Influence of carrier injection on resistive switching of TiO_2 thin films with Pt electrodes

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The influence of electron injection on the electric-pulse-induced resistive switching of Pt/TiO_2 thin film/Pt structure was studied by current-voltage (*I-V*) measurements. The electron injection was increased by annealing the sample in a N_2 atmosphere or measuring the *I-V* characteristics at high temperatures (>100 °C). The switching from the high-resistance state (HRS) to the low-resistance state by a filamentary mechanism was suppressed when the carrier injection by Schottky emission or space-charge-limited conduction (SCLC) was excessive. Interfacial potential barrier played a crucial role in determining the carrier injection. Switching was observed (not observed) when the HRS resistance was low (high) although SCLC was observed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2361268]

Resistive switching in simple binary transition metal oxide thin films, such as NiO and TiO_2, attracts great interest for a possible application in nonvolatile memory devices[1,2] due to the possible low required current for switching compared to phase change memories and a simple fabrication process compared to more complex materials such as $(Pr_{1-x}Ca_x)MnO_3$ (Refs. 3 and 4) or Cr-doped $SrZrO_3$.[5] TiO_2 thin films show reliable resistance switching with a resistance ratio as large as $>10^3$ between the low and high resistive states.[2] Recently, the authors reported that resistive switching in TiO_2 thin films with Pt-top and Ru-bottom electrodes has a close relationship with the formation and rupture of conducting filaments using current-density–voltage (*J-V*) measurements and conductive atomic force microscopy.[2] The low-resistance state (LRS) [high-resistance state (HRS)] has a high (low) density of conducting filaments with a higher (lower) specific conductivity per filament.[2] It was also reported that the dominant parameter that governs the switching mechanism of TiO_2 films is the power that is imparted to the film during switching.[6]

To acquire further insight into the resistive switching phenomenon in TiO_2 thin films, the influence of the metal (Pt) electrode/TiO_2 interface was studied. Because the formation and rupture of conducting filaments in these films have a close relationship with local heating by current flow through the filaments, it can be anticipated that the metal/oxide interface property, especially the potential barrier height (ϕ_b), largely affects the switching phenomenon. In this work, Pt/TiO_2 interfaces with a different interface ϕ_b for electron injection were fabricated and the electron injection effects on resistive switching were investigated. The electron injection was further controlled by measuring the current-voltage (*I-V*) characteristics at higher temperatures (100 °C), and the correlation between the switching behavior and electrical conduction property was investigated.

Samples were fabricated with a 40-nm-thick TiO_2 thin film, which was deposited by a plasma-enhanced atomic layer deposition at 300 °C using Ti-tetraisopropoxide as precursor and plasma activated O_2 as oxidant on a 100-nm-thick sputtered $Pt/SiO_2/Si$ substrate. The as-grown TiO_2 film was crystallized with polycrystalline anatase structure. Then, Pt-top electrodes with a diameter of 80 μm were fabricated by a lift-off photolithography process.

Some of the samples were tested at the as-deposited state (sample A). The as-deposited samples showed a lower leakage current due to a high ϕ_b and a reliable switching behavior. The other samples were annealed at 500 °C for 30 s under a N_2 atmosphere (sample N) which induced a large leakage current by the reduced ϕ_b and nonswitching behavior as shown later. It should be noted that ϕ_b is not only a function of the metal work function but is also strongly dependent on other fabrication processes.

In the following, the resistive switching behavior of the films was measured by an HP4155A semiconductor parameter analyzer from room temperature (RT) to 100 °C with biased top and grounded bottom electrodes.

Approximately 20 capacitors from sample A were tested and all showed a reliable switching behavior with a HRS and LRS resistance ratio $>10^4$ at $V<\sim 0.1$ V after an initial soft breakdown (so-called forming process) at ~3.5 V. The compliance current was set to 20 mA. Before the initial soft breakdown, the measured current was $\sim 10^{-11}-10^{-10}$ A. Figure 1(a) shows typical log *I*-log *V* curves of a capacitor from sample A which shows a resistance ratio of $\sim 5\times 10^5$ (at 0.02 V) measured at temperatures ranging from 40 to 100 °C. Here, the LRS *I-V* curves were measured at 40 and 100 °C several times and show an Ohmic behavior (slope of 1) up to the reset voltage (V_{reset}) where the switching from LRS to HRS occurs. The LRS *I-V* graphs show an almost temperature independent behavior without any systematic variation. Therefore, the LRS state is not dealt with in this letter. Actually, the LRS→HRS transition was always observed as long as the reverse transition (HRS→LRS) was observed. HRS also shows an Ohmic behavior up to ~0.5 V

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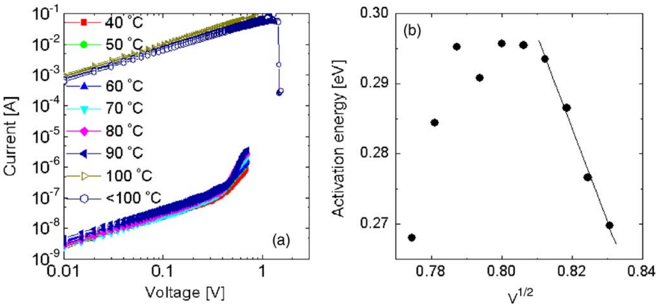

FIG. 1. (Color online) (a) $\log I$-$\log V$ curves and (b) variation in E as a function of $V^{1/2}$ of sample A.

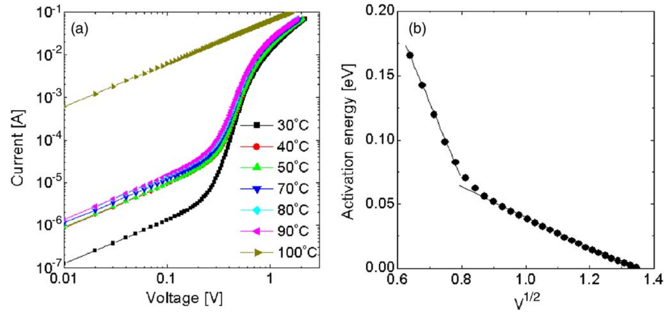

FIG. 2. (Color online) (a) $\log I$-$\log V$ curves and (b) variation in E as a function of $V^{1/2}$ of sample N.

at all temperatures, suggesting that there are residual local metallic filaments in HRS.[2] When $V > \sim 0.5$ V, HRS begins to deviate from the Ohmic behavior. It was found that the variation in Ohmic I with the temperature in HRS was relatively random from measurements of several different capacitors. It appeared that the metallic conduction effect is interfered with the random generation of tiny filaments during the switching and even in the repeated measurements in HRS.

It is natural to assume that the Pt/TiO_2 junction has a Schottky nature due to the high work function of Pt and the n-type nature of TiO_2. Therefore, the I-V behavior of HRS in the high V region ($> \sim 0.5$ V) was investigated based on the Schottky conduction mechanism which has a highly nonlinear I-V character (the slope in $\log I$-$\log V$ plot is much larger than 1). It has to be noted that Schottky conduction (or any other conduction mechanism) can hardly be observed in the LRS due to the overwhelmingly large Ohmic current via the LRS filaments.

One of the difficulties in Schottky or any other conduction mechanism analysis in such a switching system is the switching from HRS to LRS itself at a set voltage (V_{set}). In this case, V_{set} was ~ 1.5 V. Once the sample switched to LRS, switching back to HRS by applying V_{reset} does not guarantee the identical HRS due to the stochastic nature of the filament formation and rupture. Therefore, V should be limited to less than $\ll 1.5$ V during the I-V measurement at various temperatures. Although voltage application up to ca. 1 V does not induce an immediate HRS→LRS switching at lower temperatures, repeated measurements at the same pad (greater than ten times) at higher temperatures (>70 °C) result in switching. Therefore, in this case, the maximum V was limited to 0.7 V. Even with this relatively low maximum V, a small number of filaments still formed during the measurements and increased the Ohmic current during repeated measurements (measurement was performed from low to high temperature). The nonlinear parts of the I-V were not crucially influenced by this effect.

Schottky analysis followed the standard procedure; the various I-V curves were plotted on $\ln(I/T^2)$ vs $V^{1/2}$ (T is temperature) and the Schottky V region was found. Then, $\ln(I/T^2)$ was plotted with respect to $1/T$ in the Schottky V region, and the variation of the activation energies ($E = \phi_b - \beta V^{1/2}$, where β is the Schottky coefficient) obtained from the slopes was plotted as a function of $V^{1/2}$ [Fig. 1(b)]. During the analysis, it was found that the V and T regions for Schottky fitting were quite narrow due to the interference with the Ohmic current and others.

Figure 1(b) shows that Schottky conduction occurs in a narrow V region (0.66–0.69 V) and T region (40–90 °C). At lower voltages, the Ohmic current influence becomes large and at higher V another conduction mechanism begins to appear which is probably space-charge-limited conduction (SCLC) as shown later. The extrapolation of E to $V=0$ showed that ϕ_b is 1.37 eV.

Sample N did not show any reliable switching at room temperature. Initially, the sample showed a rather high leakage current level ($\sim 10^{-7}$ A) compared to sample A and did not show a clear soft breakdown and HRS→LRS switching at RT. After several I-V sweeps at RT, the I-V curves measured at various temperatures had the characteristics as shown in Fig. 2(a). The HRS state was maintained after the application of up to 2 V. A further increases in V at room temperature resulted in a complete breakdown of the sample. Similarly to sample A, HRS shows an Ohmic behavior up to ~ 0.3 V and a highly nonlinear behavior at higher voltages. In this case, due to the lack of the HRS→LRS switching, the measured V region was extended to 2 V. It can be observed that a I-V sweep at 30 °C formed the HRS filaments and the Ohmic HRS current slightly increased afterwards. Repeated measurements up to 90 °C suddenly switched the sample to LRS at 100 °C which was not possible at room temperature even with a higher number of I-V sweeps. This suggests that the high temperature helps forming the strong filaments which are necessary to create the LRS without a complete breakdown.

Figure 2(b) shows the variation in E as a function of $V^{1/2}$ of sample N obtained from the same Schottky analysis as used for sample A. The linear extrapolation in the V region from 0.4 to 0.65 V shows that $\phi_b = 0.55$ eV, which is the reason for the high leakage current of sample N. The I-V curve at $V > \sim 0.7$ V shows a behavior which is certainly different from Schottky conduction [Fig. 2(b)]. This appears to be related to SCLC as shown in the high V region ($> \sim 0.9$ V) in Fig. 2(b). The $\log I$-$\log V$ curve shows an almost linear behavior with a slope of ~ 2 which is quite close to the SCLC character.[7] An excessive electron injection results in negative charge accumulation in the TiO_2 film which results in SCLC. A high V can also induce Fowler-Nordheim (FN) tunneling. However, FN simulation using the same ϕ_b and other properly assumed parameters indicated that the FN current should be a few orders of magnitude higher than the current observed in the experiment.

It is now understood that the high and low ϕ_b have something to do with the reliable switching and nonswitching, respectively. To further elucidate the underlying influ-

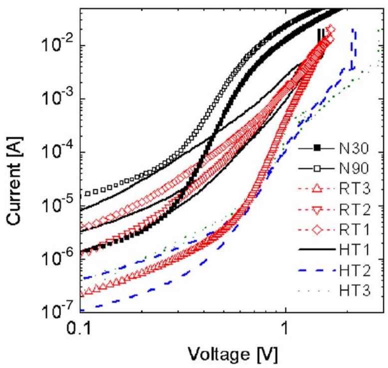

FIG. 3. (Color online) log *I* vs log *V* curves of sample A at RT (red symbols) and 100 °C (black line, blue dash, and dark green dot). *I*-*V* curves of sample N (black square) at 30 and 90 °C are also included for comparison.

ence of the charge injection on the switching, the following experiments were performed.

Among the many capacitors on sample A, a capacitor with a slightly higher HRS current (10^{-7}–10^{-6} A at 0.1 V) was selected and many *I*-*V* sweeps were performed at RT and 100 °C (Fig. 3). For comparison, the *I*-*V* data of sample N at 30 and 90 °C are also included in Fig. 3. There is a certain trend in the HRS→LRS switching behavior. First, at RT [red symbols (color online)], three *I*-*V* curves are shown (labeled as RT1, RT2, and RT3). RT3 shows a low current in the Ohmic region ($< \sim 0.3$ V), suggesting that the HRS filament density was low. As *V* increases, *I* strongly increases according to the Schottky mechanism [compare the slope with that of sample N at 30 °C; the computer simulation of Schottky *I*-*V* curves showed that the shape (slope) is almost exclusively determined by ϕ_b] up to V_{set}. RT1 and RT2 show a much higher *I* in the Ohmic region ($> \sim 0.1$ V), suggesting that the HRS filament density was high. The smaller slope in the non-Ohmic region ($> \sim 0.2$ V) suggests that the contribution from the SCLC is high in this case. This slope cannot be generated by summing up the extrapolated Ohmic currents up to the high *V* region and the Schottky current (RT3) (calculated data not shown).

However, the smaller *I* level compared to sample N in the non-Ohmic *V* region suggests that ϕ_b is still higher than that of sample N. RT1, RT2, and RT3 show almost identical V_{set} (~1.6 V) and I_{set} (~13 mA).

When *T* was increased to 100 °C, the V_{set} variation becomes large. However, there appears to be a close relationship between the non-Ohmic behavior and V_{set}. The HRS *I* -*V* curves at 100 °C (HT) can be grouped into three groups [HT1 (black line), HT2 (blue dash, color online), and HT3 (dark green dot, color online)] which have a V_{set} of ~1.5, 2.1, and 3.0 V, respectively. It can be easily anticipated that HRS→LRS switching becomes difficult as V_{set} increases. The HT1 group shows an almost identical behavior to RT1 and RT2. Therefore, it can be understood that switching was observed when the HRS resistance was low irrespective of *T*, although the non-Ohmic behavior follows the SCLC. This is a quite natural conclusion considering the fact that the HRS→LRS switching is a power driven (thermal phenomena) event, so that the higher the HRS current is the higher is the thermal energy to form strong filaments.

Now, an interesting comparison can be made between RT3 and HT3. Both have a low HRS current in the Ohmic region ($> \sim 0.3$ V), but RT3 follows the Schottky behavior whereas HT3 shows a behavior that is close to SCLC (especially at $V > \sim 1$ V) in the high *V* region. When the SCLC is dominant, V_{set} increases to a high value. The small *I* in the SCLC region suggests that ϕ_b is high. Therefore, the high ϕ_b does not necessarily guarantee repetitive switching.

There are other cases at HT in which the Ohmic current is low but follows the Schottky behavior (data not shown for clarity of Fig. 3). These cases always result in a V_{set} of ~1.5 V. HT2 shows a behavior in between HT1 and HT3.

Now, the question is why the SCLC results in difficulties in switching. The low *I* level in the non-Ohmic region of HT3 suggests that ϕ_b is high so that the SCLC may not result from the usual electron injection from the Pt/TiO_2 interface (as for sample N). Therefore, it was assumed that the electrons are injected from treelike filaments[8] into the matrix region of the TiO_2 film for the HT3 case. When this type of electron injection occurs, the bulk of the TiO_2 film becomes negatively charged and SCLC may appear although ϕ_b is high. The loss of conduction electrons into the matrix region also slows down the filament formation by a reduced heat generation. In addition, the SCLC retards the overall current flow due to the effective reduction of the electric field at the interface. Therefore, switching becomes difficult (V_{set} becomes high). This kind of electron loss from the filaments to the matrix may depend on the detailed structure of the filaments and the film's microstructure which renders the V_{set} distribution large. It appears that a high *T* enhances electron injection from the filaments to the matrix.

It may also be probable that the accumulated charges interact with charged defects that percolate to eventually form filaments in a way that is not clearly understood at this moment. This might constitute one of the reasons for the suppression of the switching at RT in sample N in addition to the reduction of the effective electric field by the SCLC effect.

In summary, the influence of electron injection on the HRS→LRS switching of TiO_2 thin films with Pt electrodes was investigated. Reliable switching was observed when ϕ_b was high and no SCLC was observed. When ϕ_b was high but SCLC was observed, probably due to electron leakage from the HRS filaments to the matrix region at high *T*, V_{set} became large. When ϕ_b was low, a strong SCLC was inevitably obtained and switching became improbable. Therefore, a high ϕ_b is one of the prime prerequisites for stable resistance switching in TiO_2 thin films.

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[1] I. G. Baek, M. S. Lee, S. Seo, M. J. Lee, D. H. Seo, D.-S. Suh, J. C. Park, S. O. Park, H. S. Kim, I. K. Yoo, U-In Chung, and J. T. Moon, Tech. Dig. - Int. Electron Devices Meet. **2004**, 587.
[2] B. J. Choi, D. S. Jeong, S. K. Kim, S. Choi, J. H. Oh, C. Rohde, H. J. Kim, C. S. Hwang, K. Szot, R. Waser, B. Reichenberg, and S. Tiedke, J. Appl. Phys. **98**, 033715 (2005).
[3] A. Asamitsu, Y. Tomioka, H. Kuwahara, and Y. Tokura, Nature (London) **388**, 50 (1997).
[4] S. Q. Liu, N. J. Wu, and A. Ignatiev, Appl. Phys. Lett. **76**, 2749 (2000).
[5] Y. Watanabe, J. G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S. J. Wind, Appl. Phys. Lett. **78**, 3738 (2001).
[6] C. Rohde, B. J. Choi, D. S. Jeong, S. Choi, J.-S. Zhao, and C. S. Hwang, Appl. Phys. Lett. **86**, 262907 (2005).
[7] M. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970), p. 9.
[8] H. Fowler, J. E. Devaney, and J. G. Hagedorn, IEEE Trans. Dielectr. Electr. Insul. **10**, 73 (2003).