

Nonvolatile Unipolar and Bipolar Resistive Switching Characteristics in Co-doped TiO₂ Thin Films with Different Compliance Currents

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The resistive switching behavior of 100nmthick Co-doped TiO₂ thin films grown by using a conventional rf magnetron sputtering system was investigated by using structural and electrical measurements. The Co-doped TiO₂ thin films display a rutile phase and a column-like structure. An unusual result, a switching transition from a unipolar to a bipolar behavior, was clearly observed at a high compliance current. The experimental results suggest that the switching transition is related to the formation of trap sites (CoO_x, TiO_{2-x}, and Co_x-Ti_{1-x}-O₂) under large electrical stress conditions. The improved reproducible switching properties of our Co-doped TiO₂ materials under forward and reverse bias stresses demonstrate the possibility of future non-volatile memory elements.

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I. INTRODUCTION

The nonvolatile memory (NVM) has recently become an indispensable part of the semiconductor industry due to the popularity of modern portable and mobile electronic devices. Therefore, various next-generation NVMs are being considered, such as the phase change memory (PRAM), the nano floating gate memory (NFGM), the polymer memory (PoRAM), and the resistive random access memory (ReRAM) recently [1–4]. Among them, the ReRAM is an interesting and promising competitor in the NVM class because of its low-power operation, high-density integration, high-speed access time, and ease of operation [5–8]. In addition, the ReRAM is believed to have fewer inherent scaling problems than capacitance-based RAMs, such as dynamic RAMs and ferroelectric RAMs [9]. The possibility of simplifying the cell structure of the ReRAM, which can process program data at high-speeds and low power consumption, makes it possible to reduce the device size. This ReRAM technology also uses materials that are highly compatible with conventional complementary metal-oxide semiconductor

(CMOS) processes, allowing existing production lines to be used. Therefore, the resistive switching behaviors of ReRAM have been greatly researched for various materials, as mentioned above. However, the corresponding resistive switching mechanisms have yet to be clarified in detail because the fundamental issues associated with resistive switching are still not clear.

In this letter, we report on the unusual electrical switching properties of Co-doped TiO₂ films. The structural properties of the Co-doped TiO₂ films were characterized using a X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, an unusual switching transition from a unipolar to a bipolar switching behavior was clearly observed in Co-doped TiO₂ films when the resistance was with varying a function of electrical stress. These experimental results might provide useful information for better understanding the origin of the I-V hysteresis loop and the principle of resistive switching in our Co-doped oxide materials.

II. EXPERIMENTS AND DISCUSSION

The metal/insulator/metal (MOM) heterojunction device of Pt/Co-doped TiO₂/Pt was deposited by using

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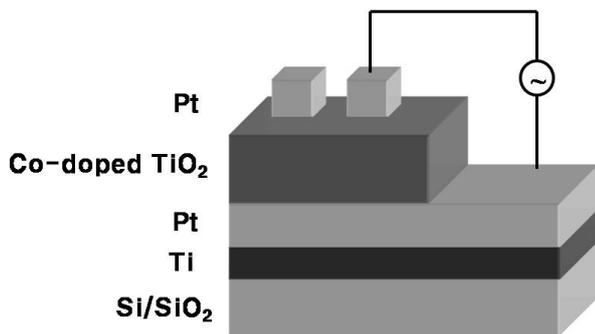


Fig. 1. Schematic structure of the Co-doped TiO_2 film.

the conventional dc and rf sputtering technique. A Pt(100 nm)/Ti(50 nm) bottom electrode was prepared on a SiO_2/Si substrate by using a dc sputtering system. A 100-nm polycrystalline Co-doped TiO_2 layer was deposited on the Pt/Ti/ SiO_2/Si substrate by using reactive rf sputtering at 150 W. The Co-doped TiO_2 films were deposited by using a pure Co-doped (at 3%) TiO_2 target at 5 mTorr, which was maintained by using argon gas. For the electrical measurement, a Pt top electrode was deposited by using a dc sputtering system and a photolithographic lift-off process. The thickness of the top electrode was 100 nm, and the diameters of the electrodes were 200 μm . Fig. 1 shows the basic structure of a Pt/Co-doped TiO_2 /Pt MOM heterostructure. The structural properties of the Co-doped TiO_2 layer were analyzed by using XRD and SEM. Subsequently, we investigated the switching properties and the electrical properties of the Co-doped TiO_2 layer by using a Keithley source-measurement unit.

The structural properties of Co-doped TiO_2 films grown on SiO_2/Si substrates were analyzed by using XRD and SEM, as shown in Fig. 2. As shown in Fig. 2 (a), the XRD pattern clearly exhibits rutile (110) and (101) peaks, implying the formation of the rutile phase in the Co-doped TiO_2 films. These patterns are typical characteristics of the polycrystalline rutile structure of Co-doped TiO_2 . No other phases (CoO_x , TiO_{2-x} , and $\text{Co}_x\text{-Ti}_{1-x}\text{-O}_2$) were observed in the as-grown Co-doped TiO_2 films. In addition, we observed a slight shift in the position of the main peak, resulting from an increase in the number of oxygen vacancies and the residual strain between the Co-doped TiO_2 films and the substrates. The surface and cross-sectional SEM images of Co-doped TiO_2 films on SiO_2/Si substrates are shown in Fig. 2 (b). As shown in this figure, the Co-doped TiO_2 film has a polycrystalline structure with a small grain size and a column-like structure. Therefore, our Co-doped TiO_2 film had the rutile and column-like structure of a polycrystalline phase.

The representative I-V characteristics of the Co-doped TiO_2 film after the forming process at about 7 V (not included in this paper) are shown in Fig. 3. Fig. 3 (a) shows unipolar switching behaviors of the Co-doped

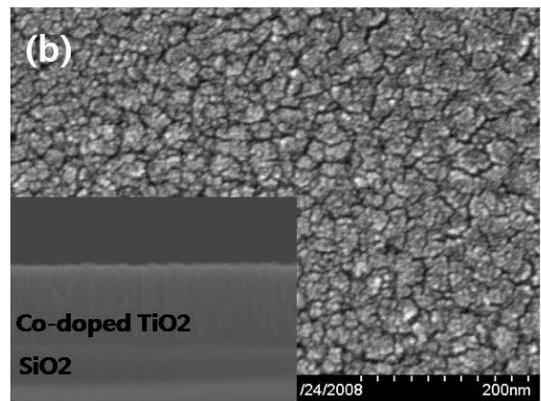
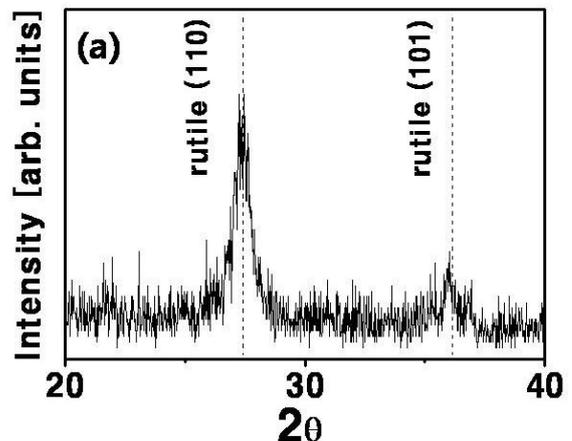


Fig. 2. (a) X-ray diffraction pattern and (b) scanning electron microscope surface image of the Co-doped TiO_2 film. The inset is a cross-sectional image of the Co-doped TiO_2 film.

TiO_2 film with a 1-mA compliance current. As shown in this figure, the Co-doped TiO_2 film with a 1-mA compliance current had a resistance ratio of roughly 3 orders magnitude for the ration of the high-resistance state (HRS; off state) to the low-resistance state (LRS; on state). The set and reset voltages are about 2.7 V and 0.8 V, respectively. This unipolar switching mechanism of binary oxide materials might be explained in terms of the formation of a conduction path which was generated by the movement of oxygen vacancies under an electrical field during the forming and set process [10–12]. In contrast to the unipolar switching in the Co-doped TiO_2 film with a 1-mA compliance current, the Co-doped TiO_2 film with a 10-mA compliance current shows bipolar switching (Figs. 3 (b)). Bipolar switching means that the bias voltage must change the polarity to switch between different resistance states. After the injection of a 10-mA compliance current, the sample starts in the LRS when sweeping the voltage from zero to negative voltage. By applying negative voltage above a critical value, the sample switches from the LRS to the HRS. By applying a positive voltage, the sample resistance switches back to the LRS. The local establishment of trap sites at the set

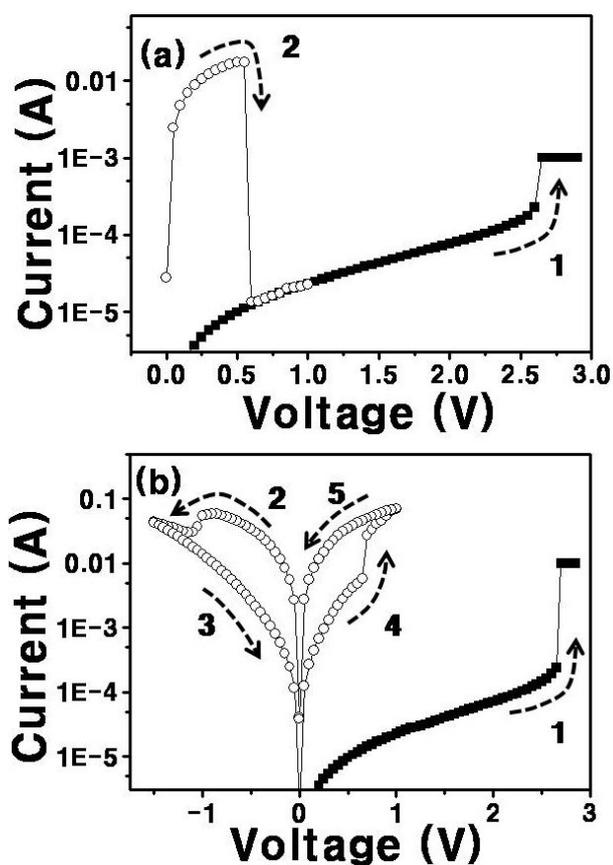


Fig. 3. Typical resistive switching I-V curves of (a) unipolar switching (1-mA compliance current) and (b) bipolar switching (10-mA compliance current) in Co-doped TiO₂ film.

process (10-mA compliance current) might be the reason for the bipolar switching in our Co-doped TiO₂ film. The doped Co ions are not combined in the Co-doped TiO₂ film, as shown by the X-ray photoelectron spectroscopy results (not included in this paper). Therefore, the unipolar switching behavior in Co-doped TiO₂ film is caused by only the TiO₂ materials (low compliance current (1 mA)). When a high compliance current (10 mA) is applied in the Co-doped TiO₂ film, a sufficient migration of oxygen ions occurs, so the doped Co ions can extract the oxygen ions from the TiO₂ bonding, resulting in oxygen ions combining with another metal ions due to the large electrical stress, thus, the interior of the Co-doped TiO₂ film forms another bonding state (CoO_x, TiO_{2-x}, and Co_x-Ti_{1-x}-O₂). When electrons are injected and trapped in trap sites (*e.g.*, CoO_x, TiO_{2-x}, Co_x-Ti_{1-x}-O₂) by applying a negative voltage, a local electric field is formed in the Co-doped TiO₂ film, resulting in a decrease in the conductivity and, thus, an increase in the resistance. Inversely, when a negative voltage is applied, electrons are ejected out of the trap site and as a result, the conductivity increases, corresponding to the set process.

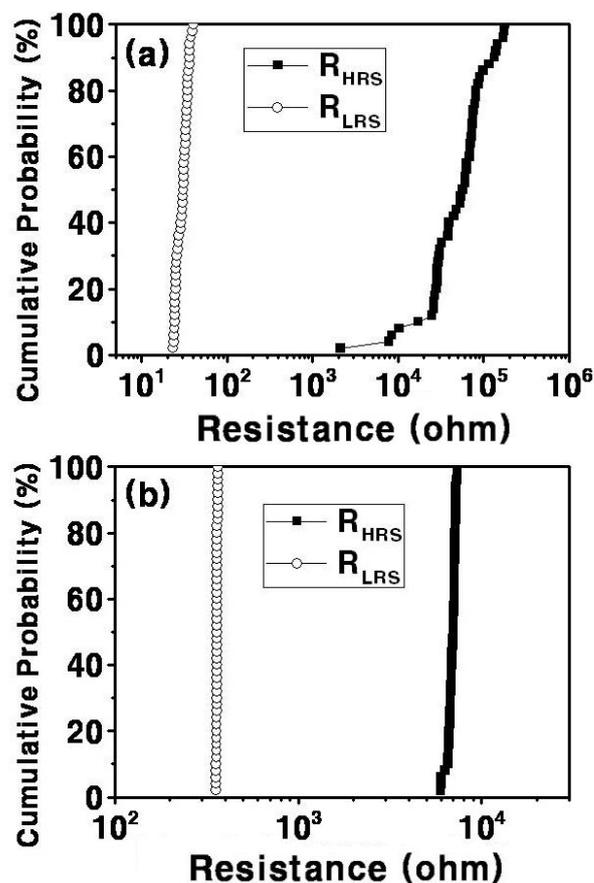


Fig. 4. Distribution of the resistance of (a) unipolar switching and (b) bipolar switching in the Co-doped TiO₂ film (read voltage: 0.2 V).

Figure 4 presents the device-to-device distribution of the resistance states during 50-set/reset switching cycles (unipolar switching: $V_{set} = 2$ V, $V_{reset} = 0.8$ V and bipolar switching: $V_{set} = 1$ V, $V_{reset} = -1.3$ V, readout voltage: 0.2 V). As shown in Figs. 4(a) and (b), R_{LRS} exhibits a more concentrated distribution than R_{HRS} , and no overlap between the R_{LRS} and the R_{HRS} is observed. However, it is enough to use the periphery circuits to probe the different resistance states because there are sharp difference (about 1 order) between the HRS and the LRS in our sample. In addition, the bipolar switching (10-mA compliance current) in the Co-doped TiO₂ film shows a more uniform distribution than the unipolar switching (1-mA compliance current) in the Co-doped TiO₂ film, which is due to random and unstable formation of a conduction path in unipolar switching while in bipolar switching, a stable resistance was obtained because a uniform number of electrons are trapped in trap sites (*e.g.*, CoO_x, TiO_{2-x}, and Co_x-Ti_{1-x}-O₂) on the Co-doped TiO₂ film.

The retention characteristics of the fabricated Co-doped TiO₂ film in the LRS and the HRS were measured at room temperature. Fig. 5 shows the current variation

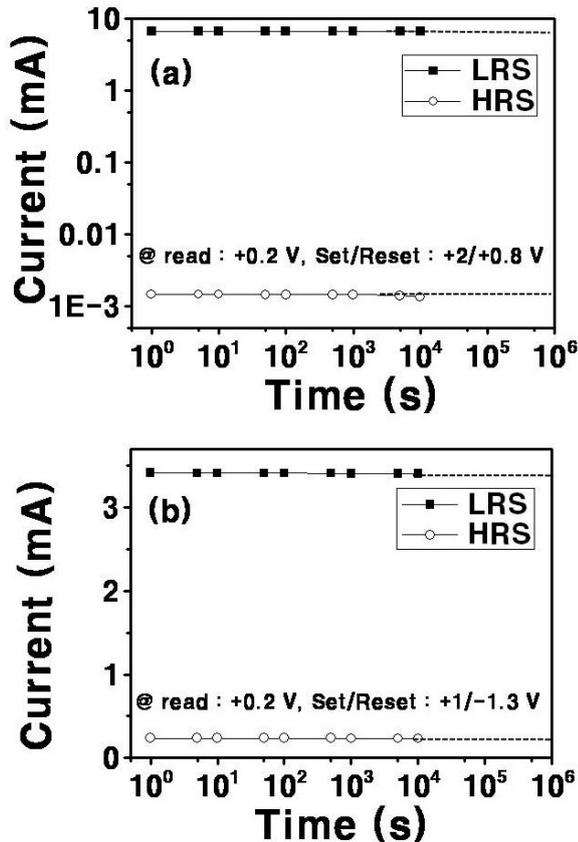


Fig. 5. Retention test of (a) unipolar switching and (b) bipolar switching in the Co-doped TiO_2 film (read voltage: 0.2 V).

over time for both the HRS and the LRS of unipolar switching and bipolar switching in the Co-doped TiO_2 film. The readout voltage was 0.2 V. Moreover, our film had an operational voltage (unipolar switching: $V_{set} = 2$ V, $V_{reset} = 0.8$ V and bipolar switching: $V_{set} = 1$ V, $V_{reset} = -1.3$ V). As can be seen, the HRS and the LRS were retained for 10^4 s without using an external bias voltage, and there is no remarkable degradation, confirming the nonvolatile nature and the nondestructive readout property of our devices.

III. CONCLUSION

We observed a switching transition from unipolar to bipolar switching in Co-doped TiO_2 films, which does not occur in typical binary oxide materials. We expect that

the bipolar switching in our structure is related to the formation of trap sites (CoO_x , TiO_{2-x} , and $\text{Co}_x\text{-Ti}_{1-x}\text{-O}_2$) under large electrical stress conditions. These novel Co-doped TiO_2 films could give rise to the promise of future non-volatile memory applications if superior memory characteristics, such as multi-level switching, long retention time, simple structure, and good uniformity, are considered.

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