A Comprehensive Study of the Resistive Switching Mechanism in Al/TiO$_x$/TiO$_2$/Al-Structured RRAM

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Abstract—The conduction mechanism and resistive switching properties in a resistive-random-access-memory device composed of Al(top)/TiO$_x$/TiO$_2$/Al(bottom) are investigated in this paper. The active-top-electrode (TE) material aluminum interacted with the TiO$_2$ layer and induced an oxygen-deficient TiO$_x$ layer near the TE. The naturally formed oxygen-deficient TiO$_x$ layer was confirmed by a transmission-electron-microscope energy-dispersive X-ray spectrometry analysis. The oxygen-deficient TiO$_x$ region acted as a trap for electrons and contributed to the resistive switching. The proposed mechanism and measured data are verified through simulation of a two-variable resistor model.

Index Terms—Oxygen vacancy, resistive random access memory (RRAM), resistive switching, TiO$_x$.

I. INTRODUCTION

RESISTIVE random access memory (RRAM) has attracted considerable attention due to superior characteristics that include its simple metal–insulator–metal (MIM) structure, high density integration, and fast write/erase operation. Promising candidate materials for RRAM devices are doped perovskite SrZrO$_3$ [1], ferromagnetic materials such as (Pr, Ca)MnO$_3$ [2], and binary transition metal oxides such as NiO [3], TiO$_2$ [4], and Cu$_x$O [5]. Although the switching characteristics have been explained by many theories, the switching mechanisms are not clearly understood. For example, much work remains in such areas as space-charge-limited conduction [4], Schottky barriers with interface states [6], [7], electrochemical migration at the interface [8], and trap charging and discharging [3], [9].

Recently, the resistive switching of active-top-electrode (TE)-induced junctions has begun to draw an increasing amount of attention [10]–[13]. In contrast to inert Ag or Pt TE-based junctions, active-TE-based junctions have unique features such as bipolar resistive switching, a low-resistance state (LRS) dominated by a uniform interface rather than a filamentary interface (as determined in electrode-area experiments), a long switching time, and opposite cycling directions compared with inert-TE-based junctions. All of the features in active-TE-based junctions are interpreted by the formation and dissociation of the oxidized active-TE material at the interface rather than by the previously proposed conducting filaments in inert Ag or Pt TE-based junctions. In an earlier work by the authors involving the Al/TiO$_2$/Al structure [4], the active material aluminum was used as the TE. It was found in that study that only the TiO$_x$ layer near the TE region, not the entire TiO$_2$ layer, contributed to the resistive switching and that the resistive switching was governed by the trap-controlled space-charge-limited current (SCLC). However, a suitable switching model and an interpretation of the resistive switching could not be provided.

In other research concerning resistive switching, Williams et al. recently reported a new concept related to resistive switching behavior when they introduced a device structure consisting of Pt(top)/TiO$_2$/TiO$_x$/Pt(bottom) [14], [15]. An oxide layer with an engineered oxygen vacancy distribution was produced using two-step deposition methods to investigate the switching mechanism. In that case, the movement of oxygen vacancies from the TiO$_2$ to the TiO$_2$ layer was a dominant factor of the switching property.

In this paper, the switching behavior of the Al(top)/TiO$_x$/TiO$_2$/Al(bottom) structure is carefully analyzed and compared to that of the aforementioned Pt(top)/TiO$_2$/TiO$_x$/Pt(bottom) structure. Although oxygen vacancies represent the dominant factor that governs the switching characteristics of both devices, regardless of structural similarities, the switching mechanisms are clearly different from that in the previous works [14], [15]. Hence, a new resistive switching mechanism in the Al(top)/TiO$_2$/TiO$_x$/Al(bottom) structure is proposed and verified by a simulation based on a two-variable resistor model.

II. EXPERIMENT

The device was fabricated as a conventional crossbar MIM structure whose electrode area is 10 $\mu$m $\times$ 10 $\mu$m. Aluminum with a thickness of 150 nm was used for the TE and bottom electrode (BE). Both the TE and BE were prepared by dc sputtering. They were patterned by conventional photolithography and a wet-etching process. TiO$_2$ thin film with a thickness of 10 nm was deposited on the BE using plasma-enhanced atomic layer deposition. Titanium tetraisopropoxide was used as a precursor, and the film growth rate was 0.5 Å/cycle. All measurements were performed by a conventional two-probe method at room temperature. Unless specified, all bias sweeps were conducted in the direction 0 V $\rightarrow$ −3 V $\rightarrow$ 0 V $\rightarrow$ 3 V $\rightarrow$ 0 V.

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III. OXYGEN-DEFICIENT LAYER

Fig. 1 shows a transmission-electron-microscope (TEM) image of the fabricated Al(TE)/TiO$_x$/TiO$_2$/Al(BE) device. As shown in Fig. 1, a TiO$_2$ layer with a thickness of 10 nm was deposited. However, between the TE and the TiO$_2$ layer, another layer (∼5 nm) was newly generated. To identify this layer, a TEM energy-dispersive X-ray spectrometry (TEM-EDX) analysis was carried out. Fig. 2 shows the scanned atom profiling between TE and BE by TEM-EDX analysis. From these data, it is found that an oxygen-deficient layer was preferentially produced in the TiO$_2$ layer near the TE naturally. It was also observed that some fraction of the aluminum in the TE diffused into the TiO$_2$ layer.

The newly generated layer (the oxygen-deficient layer) can be considered as an Al-doped TiO$_2$ layer. Generally, oxygen vacancies in TiO$_2$ are known to act as n-type dopants, transforming the insulating oxide into an electrically conductive doped semiconductor [16], [17]. This presence of n-type dopants in the form of oxygen vacancies in TiO$_2$ was verified by analysis of the MIM structure, which used an inert metal electrode. However, for the Al-doped TiO$_2$, Al$_{3+}$ substitutes for Ti$_{4+}$ in the TiO$_2$, and oxygen vacancies can be produced by diffused Al$_{3+}$ [18]. It is improbable that an Al$_{3+}$ ion in TiO$_2$ acts as a deep trap and captures an electron; instead, an oxygen vacancy traps an electron [19], [20]. Therefore, it is speculated that oxygen vacancies in the TiO$_x$ layer of the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) device act as traps for electrons.

IV. ELECTRICAL CHARACTERISTICS

Fig. 3 shows the typical current–voltage (I–V) characteristics of the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) device that produces the bipolar resistive switching. For electrical testing, a bias voltage was applied to the TE, while the BE was grounded. A high-resistance state (HRS) and an LRS were switched by a specific bias consisting of a negative set voltage ($V_{SET}$) and a positive reset voltage ($V_{RESET}$). The resistance ratio between the HRS and LRS was approximately $10^2$ at −0.5 V under a compliance current of 2.5 mA, which was applied to prevent device breakdown. The initial state of the device was HRS, and a forming process was not required for this type of resistive switching. From a previous analysis by the authors [4], it was verified that the resistive switching was governed by trap-controlled SCLC in the only TiO$_x$ layer near the TE.
Fig. 5 (a) $I$–$V$ curve between contact $\gamma$ and $\delta$. The resistive switching property was not observed in the TiO$_2$/Al(BE) junction. (b) Typical $I$–$V$ curve of an Al($\alpha$)/TiO$_x$/TiO$_2$/Al($\gamma$) device. Only negative polarity of $V_{SET}$ was observed. (c) Bias sweeps were conducted in the direction 0 V → $-3$ V → 0 V → 3 V → 0 V in the Al($\alpha$)/TiO$_x$/Al($\beta$) device, and $V_{SET}$ was observed at a negative bias. (d) Bias sweeps were conducted in the direction 0 V → 3 V → 0 V → $-3$ V → 0 V in the Al($\alpha$)/TiO$_x$/Al($\beta$) device, and $V_{SET}$ was observed at a positive bias.

To investigate the interface property in the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) structure, a four-contact electrical measurement was performed, as shown in Fig. 4. When both positive and negative voltages were applied between contacts $\gamma$ and $\delta$, resistive switching behavior was not observed, and only a symmetric $I$–$V$ curve was shown by means of the TiO$_2$/Al(BE) Schottky barrier junction, as shown in Fig. 5(a).

On the one hand, during repetitive resistive switching between contacts $\alpha$ and $\gamma$, as shown in Fig. 5(b), no change of the $I$–$V$ characteristics between contacts $\gamma$ and $\delta$ was observed at either a positive or a negative bias. This implies that the oxygen-deficient TiO$_x$ region responds to the external bias change, whereas the TiO$_2$/Al(BE) region does not contribute to the resistive switching. These characteristics are consistent with the aforementioned previous work [4] and are quite different from the resistive switching behaviors observed in the Pt(TE)/TiO$_2$/TiO$_x$/Pt(BE) device. According to the model proposed by Williams et al. [15], [16], switching is observed from HRS to LRS when negative voltage applied to the TE attracts positively charged mobile oxygen vacancies ($V^2_2^+o$) toward that electrode, as shown in Fig. 6. Consequently, the top Pt(TE)/TiO$_2$ rectifying nonohmic interface became an ohmiclike interface by $V^{2+}_o$. Therefore, if this model is adapted to the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) structure, $V_{SET}$ should have positive polarity to drive the $V^{2+}_o$ from the oxygen-deficient TiO$_x$ layer toward the TiO$_2$/Al(BE) nonohmic interface. In addition, this nonohmic TiO$_2$/Al(BE) interface should become an ohmic interface after the SET process. However, this is not consistent with the measured data. Therefore, for the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) structure, the negative polarity of the $V_{SET}$ can be explained as due to the movement of negative charges, i.e., electrons, inducing resistive switching rather than as due to the movement of positive charges by $V^{2+}_o$. It is believed that this distinctive characteristic originates from the existing forming process. After the electrical forming process,
V. Two-Variable Resistor Model

The appearance of both positive and negative polarities of $V_{SET}$ in the Al(TE)/TiO$_x$/Al(TE) device can be understood using a two-variable resistor model. Creation of the two-variable resistor model began with several assumptions.

1) Oxygen vacancies in the oxygen-deficient layer (TiO$_x$) act as traps for electrons, and they are uniformly distributed in the TiO$_x$ layer.

2) The TiO$_x$ layer is divided into two parts: a good conducting part of thickness $w(t)$ (i.e., $R_{on}$) and a less conductive part of thickness $D - w(t)$ (i.e., $R_{off}$).

3) The filled-trap region of TiO$_x$ shows good conductivity (i.e., $R_{on}$).

4) The unfilled-trap region of TiO$_x$ shows poor conductivity (i.e., $R_{off}$).

Before applying bias to Al(TE)/TiO$_x$/Al(TE) device, the initial TiO$_x$ film was in HRS. Therefore, the initial TiO$_x$ film (= unfilled-trap region of TiO$_x$) was considered as $R_{off}$. It should be noted that this model is only applied in the Al(TE)/TiO$_x$/Al(TE) device and not in the Al(TE)/TiO$_x$/TiO$_2$/Al(BE) device.

The total resistance of the TiO$_x$ layer is determined by a serially connected two-variable resistor consisting of a low-resistance resistor ($R_{on}$) and a high-resistance resistor ($R_{off}$). The thickness of this two-variable resistor, i.e., $w(t)$, represents the length of the filled-trap region of TiO$_x$. In addition, $D$ is the total thickness of TiO$_x$, as shown in Fig. 7. Thus, the total resistance can be described by the following equation:

$$R_{total} = R_{on} \frac{w(t)}{D} + R_{off} \left(1 - \frac{w(t)}{D}\right).$$  \hfill (1)

In this case, oxygen vacancies act as electron traps. As the applied bias is increased, electrons are injected from the electrode, and the traps are gradually filled. Injected carriers exceeding the traps contribute to the excess current. As an increase in the current implies a decrease in the resistance in the TiO$_x$ film, the filled-trap region can be considered as $R_{on}$. The region of $R_{on}$ is widened as the applied bias is increased, and the device then switches from HRS to LRS as a result. Therefore, $w(t)/D$ is one at LRS and zero at HRS. Fig. 8(a) shows the applied bias and $w(t)/D$ as a function of time. When all bias sweeps were conducted in the direction $0 \text{~V} \rightarrow -3 \text{~V} \rightarrow 0 \text{~V} \rightarrow 3 \text{~V} \rightarrow 0 \text{~V}$, the initial value of $w(t)/D$ was zero because the initial TiO$_x$ was in HRS. Near $V_{SET} (\approx -2.3 \text{~V})$, the value of $w(t)/D$ decreased abruptly, which implies a transition from HRS to LRS. In this transition, the exponential function between $w(t)/D$ and time (i.e., $w(t)/D$ is proportional to $\exp(V)$; applied voltage $V$ is linearly varied with constant time interval, so $V$ is proportional to time) was chosen to fit the simulation result to the measurement data. The physics of this exponential relationship is under investigation. In contrast, near $V_{RESET} (\approx 2.3 \text{~V})$, the value of $w(t)/D$ decreased abruptly, which implies a transition from LRS to HRS. In this transition, the exponential function was also chosen. In addition, to calculate (1), $R_{off} = 3 \text{~M} \Omega$ was assigned. This was the measured data from the Al(TE)/TiO$_x$/Al(BE) device. In addition, the ratio of $R_{off}/R_{on}$ was assigned by the maximum resistance ratio ($\approx 100$) between HRS and LRS from the
Fig. 8 (a) Relationship between the applied bias and the variation of the filled-trap region as a function of time. (b) Calculated $I$–$V$ curves according to (1).

Fig. 9 Calculated $I$–$V$ curves of the Al(TE)/TiO$_x$/Al(TE) device and the measured data.

well fitted to the measured data in which the resistive switching is explained by the proposed model, thickness variation of the filled-trap region of the TiO$_x$ layer. For a generalized model to describe the $I$–$V$ characteristic in the entire Al(TE)/TiO$_x$/TiO$_2$/Al(BE) device, this simple two-variable resistor model should be refined with further investigation.

VI. CONCLUSION

The distinct resistive switching properties in active Al TE-based TiO$_x$ have been investigated in this paper. The formation of an oxygen-deficient TiO$_x$ layer was confirmed by TEM-EDX analysis. Oxygen vacancies in an oxygen-deficient TiO$_x$ layer act as electron traps, and the variation of a filled-trap region in an oxygen-deficient TiO$_x$ layer contributes to resistive switching. This resistive switching characteristic is properly explained by the two-variable resistor model. The simulation results from the proposed model provide additional information to help in understanding the intrinsic nature of resistive switching in the MIM structure.

REFERENCES


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