Effect of Top Electrode Material on Resistive Switching Properties of ZrO_2 Film Memory Devices

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***Abstract*—The influence of top electrode material on the resistive switching properties of ZrO_2-based memory film using Pt as a bottom electrode was investigated in this letter. In comparison with Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices, the Ti/ZrO_2/Pt device exhibits different resistive switching current–voltage (I–V) curve, which can be traced and reproduced by a dc voltage more than 1000 times only showing a little decrease of resistance ratio between high and low resistance states. Furthermore, the broad dispersions of resistive switching characteristics in the Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices are generally observed during successive resistive switching, but those dispersions are suppressed by the device using Ti as a top electrode. The reliability results, such as cycling endurance and continuous readout test, are also presented. The write-read-erase-read operations can be over 10^4 cycles without degradation. No data loss is found upon successive readout after performing various endurance cycles.**

***Index Terms*—Nonvolatile memory, resistive random access memory (RRAM), resistive switching, ZrO_2.**

I. Introduction

THE next-generation nonvolatile memory (NVM) has attracted extensive attention due to the conventional memories approaching their scaling limits. Several types of NVMs, such as ferroelectric random access memory, magnetic random access memory, and resistive random access memory (RRAM), are being investigated. Among various NVMs, the RRAM that is composed of a simple metal-insulator-metal (M-I-M) structure has the merits of low power consumption, high-speed operation, and high-density integration. Due to these excellent characteristics, a number of metal oxides, such as $SrZrO_3$ [1], $Pr_{1-x}Ca_xMnO_3$ [2], [3], Nb_2O_5 [4], TiO_2 [5], [6], NiO [7], and ZrO_2 [8], have been studied. However, there is an important issue risen about how to minimize the dispersions of resistive switching parameters such as the resistance values of ON-state (R_{ON}) and OFF-state (R_{OFF}), and the required voltages to switch from OFF-state to ON-state (V_{ON}), and vice versa (V_{OFF}), which is needed to overcome. It is because that after a long-time operation, the dispersions of these parameters lead to severe control and readout hazards. By means of inserting thin IrO_2 layers at M–I interfaces, the reduction of dispersion was shown due to the enhancement of crystalline insulator [9]. Moreover, reducing the active memory area to sub-100-nm size by a plug-contact-type bottom electrode was also able to reduce the dispersion into a sharp distribution [10].

In this letter, we report a more effective and convenient method to reduce the dispersions of the resistive switching parameters by replacing conventional Pt or Al top electrode with Ti top electrode.

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II. Experiments

The 70-nm-thick ZrO_2 films were deposited on Pt/Ti/SiO_2/Si substrate at 250 °C by a radio-frequency (RF) magnetron sputtering. All 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 M-I-M structure, the Al top electrode was deposited by a thermal evaporation to fabricate Al/ZrO_2/Pt structure. The top electrodes of Pt and Ti were deposited by an RF magnetron sputtering to form Pt/ZrO_2/Pt and Ti/ZrO_2/Pt structures. All the top electrodes were formed at ambient temperature with a diameter of 250 μm patterned by the shadow mask process. Agilent 4155C semiconductor parameter analyzer was used to measure the current–voltage (I–V) characteristics of the ZrO_2 film memory device. For dynamic measurement, Agilent 81110A was employed to generate voltage pulses to change the resistance of the device, and the Agilent 4155C was used to measure the current of the device. All the measurements were performed at room temperature.

III. Results and Discussion

Fig. 1(a) shows the typical I–V curve of the Ti/ZrO_2/Pt device. First, using the dc voltage sweep method with a current compliance of 5 mA, there, a sudden increase of current occurs near 8.8 V and, then, is limited at 5 mA, which is called forming process. The forming process is similar for all the three devices. After the forming process, the Ti/ZrO_2/Pt device reaches its low resistance state, called ON-state. By sweeping a voltage bias to negative over V_{OFF}, the device is switched from the low resistance state to the high resistance state (OFF-state). On the contrary, the voltage sweep toward positive over V_{ON} is performed to switch back to the ON-state, and there is no current compliance needed again, which is different from the

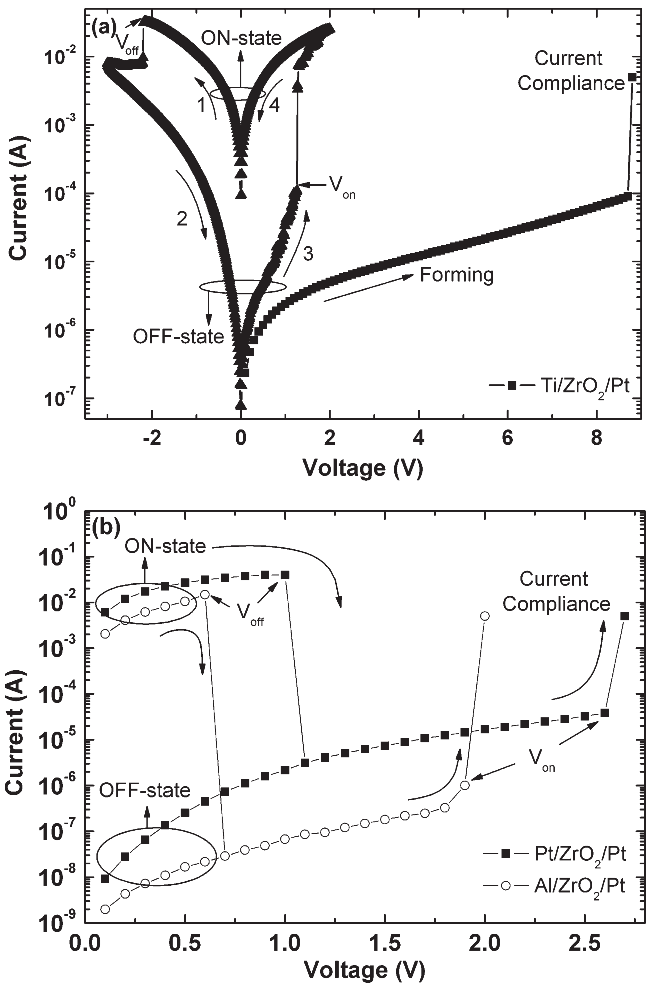

Fig. 1. Typical resistive switching I–V curves of Ti/ZrO_2/Pt, Pt ZrO_2/Pt, and Al ZrO_2/Pt devices, respectively.

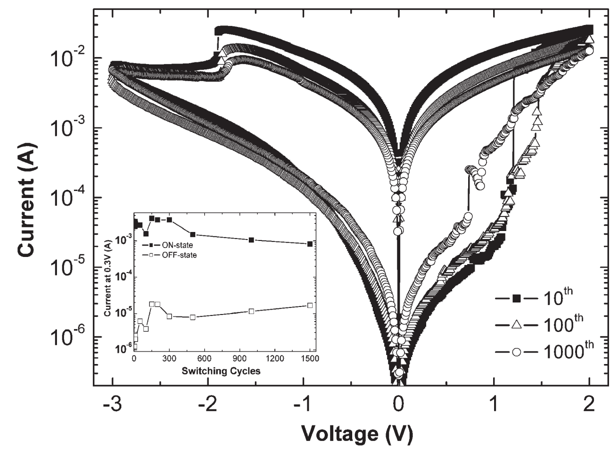

Fig. 2. 10th, 100th, and 1000th I–V curves in the Ti/ZrO_2/Pt device during continuous dc voltage switching cycles. The inset shows that the current of the ON-state gradually decreases and that of the OFF-state gradually increases during continuous switching cycles.

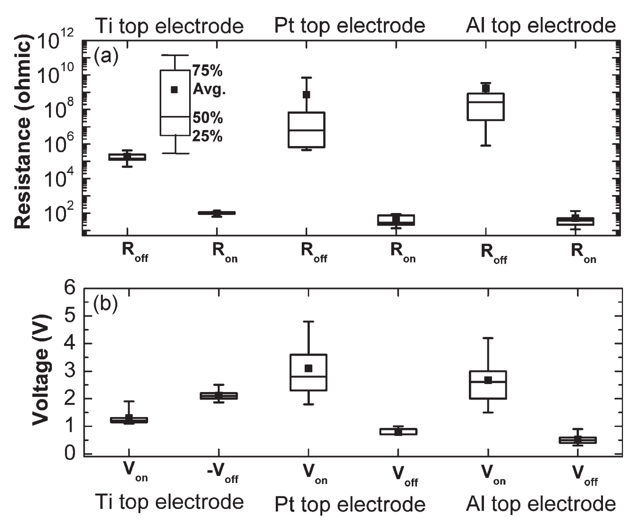

Fig. 3. Variations of the resistive switching parameters in the Ti/ZrO_2/Pt, Pt/ZrO_2/Pt, and Al/ZrO_2/Pt devices, respectively. R_{ON} and R_{OFF} are resistances measured at 0.3 V for each device.

reported Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices [11]. The typical I–V curves of Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices are unipolar [as shown in Fig. 1(b)], which apply the positive (negative) voltage to switch them to OFF-state and back to ON-state with a current compliance by applying the positive (negative) voltage again. It was reported that the oxygen content and oxygen-related defects had great influences on the resistive switching characteristics [6], [7], [9], [11], [12]. Therefore, the different I–V curve of Ti/ZrO_2/Pt device from those of Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices might be attributed to the lower work function (4.3 eV) of titanium, or that titanium served as oxygen gettering material to induce the oxygen vacancies at Ti/ZrO_2 interface, which would modify the oxygen vacancies distribution within ZrO_2 memory film further leading to better resistive switching characteristics.

The resistive switching of Ti/ZrO_2/Pt device (I–V curve) can be traced and reproduced over 1000 times. The 10th, 100th, and 1000th cycle I–V curves of Ti/ZrO_2/Pt device are shown in Fig. 2, and there is only a little distortion between them. During the successive resistive switching by dc voltage, there is no "set fail" phenomenon observed, which is a failure of resistive switching from OFF-state to ON-state [9]. Moreover, as the continuous resistive switching cycle increases, the ON-state current (measured at 0.3 V) gradually decreases while the OFF-state current (measured at 0.3 V) gradually increases, which causes the resistance ratio between ON-state and OFF-state to decrease, as shown in the inset of Fig. 2.

Fig. 3 shows the statistical charts of the resistive switching parameters for various top electrode devices during continuous resistive switching by dc voltage. Both R_{ON} and R_{OFF} of different devices are measured at 0.3 V. The R_{ON}, R_{OFF}, V_{ON}, and V_{OFF} of the Ti/ZrO_2/Pt device obviously have sharp distributions, and the dispersions are reduced in comparison with the Pt/ZrO_2/Pt and Al/ZrO_2/Pt devices. Consequently, the Ti/ZrO_2/Pt device with good uniformity and stability of switching parameters has high potential for possible NVM applications.

The electrical pulse-induced resistance change effect was also performed in Ti/ZrO_2/Pt device (Fig. 4). After adding a -3-V 10-μs voltage pulse on the device, the state is switched to OFF-state and measured at 0.3 V. Then, adding a $+6$-V 10-μs voltage pulse on the device, the OFF-state is changed to ON-state and measured at 0.3 V. The polarity of the resistance switching

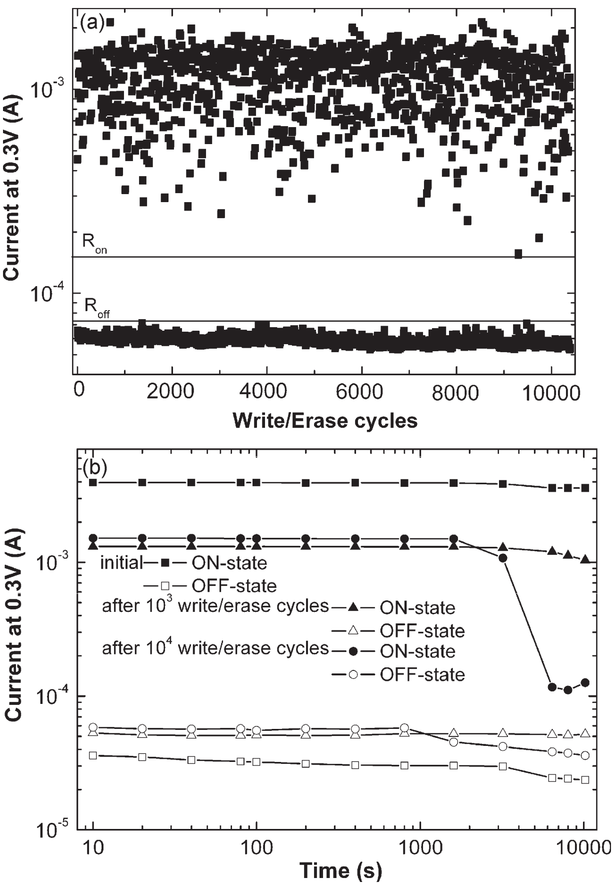

Fig. 4. (a) Dynamic pulse resistive switching of a $Ti/ZrO_2/Pt$ device for a "write-read-erase-read" sequence over 10^4 cycles. (b) Nondestructive readout properties of a $Ti/ZrO_2/Pt$ device. Before 10^4 write/erase cycles, both ON-state and OFF-state are kept stable. However, it shows a little drop of R_{ON} after 10^4 write/erase cycles.

is the same as that of the dc voltage sweeping operation. The write/erase operation indicated in Fig. 4(a) demonstrates that the device can be switched over 10^4 cycles without degradation. Fig. 4(b) depicts the stability of the $Ti/ZrO_2/Pt$ device under an ongoing bias voltage of 0.3 V after 10^3 and 10^4 write/erase cycles. The initial ON-state and OFF-state are kept stable more than 10^4 s, indicating that the resistance states are not varied during 10^{12} read pulses (10 ns). Even after 10^3 write/erase cycles, both ON-state and OFF-state are almost kept at the same current values. Therefore, important properties of nondestructive readout and good reliability are demonstrated in this device. However, after 10^4 write/erase cycles, the current of the ON-state shows a little drop, but remains higher than that of the OFF-state, which would not cause a readout hazard.

However, there are various remaining questions needed to be studied, such as the possibility of oxidation of top electrode, nanodomain switch, conduction paths formation in the $Ti/ZrO_2/Pt$ device, to provide more detailed explanations about why the $Ti/ZrO_2/Pt$ device exhibits better resistive switching characteristics.

IV. Conclusion

The effect of the top electrode material on the switching behaviors of ZrO_2 film memory devices was investigated. It was found that the $Ti/ZrO_2/Pt$ device exhibited better resistive switching properties in comparison with $Pt/ZrO_2/Pt$ and $Al/ZrO_2/Pt$ devices. It was demonstrated in the $Ti/ZrO_2/Pt$ device that it can be traced and reproduced over 1000 times with a little decrease of the resistance ratio between ON-state and OFF-state. The dispersions of resistive switching parameters such as, R_{ON}, R_{OFF}, V_{ON}, and V_{OFF}, were minimized showing sharp distributions. The $Ti/ZrO_2/Pt$ device with the write/erase operations over 10^4 cycles without degradation and the good stability of ON-state and OFF-state has high potential for NVM applications.

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