.

Figures 5(a) and 5(b) show simulated I-V curves for $T_b/T_c = 0.3$ and 0.75, respectively. We set $v_{\rm on} = 1.0$ and $I_{\rm comp} = 0.5$ in arbitrary units. For the off and on states of the circuit breaker, we adopted values of c and a from the literature [20]. For lower T_b simulations, we approximated $r_h/r_l = 10\,000$ [19]. As shown in Fig. 5(a), the results show typical memory RS. On the other hand, for higher T_b, we used $r_h/r_l = 100$, representing the observed change in resistance from 118 to 300 K as shown in Fig. 3. The obtained I-V curves in Fig. 5(b) represent those of threshold RS. For completeness, we also obtained an I-V curve while we gradually decreased V after it reached the formed state. As shown in the inset of Fig. 5(b), these results agreed quite well with our observed I-V curves for the threshold RS shown in Fig. 2(d). Our simulations demonstrate that both memory and threshold RS could be described by the unified percolation model [19].

The type of unipolar RS effect could be determined by competition between Joule heating and thermal dissipation processes, especially in the hottest bond. When $T_{\rm loc}$ approaches T_c, Eq. (1) becomes

$$\frac{dT_{\rm loc}}{(T_c - T_b)} \sim \left[\frac{1}{\tau_1} - \frac{1}{\tau_2}\right]dt, \qquad (2)$$

where $\tau_1 = c(T_c - T_b)/(v_{\rm on}^2/r_h)$ and $\tau_2 = c/a$. Note that the first and second terms come from Joule heating and thermal dissipation processes, respectively. If $[1/\tau_1 - 1/\tau_2]$ becomes positive, i.e., $\tau_1 < \tau_2$, $T_{\rm loc}$ increases above T_c as time progresses. The hottest bond will then become unstable. On the other hand, if $[1/\tau_1 - 1/\tau_2]$ becomes negative, i.e., $\tau_1 > \tau_2$, $T_{\rm loc}$ cannot reach T_c as time passes, leaving the filament stable, as in memory RS. In our experimental studies, temperature was shown to induce a change of τ_1 (due to T_b and r_h changes), resulting in a change in the unipolar RS type.

In summary, our study indicates that memory and threshold resistance switching effects for NiO films could come from the same origins, i.e., formation and rupture of conducting filamentary paths. Using a simple unified picture based on a dynamic and reversible percolation model, we explained how both memory and threshold resistance switching effects can occur in the same sample and can be controlled by temperature. This work provides a clear picture on how the unipolar resistance switchings can occur.

This work was supported financially by the Creative Research Initiatives (Functionally Integrated Oxide Heterostructure) of the Ministry of Science and Technology (MOST) and the Korean Science and Engineering Foundation (KOSEF).

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[19] In reality, the heat will be dissipated by thermal conduction to neighboring medium. And an increase in $T_{\rm loc}$ will increase r_l and decrease r_h. Recently, we performed another series of RCB network simulations which take into account of these more realistic effects, and obtained essentially the same results in Fig. 5. The results will be published elsewhere.
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