Resistive Switching Mechanisms of V-Doped $SrZrO_3$ Memory Films

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***Abstract*—The resistive switching behaviors of sputtered V-doped $SrZrO_3$ (V:SZO) memory films were investigated in this letter. The current states of the memory films were switched between high current state (H-state) and low current state (L-state). The resistance ratio of the two current states was over 1000 at a read voltage. The switching mechanism from L- to H-state corresponds to the formation of current paths. However, this mechanism from H- to L-state is thought to be due to the fact that the defects present in the V:SZO film randomly trap electrons, and hence, the current paths are ruptured. The conduction mechanism of the H-state is dominated by ohmic conduction, whereas the L-state conduction is dominated by Frenkel–Poole emission. The polarity direction of the resistive switching is an intrinsic property of the $SrZrO_3$ oxides. The V:SZO films with high uniformity and good stability are expected to be used in nonvolatile memory.**

***Index Terms*—Conduction mechanism, nonvolatile memory (NVM), resistive random access memory (RRAM), resistive switching, $SrZrO_3$.**

I. Introduction

Due to the popularity of portable equipment, such as mobile phone and MP3 player, the nonvolatile memory (NVM) plays an important role in the semiconductor industry. One of the promising candidates of next-generation NVMs is the resistive random access memory (RRAM) because of its superior properties including reproducible resistive switching, low power consumption, high operation speed, long retention time, small size, and simple structure. The reproducible resistive switching behaviors were observed on various kinds of perovskite oxides [1]–[5] and transition metal oxides [6]–[9]. However, some controversies regarding resistive switching mechanisms still exist. Recently, perovskite oxides, such as doped $SrTiO_3$ [3] and $SrZrO_3$ (SZO) [4], [5], have attracted wide attention due to its superior resistive switching behaviors. In this letter, we report the resistive switching mechanisms of V-doped $SrZrO_3$ (V:SZO) films deposited by the sputter method. In addition, the conduction mechanisms in both low current state (L-state) and high current state (H-state) are studied. The good stability and high uniformity of the films are also demonstrated.

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II. Experiment

A 200-nm-thick SiO_2 oxide film was thermally grown on (100) silicon wafers in an oxidation furnace to perform an isolation layer. Second, a 150-nm-thick $LaNiO_3$ (LNO) conducting film was deposited on the SiO_2/Si substrates at 250 °C using a radio-frequency magnetron sputter system. The LNO films were heat-treated by the rapid thermal annealing furnace in O_2 ambient at 700 °C for 1 min. Then, a 45-nm-thick 0.3-mol% V:SZO film was deposited on the LNO bottom electrode at 500 °C by the radio-frequency magnetron sputter. Based on X-ray diffraction, the 45-nm-thick V:SZO film has a (100) highly preferred orientation polycrystalline structure. Finally, a 300-nm-thick Al top electrode was deposited by a thermal evaporation system to form the metal–insulator–metal (MIM) sandwich structure. The area of the top electrode defined by a shadow mask was 4.9×10^{-4}cm^2. The electrical measurement was performed by an Agilent 4155C semiconductor parameter analyzer.

III. Results and Discussion

Fig. 1(a) depicts the plot of current versus bias voltage of the V:SZO-based MIM device. While negative voltage is applied on the top electrode, the current rapidly increases at -13 V and switches the device from L- to H-state (ON). The state holds on H-state after sweeping the bias voltage from -18 to 0 V. Subsequently, the bias voltage sweeps to positive and changes the device from H- to L-state (OFF) after passing a transition region that performs the negative differential resistance. The state firmly holds on L-state after sweeping the bias voltage from $+18$ to 0 V. The resistance ratio of the two current states is over 1000 times at a low voltage. The resistances of H-state and L-state are 10 kΩ and 100 MΩ at -1 V, respectively. The polarity direction of the resistive switching is an intrinsic property of the SZO oxides. This resistive switching cycle can be traced and reproduced more than 100 times. In the ON process, the biased electrons found one or few conduction paths consisting of possible point defects, such as oxygen vacancies ($V_o^{\bullet}$, $V_o^{\bullet\bullet}$) and ionic and electronic defects associated with Zr replacement by V ($V_{Zr}^{\bullet}$, e$'$). Simultaneously, the electrons hopped passing through the V:SZO film in these paths and causing the current to dramatically increase. Consequently, the resistive switching mechanism of the ON process

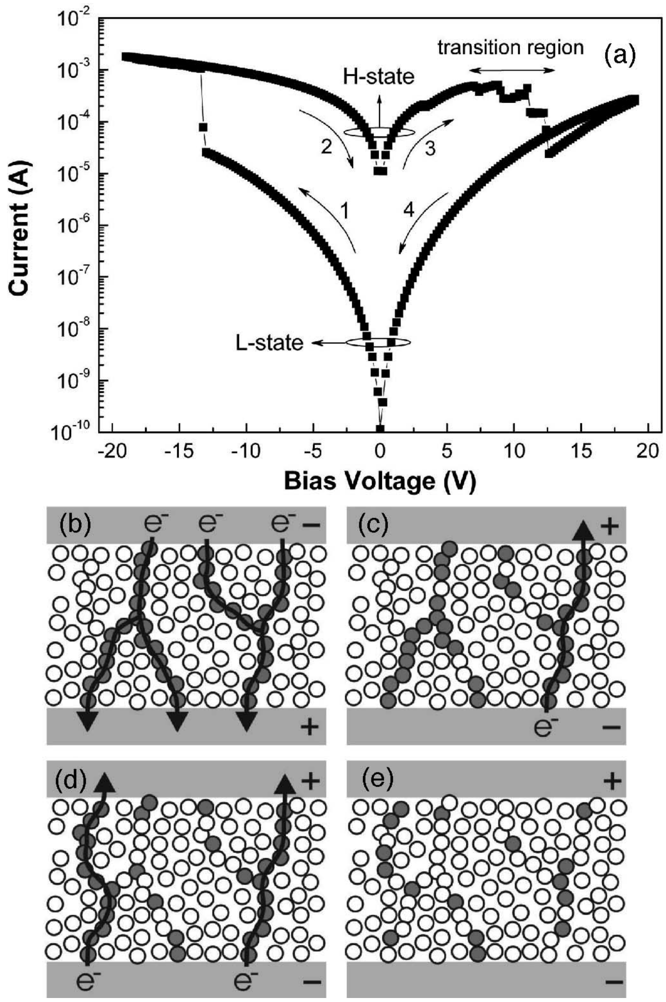

Fig. 1. (a) Resistive switching property of the V:SZO-based MIM device. Hypothetical diagram of the current paths: (b) ON process and (c, d, e) OFF process.

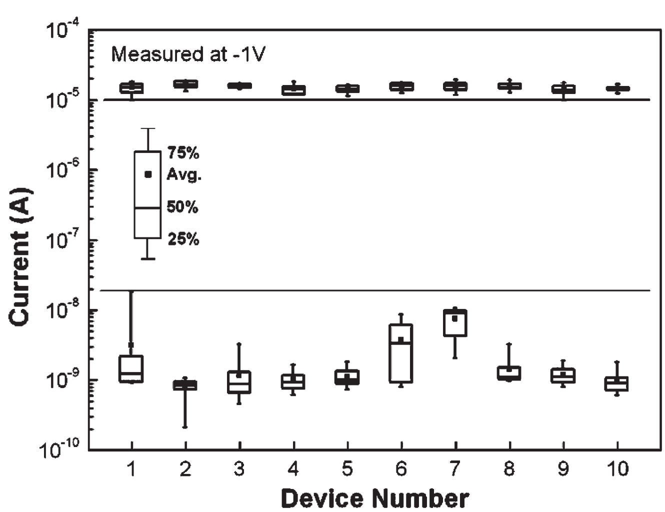

Fig. 2. Uniformity and stability of both L-state and H-state of the V:SZO-based MIM device.

was considered to affect the formation of current paths [2]. Fig. 1(b) shows the hypothetical diagram of the current paths of the ON state. On the other hand, the mechanism of the

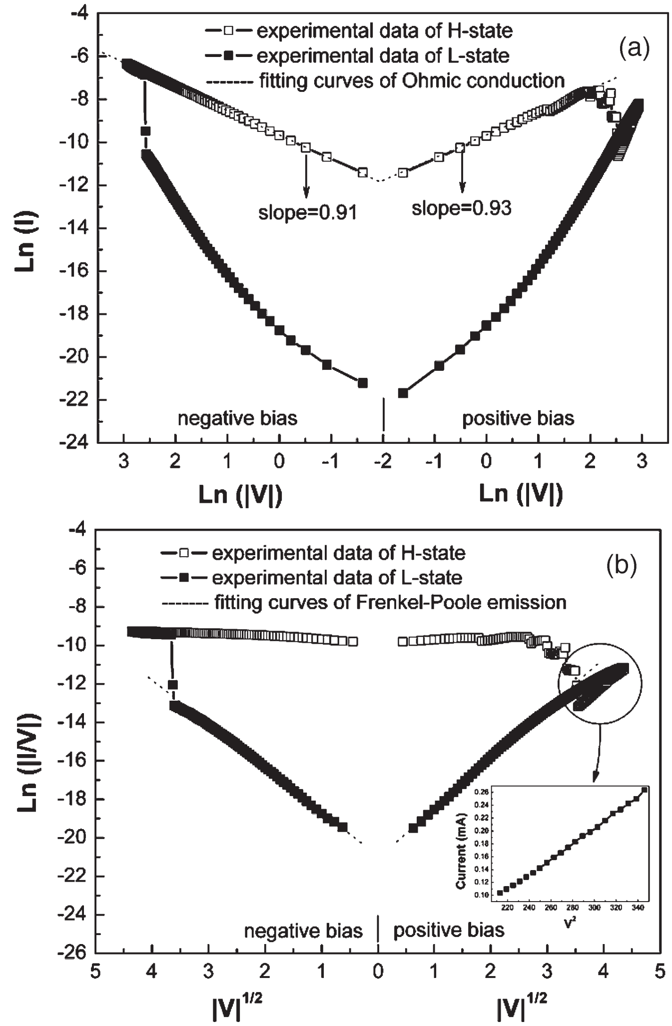

Fig. 3. Fitting curves of (a) ohmic conduction and (b) Frenkel–Poole emission for both L-state and H-state of the V:SZO-based MIM device. The inset of (b) shows the fitting curve of the space-charge-limited current of L-state when the bias voltage is over 13 V.

OFF process is believed to cause the current paths to rupture. The defects in the V:SZO film would trap electrons randomly while the positive bias voltage is applied. In the transition region, the current decreases while the trapping just occurs at the current paths, and hence, a part of the current paths is ruptured [as shown in Fig. 1(c)]. However, the current does not decrease to the stable L-state at a time because the current could flow through other unruptured or newly formed current paths [Fig. 1(d)]. Nevertheless, the current should return to the stable L-state after passing through the transition region (13 V) while the defects in the V:SZO film trap electrons to some degree, and hence, the paths could be considered ruptured [Fig. 1(e)]. Such switching behaviors show that the OFF process is more complicated and consumes more power than the ON process, which shows the same tendency with the different transition speeds between the two current states by dynamic pulse voltage analyses [4].

Fig. 2 shows the statistical chart of both H-state and L-state measured at -1 V. The resistive switching behaviors can be observed in more than 90% of V:SZO-based MIM devices. In

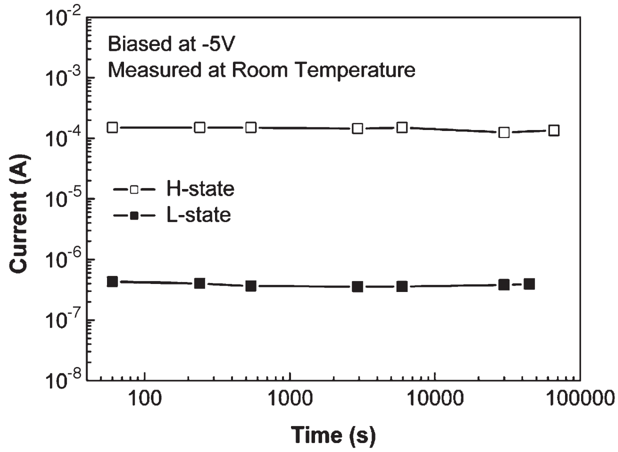

Fig. 4. Nondestructive readout property of the V:SZO-based MIM device.

the chart, H-state performs more stable than L-state due to the stable conductivities of the current paths in the V:SZO films. The resistance ratio of the two current states is over 500 for the worst case and over 1000 in general. Consequently, the uniformity and stability of the V:SZO-based MIM devices are good enough for possible NVM applications.

The plots of $\mathrm{Ln}(I)$ versus $\mathrm{Ln}(|V|)$ for both H-state and L-state of the V:SZO film shown in Fig. 3(a) depict that the slopes of the H-state curves are very close to unity, which indicates that the H-state is dominated by ohmic conduction, which is related to thermally excited electrons hopping from one isolated state to the next [10]. Furthermore, the MIM device structure with asymmetric top and bottom electrodes shows the symmetric fitting curves of H-state between the positive and negative bias conditions. Therefore, the H-state current could relate to the bulk conduction of the V:SZO film rather than the interface effect. On the other hand, the L-state curves are not straight lines, which imply that the L-state is dominated by other conduction mechanisms. The L-state follows the Frenkel–Poole emission due to field-enhanced thermal excitation of trapped electrons into the conduction band, as indicated by the linear fittings to the experimental data for the V:SZO film shown in Fig. 3(b). However, the fitting curves of the L-state are not absolutely straight lines when the device is swept over the OFF voltage (13 V). The inset of Fig. 3(b) exhibits the linear fitting of the trap-controlled space-charge-limited current when the device is swept over 13 V. Either Frenkel–Poole emission or space-charge-limited current is controlled by the trapped electrons. Therefore, the Frenkel–Poole mechanism dominates at the sweeping voltage less than 13 V, whereas the space-charge-limited current becomes predominant at the sweeping voltage over 13 V.

Fig. 4 shows the stability of the V:SZO memory film under an ongoing bias voltage of -5 V for more than 40 000 s, which indicates that the current states are not varied after applying 4×10^{12} read pulses (10 ns). Therefore, an important property of nondestructive readout is demonstrated.

IV. Conclusion

The resistive switching properties of V:SZO-based MIM device were investigated. The switching mxechanism from L- to H-state corresponds to the formation of the current paths. However, the current switches from H- to L-state due to the defects randomly trap electrons, and hence, the current paths are ruptured. The conduction mechanism of H-state is ohmic conduction, whereas the L-state conduction is dominated by Frenkel–Poole emission at a bias voltage < 13 V but by the space-charge-limited current mechanism at > 13 V. Both H- and L-state conduction mechanisms are bulk controlled, not interface controlled. The type and concentration of the defects is a prominent factor to affect the switching properties of V:SZO films.

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