



Article Effects of Sm₂O₃ and V₂O₅ Film Stacking on Switching Behaviors of Resistive Random Access Memories

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Abstract: In this work, the resistive switching characteristics of resistive random access memories (RRAMs) containing Sm_2O_3 and V_2O_5 films were investigated. All the RRAM structures made in this work showed stable resistive switching behavior. The High-Resistance State and Low-Resistance State of Resistive memory (R_{HRS}/R_{LRS}) ratio of the RRAM device containing a V_2O_5/Sm_2O_3 bilayer is one order of magnitude higher than that of the devices containing a single layer of V_2O_5 or Sm_2O_3 . We also found that the stacking sequence of the Sm_2O_3 and V_2O_5 films in the bilayer structure can affect the switching features of the RRAM, causing them to exhibit both bipolar resistive switching (BRS) behavior and self-compliance behavior. The current conduction mechanisms of RRAM devices with different film structures were also discussed.

Keywords: resistive random access memory (RRAM); bipolar resistive switching behavior; thin films; electrical conduction mechanism

1. Introduction

As technology continues to advance, electronic products have become indispensable items in peoples' lives. For electronic products, memory capacity has a key impact on electronic computing speed and efficiency. Due to their superior features, such as simple structure, low power consumption, high-speed operation, small device area, and nonvolatile properties, resistive random access memories (RRAMs) have attracted extensive attention for next-generation nonvolatile memory applications [1,2]. Several transition metal oxides (TMOs) such as ZnO, TiO₂, MgO, SrTiO₃, and V₂O₅ exhibit reproducible resistive switching properties [3–7]. Among them, V₂O₅ exhibits a metal-insulator transition (MIT) at a relatively low temperature of 280 °C. During the MIT process, the crystal structure, optical parameters, and conductivity of V₂O₅ change significantly. Therefore, V₂O₅ has potential applications for RRAMs [8]. On the other hand, Sm₂O₃, one of the rare earth oxides (REOs), has a large energy band gap, high thermal stability, good chemical stability, good thermal stability, low leakage current density, high breakdown electric field, and low trapping rates. Because of these superior properties, Sm_2O_3 has been investigated as a high-k material which could replace SiO₂ in Complementary Metal-Oxide-Semiconductor (CMOS) devices [9–13]. There are two different resistive switch behaviors in RRAMs: unipolar resistive switching (URS) behavior and bipolar resistive switching (BRS) behavior [14]. Generally, BRS features faster switching speed, lower operation power, and better endurance than URS [15], while URS has a higher Resistance OFF/ON (R_{OFF}/R_{ON}) ratio, easy reading operation, and higher memory density [16]. In this work, the resistive switching characteristics of RRAMs containing Sm_2O_3/V_2O_5 bilayer films were investigated. The effects of the Sm_2O_3 and V_2O_5 film stacking sequence on the switching behavior were also discussed. It would be advantageous to develop scalable RRAM devices exhibiting both bipolar and unipolar switching behaviors.

2. Experimental

In this work, four different kinds of RRAM structures were made. The first RRAM structure was a V₂O₅/TiN/SiO₂/Si substrate where a V₂O₅ film was deposited by radio frequency (RF) magnetron sputtering at room temperature (RT). A two-inch V₂O₅ target for the V₂O₅ sputtering deposition was made through a ceramic powder process, as described in our previous work [17]. The sputtering conditions for the V₂O₅ film deposition were an RF power of 75 W and an argon working pressure of 30 mTorr for 10 min. The second structure was a Sm₂O₃/TiN/SiO₂/Si substrate where a Sm₂O₃ film was deposited by RF magnetron sputtering at RT. The sputtering conditions for the Sm₂O₃ film deposition were an RF power of 30 mTorr at an oxygen to argon ratio of 1:10 for 5 min. The third structure was a Sm₂O₃/V₂O₅/TiN/SiO₂/Si substrate where V₂O₅ and Sm₂O₃ films were deposited by RF magnetron sputtering at RT, as shown in Figure 1a. The fourth RRAM structure was a V₂O₅/Sm₂O₃/TiN/SiO₂/Si substrate where deposited by RF magnetron sputtering at RT, as shown in Figure 1a.

An array of circular Al top contacts with a diameter of 50 μ m and a thickness of 200 nm was deposited by RF magnetron sputtering to form the Metal-Insulator-Metal (MIM) structure for the RRAMs. An Agilent 4156C semiconductor parameter analyzer was used to measure the resistive switching characteristics of the four different RRAM devices at RT. Positive sweep is defined as current that flows from the top to the bottom electrode. During the current-voltage (*I-V*) measurements of the RRAM devices, the bias voltage was applied to the Al top electrode (TE) while the bottom electrode (BE) was grounded. The *I-V* characteristics of the RRAM devices were obtained through DC voltage sweep measurements. A forming process is needed at the beginning to activate the resistive switching (RS) behavior by applying positive and negative biases.



Figure 1. (a) The structure and deposition process of the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si device. (b) The structure and deposition process of the Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si device.

3. Results and Discussion

Typical bipolar resistive switching *I-V* curves for the Sm₂O₃ and V₂O₅ thin film RRAM devices are shown in Figure 2, and their bipolar switching characteristics were stable. Reproducible BRS behavior for the single-layer memory devices used in the initial electrical forming process was observed for the Al/Sm₂O₃/TiN/SiO₂/Si and Al/V₂O₅ /TiN/SiO₂/Si structures shown in the insert in Figure 2. The bias voltage was applied under the sweeping sequence of $1 \rightarrow 2 \rightarrow 3 \rightarrow 4$. In some studies, it has been observed that Sm₂O₃ and V₂O₅ thin films have polycrystalline structures. Oxygen vacancies easily drift through grain boundaries and dislocations, resulting in stable resistive switching behavior [7–10]. In studies of vanadium oxide films, it has been observed that these films have a stable reversible switching characteristic, and the current can be controlled by setting the current limit during the set process to reduce the power consumption [8]. Therefore, the second RRAM, which contains Al/V₂O₅/TiN/SiO₂/Si, was examined to study the effects of V₂O₅. A typical bipolar resistive switching *I-V* curve for the Al/V₂O₅/TiN/SiO₂/Si device is also shown in Figure 2, and the bipolar switching characteristic was stable. Figure 2 shows that both the Al/Sm₂O₃/TiN/SiO₂/Si and Al/V₂O₅/TiN/SiO₂/Si devices exhibited BRS behavior. As shown in Figure 2, the Al/Sm₂O₃/TiN/SiO₂/Si device had a larger R_{HRS}/R_{LRS} ratio than the Al/V₂O₅/TiN/SiO₂/Si device. In addition, the reproducible BRS behavior of the Sm₂O₃ thin film RRAM device was low, and became progressively lower in the case of V₂O₅ thin films. For the Sm₂O₃ thin film RRAM devices, leading to defects and dangling bonds. To further investigate and discuss the electrical conduction mechanism in the initial metallic filament forming process, the hopping conduction mechanism and Schottky emission conduction were inferred by ln*I-V* and ln*I-V*^{1/2} curve fitting [18,19]. For hopping conduction,

$$J = qN_a v_o e^{-q\Phi_T/kT} e^{qaV/2dkT},$$
(1)

where *N*, *a*, Φ_T , v_0 , and *d* are the density of space charge, mean of hopping distance, barrier height of hopping, intrinsic vibration frequency, and film thickness, respectively. To validate the ln*I*-*V* curve fitting, the hopping conduction equation was transformed to the straight line representation of the equation: $\frac{\partial logI}{\partial (\frac{1}{kT})} = E_C - E_F - qV_A \frac{\Delta z}{2u_a}$. The electronic activation energy barrier equation (*Ea*) and the hopping conduction distance (Δz) extraction were observed [20].

For the Schottky emission equation,

$$J = A^* T^2 \exp[-q(\Phi_B - \sqrt{\frac{qE_i}{4\pi\varepsilon_i}})/kT],$$
(2)

T is the absolute temperature, Φ_B is the Schottky barrier height, ε_i is the insulator permittivity, *k* is Boltzmann's constant, and *A** is the Richardson constant. To validate the $\ln\left(\frac{I}{T_2}\right) - \sqrt{V}$ curve fitting, the Schottky conduction equation was transformed to: $\ln\left(\frac{I}{T_2}\right) = \frac{q\sqrt{q/4\pi\varepsilon_i d}}{kT}$, where $\left(\frac{q\sqrt{q/4\pi\varepsilon_i d}}{kT}\right)$ is the slope and $\left(\frac{q\Phi_B}{kT}\right)$ is the intercept of the straight line equation [21].



Figure 2. The current-voltage (*I-V*) curves of the self-compliant Sm₂O₃ and V₂O₅ thin film resistive random access memory (RRAM) structure devices during the set/reset process.

The electrical conduction mechanisms of the Sm_2O_3 and V_2O_5 thin film RRAM devices during the set/reset process for positive and negative biases are shown in Figures 3 and 4. For the Sm_2O_3 and V_2O_5 thin films with a voltage bias applied, the electrical conduction mechanisms exhibited the hopping

conduction and Schottky emission mechanisms, as shown by the $\ln I-V$ and $\ln I-V^{1/2}$ curve fittings. The initial metal filament path processes and electrical conduction models for the $Al/Sm_2O_3/TiN/SiO_2/Si$ and $Al/V_2O_5/TiN/SiO_2/Si$ structures are shown in the insets of Figure 4a–d. In the hopping conduction mechanism, as seen from the $\ln I-V$ curve fitting in the initial metallic filament process of RRAM devices, the shallow trapped electrons jumped the activation energy barrier and induced a reduction of the leakage current. In the $Al/V_2O_5/TiN/SiO_2/Si$ structure, the I-V curves exhibited the hopping conduction mechanism for low applied voltage biases and Schottky emission conduction for high applied voltage biases. In addition, the $Al/Sm_2O_3/TiN/SiO_2/Si$ RRAM structures exhibited self-compliance properties and similar electrical conduction mechanisms to the V_2O_5 thin film RRAM shown in Figure 4.



Figure 3. The $\ln I - V$ and $\ln I - V^{1/2}$ curve fittings for the hopping conduction mechanism for (**a**) V_2O_5 and (**b**) Sm_2O_3 memory devices for the ON/OFF state. The Schottky emission conduction of the (**c**) V_2O_5 thin films and (**d**) Sm_2O_3 memory devices for the ON/OFF state.



Figure 4. The electrical conduction mechanism and metal filament path model of the self-compliant Sm_2O_3 and non-compliant V_2O_5 thin film RRAM devices for positive and negative biases.

From Figures 2–4, we can see that both the $Al/Sm_2O_3/TiN/SiO_2/Si$ and $Al/V_2O_5/TiN/SiO_2/Si$ devices exhibited bipolar resistive switching behavior. Therefore, in the third RRAM device structure we combined Sm_2O_3 and V_2O_5 films to study the effects of this on the resistive switching behavior of the RRAMs.

Typical bipolar resistive switching *I-V* curves for the Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si and Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si devices are shown in Figure 5, and the bipolar switching characteristic was stable. However, the forming voltage of the device containing a V₂O₅/Sm₂O₃ bilayer was higher than that of the devices containing a single layer of V₂O₅ or Sm₂O₃. On the other hand, the R_{HRS}/R_{LRS} ratio of the device containing a V₂O₅/Sm₂O₃ bilayer was one order of magnitude higher than that of the devices containing a single layer of V₂O₅ or Sm₂O₃. In addition, the self-compliance and non-compliance properties of the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si and Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si structures are shown in Figure 5.



Figure 5. The resistive switching characteristics of the Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si and Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si memory devices.

For the fourth RRAM device, Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si, the stacking sequence of the V₂O₅ and Sm₂O₃ films were exchanged. A typical unipolar resistive switching *I-V* curve for the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si device is shown in Figure 5. In this experiment, we found that the stacking sequence of the Sm₂O₃ and V₂O₅ films in the bilayer structure can affect the switching features of the RRAM, causing either BRS behavior or URS behavior. It was also shown that the reset process of this device displays a shrinking phenomenon compared to that of the Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si device.

In Figure 6, the electrical conduction mechanisms of the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si and Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si thin film RRAM devices during the set/reset process for positive and negative bias are shown. In the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si structure, the electrical conduction exhibited the hopping conduction mechanism, as can be seen by the ln*I*-*V* curve fitting. The ln*I*-*V*^{1/2} curve fitting and the *I*-*V* curve for the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si structure exhibited the hopping conduction mechanism, as can be seen by the ln*I*-*V* curve fitting. The ln*I*-*V*^{1/2} curve fitting and the *I*-*V* curve for the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si structure exhibited the hopping conduction mechanism in the initial metallic filament process of the RRAM device. Based on the above results obtained in dual-layer structure RRAM devices, we suggest that Sm₂O₃ thin films play an important role because of the leakage current lowering properties of shallow trapped electrons jumping the activation energy barrier [11].



Figure 6. The electrical conduction mechanisms and metal filament path models for the Al/Sm₂O₃/V₂O₅/TiN/SiO₂/Si and Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si devices when a positive bias is applied.

Figure 7 shows the initial metallic filament path forming model and the hopping conduction mechanism of the $Al/V_2O_5/Sm_2O_3/TiN/SiO_2/Si$ structure for the ON/OFF state. In Figure 7a, the initial metallic filament path forming for the RRAM device for an applied positive bias in the set state is shown. In Figure 7b, the metallic filament is slightly thinner because of the continuous oxidation reaction by oxygen atoms from the metal oxide bonds on the interface of the Sm_2O_3/TiN electrode.



Figure 7. The electrical transfer mechanisms and initial metallic filament path models for the $Al/V_2O_5/Sm_2O_3/TiN/SiO_2/Si$ and $Al/Sm_2O_3/V_2O_5/TiN/SiO_2/Si$ devices in the ON/OFF state for the (a) ON and (b) OFF states.

To discuss the excellent nonvolatile random memory devices properties, the switching cycling reliability and retention time characteristic measurements for the $Al/V_2O_5/Sm_2O_3/TiN/SiO_2/Si$ RRAM device are shown in Figure 8. For switching cycling reliability, the R_{HRS}/R_{LRS} ratio was approximately 10^3 . In another nonvolatile memory characteristic calculation, significant and apparently stable ON/OFF characteristics for different retention times in $Al/V_2O_5/Sm_2O_3/TiN/SiO_2/Si$ RRAM devices for HRS/LRS were also observed.



Figure 8. (a) Endurance cycle and (b) retention time properties of the Al/V₂O₅/Sm₂O₃/TiN/SiO₂/Si devices at room temperature, as measured at 0.2 V.

4. Conclusions

In this study, the resistive switching characteristics of RRAM devices with integrated Sm_2O_3 and V_2O_5 films were investigated. All four of the RRAM structures constructed in this work showed stable resistive switching behaviors. The R_{HRS}/R_{LRS} ratio of the RRAM device containing a V_2O_5/Sm_2O_3 bilayer was higher than those of the devices containing a single layer of V_2O_5 or Sm_2O_3 . It was found that the stacking sequence of the Sm_2O_3 and V_2O_5 films in the bilayer structure can affect the switching feature of the RRAM, leading to either BRS behavior or URS behavior. Hence, it would be beneficial to develop scalable RRAM devices that exhibit both bipolar and unipolar switching behaviors to expand their applications to nonvolatile memories.

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Conflicts of Interest: There is no conflict of interest in this experiment.

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