Modified resistive switching behavior of Zr O 2 memory films based on the interface layer formed by using Ti top electrode

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Modified resistive switching behavior of ZrO_2 memory films based on the interface layer formed by using Ti top electrode

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The influence of Ti top electrode material on the resistive switching properties of ZrO_2-based memory film using Pt as bottom electrode was investigated in the present study. When Ti is used as top electrode, the resistive switching behavior becomes dependent on bias polarity and no current compliance is needed during switching into high conducting state. This phenomenon is attributed to the fact that a series resistance between Ti and ZrO_2 film, composed of a TiO_x layer, a ZrO_y layer, and even the contact resistance, imposed a current compliance on the memory device. Besides, our experimental results imply that switching the device into high conducting state is a field driven process while switching back into low conducting state is a current driven process.
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I. INTRODUCTION

Recently, a resistive switching phenomenon observed in various oxide films in metal-insulator-metal (MIM) structures has been developed for potential nonvolatile memory application. Based on previous studies, the origin of the resistive switching is mainly associated with the intrinsic bulk property, but the interface between electrodes and oxide films also has a considerable influence on the resistive switching phenomenon. Therefore, various surface treatments and various materials with different top and bottom electrodes combinations were studied to further look into the mechanism of the resistive switching phenomenon.[1–9] Seo *et al.* investigated the resistive switching in the top electrode/NiO/Pt structures, demonstrating that, if the top electrode formed an Ohmic contact with NiO film, the effective electric field inside the film became high enough to cause the resistive switching. On the contrary, if well-defined Schottky contact was formed, there was a voltage drop across the interface so that the electric field across the NiO was too small to induce resistive switching. Choi *et al.* reported that the resistive switching has only been observed in $Al/TiO_2/Pt$ devices when applying positive bias on Al top electrode, proposing that the electrode-relative bi—or unipolar resistive switching seems to be related to the oxygen permeation through the top electrode. Sawa *et al.* studied the current-voltage (*I-V*) characteristics of different top electrodes stacked on the $Pr_{0.7}Ca_{0.3}MnO_3$(PCMO)/$SrRuO_3$ bottom electrode, concluding that a Schottky-like barrier was the main factor determining the resistive switching phenomenon. Peng *et al.* tried to explain the Schottky-like barrier causing resistive switching through the correlated work function factor influencing resistive switching of symmetric metal/PCMO/metal structures with electronegativity of different metals electrodes.

In this study, the resistive switching behavior of ZrO_2 films in MIM structure with Ti top electrode was investigated. TiO_x and ZrO_y ($y<2$) interface layers were formed at the interface of Ti top electrode/ZrO_2 film, leading to the fact that the resultant *I-V* curve was significantly different from that without TiO_x and ZrO_y interface layers. A uni-to-bipolar resistive switching translation is demonstrated to give an insight into resistive switching mechanism.

II. EXPERIMENT

40~70-nm-thick ZrO_2 films were deposited on $Pt/Ti/SiO_2/Si$ substrates at 250 °C by a radio-frequency (rf) magnetron sputtering. All ZrO_2 films were prepared at 10 mTorr, which was maintained by a gas mixture of oxygen and argon at a mixing ratio of 6:12. To achieve the MIM structure, a 150-nm-thick Ti top electrode was deposited by rf magnetron sputtering or electron beam evaporation at ambient temperature with a diameter of 250 μm patterned by the shadow mask process. The base pressure for sputtering Ti top electrode was 2×10^{-6} Torr using a cryopump and the working pressure of Ar gas (99.995%) was kept at 7.6×10^{-3} Torr during deposition process. The base pressure for electron beam evaporation was 4×10^{-6} Torr using a cryopump. Agilent 4155C semiconductor parameter analyzer was used to measure the *I-V* characteristics of the ZrO_2 film memory device at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows a schematic diagram of the device structure and measurement system. The *I-V* characteristics were measured in a two-probe configuration, and the bias voltage

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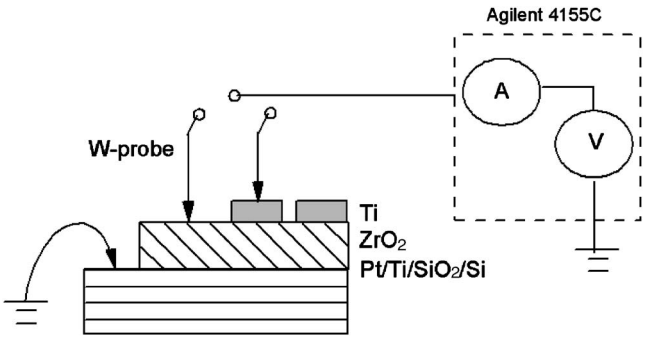

FIG. 1. A schematic diagram of the device structure and the measurement system.

was applied on Ti top electrode with the Pt electrode grounded. Figure 2 depicts that the unipolar and bipolar resistive switching phenomena can be observed by using a tungsten probe directly contacting with ZrO_2/Pt structures without Ti top electrode (W probe/ZrO_2/Pt), which demonstrates that both positive and negative voltages can perform the reproducible resistive switching. After high voltage forming process, the W probe/ZrO_2/Pt devices are switched into high conducting state (on state). on state can be switched into low conducting state (off state) by applying positive voltage bias, and back into on state again by positive or negative voltage bias, as shown in Figs. 2(a) and 2(b). Figures 2(c) and 2(d) show that on state can be also switched into off state by negative voltage bias, and back into on state by positive or negative bias. As a result, the resistive switching is independent of bias polarity, and the influence from the interface of the ZrO_2/bottom electrode and/or the interface of tungsten probe/ZrO_2 is negligible. That is because most of interface effects relate to bias polarity based on previous report,[4] but the result shown here is not related to the bias polarity. The bulk of ZrO_2 film dominates the resistive switching.

Because Ti is an oxygen-gettering metal, using Ti as the top electrode is expected to modify the oxygen content, oxygen vacancies, oxygen ions, and oxygen-related defect distribution in the ZrO_2 films, and further causes the formation of a TiO_x and a ZrO_y layer. According to the result of secondary ion mass spectrometry (SIMS) analysis, as shown in Fig. 3, the signal of TiO is detected and there is a TiO_x layer indeed formed at the interface of Ti/ZrO_2. However, the ZrO_y layer is difficult to be identified here, this is because the ZrO_y layer is so thin which is beyond the resolution of SIMS analysis. Therefore, high-resolution transmission electron microscopy (HR-TEM) observation was carried out and the result is shown in Fig. 4. A thin interface layer about few nanometers is found and believed to be ZrO_y, but the difference between Ti and TiO_x, however, is indistinguishable in the HR-TEM image. Based on the results of SIMS profile and HR-TEM image, the interface layer formed between Ti and ZrO_2 would comprise TiO_x and ZrO_y, and this device structure can be defined as Ti/IL/ZrO_2/Pt, where IL pre-

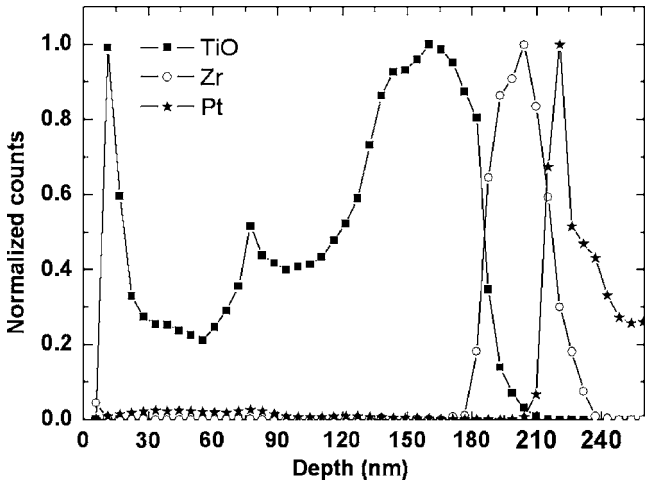

FIG. 3. SIMS depth profile of ZrO_2/Pt stack using Ti top electrode.

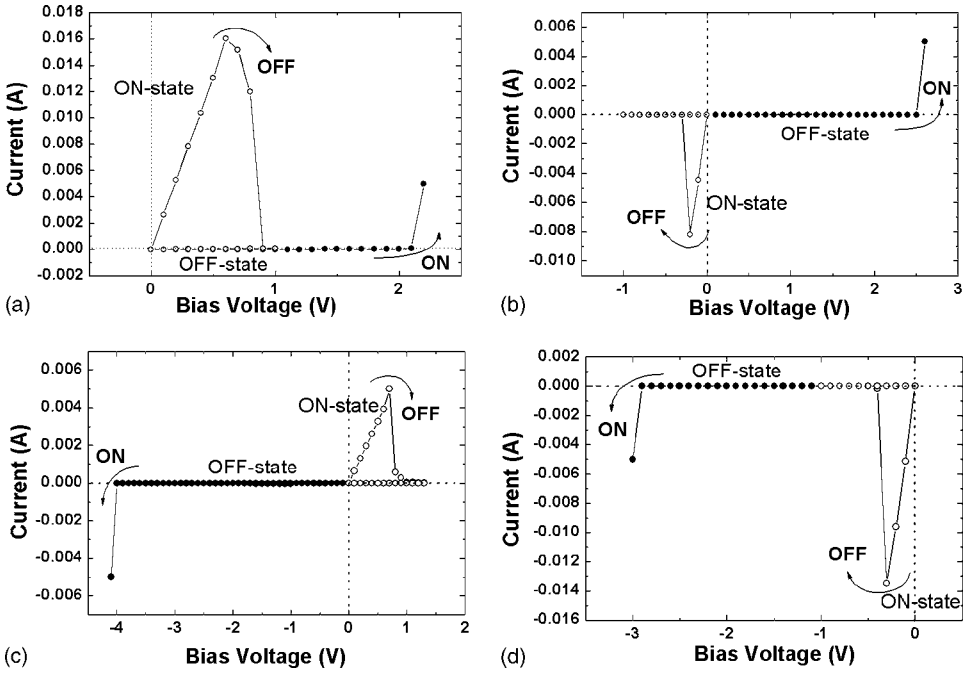

FIG. 2. Resistive switching behavior performed with positive and negative bias voltages showing unipolar and bipolar resistive switching by using tungsten probe directly in contact with ZrO_2/Pt structure.

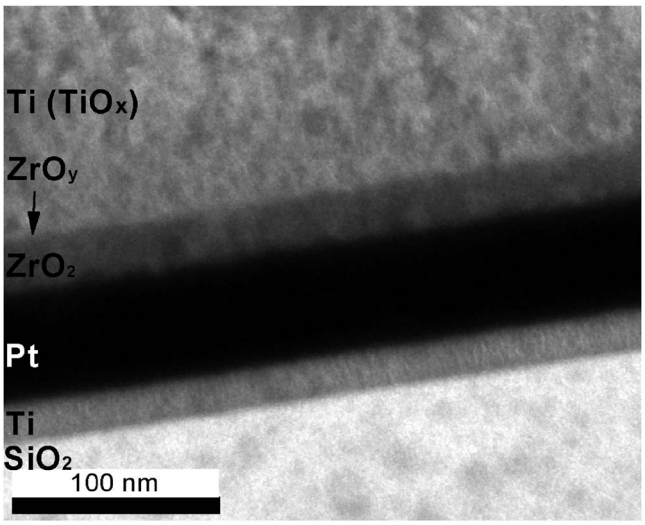

FIG. 4. Cross-sectional HR-TEM image of a thin ZrO_y interface layer formed between Ti (TiO_x) and ZrO_2.

sents interface layer consisting of TiO_x and ZrO_y. The formation of the TiO_x layer is caused by Ti metal reacting with O_2 presented in the chamber during deposition and the interdiffusion between Ti and ZrO_2 film, and the ZrO_y layer is formed due to the interdiffusion between Ti and ZrO_2 film. As a result, the TiO_x layer is much thicker compared with the thin ZrO_y layer, as shown in Fig. 3. Furthermore, it is expected that there are tiny thickness and stoichiometry variations of the TiO_x layer between two different techniques for Ti top electrode deposition in the experimental part due to different fabrication conditions, such as base pressure, working pressure, and Ar usage, but the *I-V* characteristics of these two kinds of memory devices are almost the same. Hence, one of the possible reasons attributed to this phenomenon is that the different Ti deposition techniques might induce very similar ZrO_y layers, and their TiO_x layers only play a minor role. Another possible reason might be that the variation of process-dependent interface layers in this study does not significantly change the *I-V* characteristics. Future work is going to focus on controlling the interface layers by depositing various thicknesses of Ti metal on ZrO_2 films, and to provide more detailed study about the effect of various kinds of interface layers on the electrical characteristics of ZrO_2 films.

The typical *I-V* characteristics of Ti/IL/ZrO_2/Pt device in linear scale, translating into bias polarity dependent, are shown in the Fig. 5(a). The same *I-V* characteristics are shown also as a semilogarithmic plot in the Fig. 5(b). Only by applying positive voltage bias can switch the Ti/IL/ZrO_2/Pt device into on state, and it can be switched back into off state only by negative voltage bias, demonstrating that bipolar resistive switching occurs when using Ti top electrode for the MIM structure. Before any resistive switching is performed, a forming process, which can be achieved by either positive or negative voltage bias with a current compliance of 5 mA at an absolute value of 5–8 V, is necessary for both Ti/IL/ZrO_2/Pt and W probe/ZrO_2/Pt devices. Because both Ti/IL/ZrO_2/Pt and W probe/ZrO_2/Pt devices possess the same forming process, Ti top electrode is

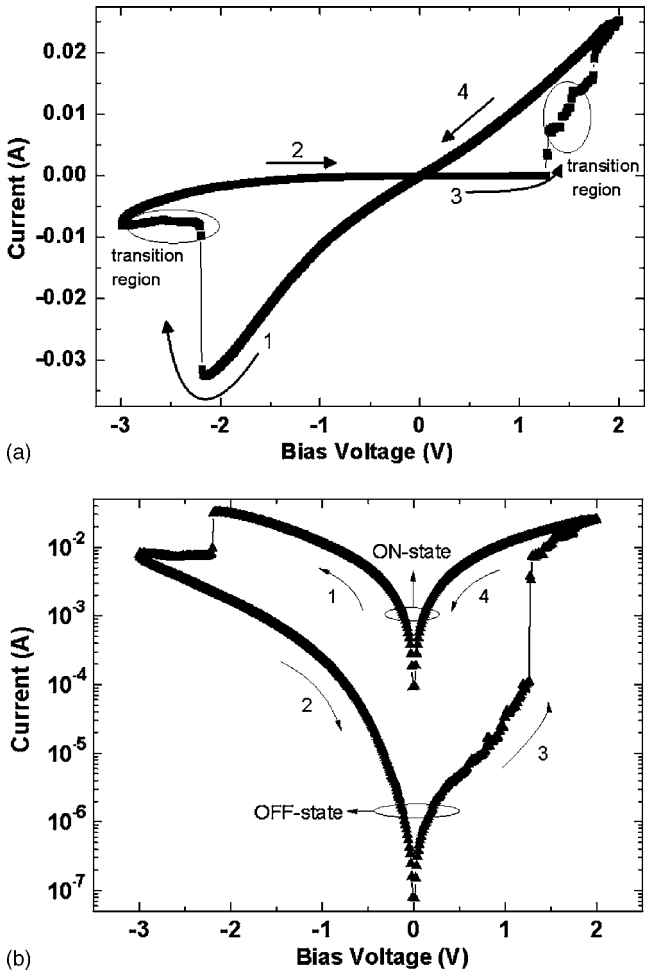

FIG. 5. (a) Typical *I-V* curve of the Ti/IL/ZrO_2/Pt device in linear scale, applying positive bias on Ti top electrode to switch the device on and negative bias to switch it off. (b) *I-V* curve in semilog scale.

believed to only modify the top part of ZrO_2 film instead of the whole film. The forming process, independent of bias polarity and of top electrode, is analogous to the time dependent dielectric breakdown (TDDB) in Pt/NiO_y/Pt devices, and it was proposed that the conducting filaments were formed during dielectric breakdown.[10] Therefore, conducting filaments are believed to be present in Ti/IL/ZrO_2/Pt and W probe/ZrO_2/Pt devices as a result of forming process. Moreover, due to the resistive switching phenomenon and similar forming process observed in both Ti/IL/ZrO_2/Pt and W probe/ZrO_2/Pt devices, we would conclude that the ZrO_2 film, instead of interface layers, dominates the resistive switching behavior, while the interface layers serve as a series resistance and an oxygen sink. We are going to elucidate how interface layers influence the resistive switching behavior in the following section.

After a forming process, the Ti/IL/ZrO_2/Pt was switched from original state into on state. Subsequently, the negative bias voltage applied on the top electrode changes the device from on state to off state, and the turn-off process is marked in region 1, as shown in Fig. 5(a). While positive voltage is applied on the Ti top electrode again to switch the device into on state, the current compliance is not needed, which is obviously different form the *I-V* curves of other

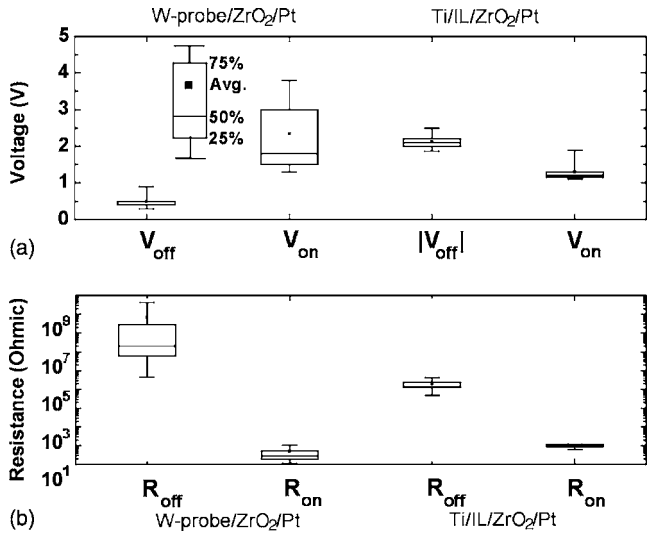

FIG. 6. Variations of the resistive switching parameters in the W-probe/ZrO_2/Pt and Ti/IL/ZrO_2/Pt devices, respectively. R_{on} and R_{off} are the resistances measured at 0.3 V for each device.

metal oxides resistive switching devices previously reported. The interface layers in series with the ZrO_2 film act as a current compliance resistance during turn-on process. Before any sudden change in ZrO_2 resistance, most of voltage drop is across the ZrO_2 film for its off state with larger resistance than that of the interface layers. After a sudden resistance change in the ZrO_2 film at 1.3 V, the resistance of ZrO_2 film is close to that of the interface layers at this time, and the voltage drop across the ZrO_2 decreases to near half of the initial value. The more the resistance of ZrO_2 film decreases, the lower the voltage drop across the ZrO_2 film is, leading to a transition region presented in the region 3. Finally, most voltage drop is across the interface layers. Consequently, the interface layers impose a current compliance during turn-on process and this way is similar to current limited by transistor gate voltage proposed by Chen *et al.*[11]

During turn-off process, the transition region also appears in region 1 due to the same reason why the TiO_x layer is still in series with the ZrO_2 film and the resistance of ZrO_2 is comparable to that of the interface layers at this moment. Moreover, the conducting filaments continue rupturing during sweeping of the bias voltage from −3 to 0 V. The characteristics of the Ti/IL/ZrO_2/Pt device, where interface layers play roles of a series resistance, are obviously demonstrated in this study. In addition to the interface layers, it is worthy noting that the contact resistance might also play an important role for the series resistance.

In general, conducting filaments are thought to be easily formed where local electrical field is especially high, and it can propagate through the insulator until conducting connections are formed between the electrodes. Consequently, the biased electrons find one or few conducting paths consisting of possible point defects, such as oxygen vacancies and other ionic and electronic defects.[7] Simultaneously, the electrons hopped passing through the insulator in these paths and causing the current to dramatically increase, and this is the on process. In Fig. 6(a), the turn-on voltage of the Ti/IL/ZrO_2/Pt device, in general, is smaller than that of the W probe/ZrO_2/Pt devices. A smaller voltage is enough to provide large effective electric field inside the ZrO_2 films leading to the formation of conducting filaments. This is due to the ZrO_2 films modified by the Ti top electrode to reduce the effective resistive switching region. Therefore, the turn-on process can be thought to be a field driven process. Moreover, the effective resistive switching region is reduced so that the Ti/IL/ZrO_2/Pt device possesses lower variations in V_{off}, V_{on}, R_{off}, and R_{on} (as shown in the Fig. 6) and lower resistance ratio between on state and off state.

Another interesting phenomenon is that the R_{on} of Ti/IL/ZrO_2/Pt device is larger than that of W probe/ZrO_2/Pt device, which might be due to the interface layers formed in series with the conducting filaments in the ZrO_2 matrix. For higher R_{on} of Ti/IL/ZrO_2/Pt device, the turn-off voltage of the Ti/IL/ZrO_2/Pt device is expected to be higher than that of the W probe/ZrO_2/Pt device under the same off current, which conforms to the statistical results, as shown in Fig. 6. Besides, some reports proposed that for the higher current compliance imposed on the device to switch into on state, higher off current was needed to switch it into off state.[12,13] Based on above results, the off process can be interpreted to be a current driven process.

On the other hand, the large variation in R_{off} may be caused by the random rupture of the conducting filaments,[14] implying that the region for filament rupture might be large. Kim *et al.* have reported that thin IrO_2 layers, located between Pt and NiO films in the device of Pt/NiO/Pt, would stabilize local oxygen migrations for filament formation and rupture, resulting in the stable resistive switching parameters.[15] In our Ti/IL/ZrO_2/Pt device, the interface layers would have the same function as the above mentioned IrO_2 layer, and fix filament formation and rupture at a certain region. Moreover, the region for filament rupture in the W probe/ZrO_2/Pt device is expected to be wider than that in the Ti/IL/ZrO_2/Pt device to some degree, leading to its R_{off} higher than that of the Ti/IL/ZrO_2/Pt device. Consequently, the value and the variation of R_{off} in the W probe/ZrO_2/Pt device are larger than those of the Ti/IL/ZrO_2/Pt device due to the different top electrode used.

The off process is believed to be related to the rupture of the conducting filaments, which is considered to occur at high resistance flaws inside the filaments by local Joule heating.[16] Kinoshita *et al.* suggested that the turn-off process may be realized by oxidization of the whole or a part of the conducting filaments on the anodic side.[8] Based on their suggestions, the off process is thought to be a current driven process due to the local Joule heating enhancing the oxidization of parts of conducting filaments, resulting in the rupture of conducting filaments. The oxidization assisted by local Joule heating effect takes place on the anodic side of the conducting filaments, which is close to the electrode with positive bias, causing the off process. It could be used to explain why the Ti/IL/ZrO_2/Pt device cannot be switched off by applying positive bias, for the reasons that the oxidization takes place in the interface layers instead in the parts of the conducting filaments near Ti top electrode. Therefore, when applying negative bias on the Ti top electrode to switch off the device, the oxidization assisted by the local Joule

heating is expected to take place in the parts of the conducting filaments near Pt electrode which is the anodic side relative to the Ti top electrode.

The detailed mechanism of resistive switching behavior remains unclear. The existence of oxygen ions and vacancies would play an important role in resistive switching,[7,17] leading to reduction and oxidization in some parts of conducting filaments. When Ti is applied with positive bias, oxygen ions migrate to the interface layers, accompanied by oxygen vacancies diffused toward Pt electrode, causing the reduction of conducting filaments and switching into on state. When Ti is applied with negative bias, electrons injected from Ti top electrode cause oxygen ions to migrate from the interface layers to oxidize the conducting filaments, switching into the off state. It has been reported in our recent paper that the $Ti/IL/ZrO_2/Pt$ device indicated a little degradation of electrical performance after successive switching cycles,[8] which might be possibly related to the evolution of the interface layers considering this work. Further study is necessary to investigate the evolution of the interface layers after degradation of the memory device and to closely look into the interrelations between the interface layers formed and original mechanism of the resistive switching behaviors.

IV. CONCLUSION

In summary, the effects of the Ti top electrode and the interface layers on the resistive switching characteristics of $Ti/IL/ZrO_2/Pt$ device were investigated in this study. It was found that such an effect leads to a translation from unipolar to bipolar resistive switching. Moreover, a series resistance formed due to the existence of the TiO_x layer, and even the contact resistance between Ti and ZrO_2 film imposed a current compliance on the memory device during turn-on process, which is different from those reported in the literatures. The turn-on process can be regarded as a field driven process and the turn-off process can be interpreted to be a current driven process owing to the local Joule heating enhancing the oxidization of anodic parts of conducting filaments.

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