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Concurrent nonvolatile resistance and capacitance switching in LaAlO_3

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We report on the correlated nonvolatile resistance and capacitance switching in $\text{Pt/LaAlO}_3/\text{Nb:SrTiO}_3$ heterostructures. The pristine devices show the typical characteristics of a Schottky junction; however, after forming, a reverse bias switches the device into a low resistance and high capacitance state while a forward bias drives it into a high resistance and low capacitance state. Our experiments suggest that both the formation of conducting filaments and the modulation of interface barrier contribute to the resistance switching. Oxygen vacancies play critical roles in determining the switching characteristics and can be controlled in the process of device fabrication. © 2011 American Institute of Physics. [doi:10.1063/1.3560257]

As the device scaling continues relentlessly, the conventional solid state nonvolatile memory (NVM) concepts are encountering severe physical challenges.¹ Recently, there have been intensive efforts on searching for emerging NVM devices to replace the flash memory beyond the 22 nm technology node.² Among these NVMs, resistance random access memory (RRAM) has attracted much attention due to its advantages such as high cell density, high operation speed, low power consumption, low cost, and good endurance.^{3–7} Although great efforts have been devoted to RRAM, many aspects of the microscopic switching mechanism remain controversial. There is a general consensus that the migration of oxygen vacancies or oxygen ions plays crucial roles in oxide resistance switching.^{8–11} In general, resistance switching in various oxides can be classified into two basic mechanisms: electrochemical redox process^{12,13} and changes in Schottky-like barrier by trapping/detrapping effects at interface.¹⁴

Lanthanum aluminate (LaAlO_3) or LAO has attracted considerable interest as a canonical dielectric due to its high dielectric constant and low leakage current.¹⁵ Recently, it has become a focus of attention after two dimensional electron gas was discovered between LAO ultrathin films and TiO_2 -terminated SrTiO_3 substrates.¹⁶ To date, however, the resistance switching behaviors of LAO thin films have not been reported. In this letter, we report on the concurrent resistance and capacitance switching behaviors in nonvolatile $\text{Pt/LaAlO}_3/\text{Nb:SrTiO}_3$ memory devices. Our experiments suggest that both the filamentary conduction and the interfacial effect coexist in the device operation, and their interplay dictates the overall characteristics.

In our experiments, LAO thin films with varied thickness from 10 to 120 nm were grown on 0.7 wt % Nb-doped SrTiO_3 (001) substrates by pulsed laser deposition. A KrF excimer laser ($\lambda=248$ nm) with an energy density of 1.2 J cm^{-2} and a repetition rate of 2 Hz was used to ablate a single-crystal LAO target. The substrate temperature was maintained at 750°C during the growth and the oxygen pressure was varied from 2×10^{-4} to 2 Pa. After growth, the crystalline structure of the films was characterized by high-resolution x-ray diffraction. The θ - 2θ patterns with sharp Bragg peaks were obtained, indicating the epitaxial growth

of c -axis oriented LaAlO_3 . Figure 1(a) shows the reciprocal space mapping (RSM) data for the (103) reflection of a LAO thin film with a thickness of 50 nm. From the RSM peaks we deduced that the in-plane and the out-of-plane lattice parameters are $3.833 \text{ \AA}$ and $3.776 \text{ \AA}$, respectively. This larger in-plane lattice constant compared to the bulk value ($3.792 \text{ \AA}$) suggests that the LAO thin film is under tensile strain.

Before the electrical measurements, Pt electrodes were deposited on the thin films using magnetron sputtering through a shadow mask. The schematic of the $\text{Pt/LaAlO}_3/\text{Nb:SrTiO}_3$ device is illustrated in Fig. 1(b). A Keithley 4200 semiconductor characterization system was used to conduct the transport measurements at room temperature. A forward (positive) voltage bias applied to the devices is defined as the current flowing from the Pt electrode to the LAO thin film. The current-voltage (I - V) curves of pristine devices show rectifying characteristics, as shown in Fig. 2(a), which can be assigned to the Schottky contact formed between the high work function Pt and the LAO thin film. To justify this, a reference device was made using a low work function metal Al as the top electrode. This reference device exhibited a symmetric I - V characteristic without hysteresis, which indicates that the Al/LAO and the LAO/Nb:SrTiO₃ interfaces are Ohmic, and the transport in Pt/LAO/Nb:SrTiO_3 is dominated by the Pt/LAO interface.

After forming with a reverse bias, bipolar resistance switching was observed in the Pt/LAO/Nb:SrTiO_3 devices. As shown in Fig. 2(a), a reverse bias sweeping switches the

FIG. 1. (Color online) (a) X-ray RSM around the (103) reflection of LaAlO_3 thin film grown on Nb:SrTiO_3 (001) substrate. (b) Schematic of the measurement configuration.

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FIG. 2. (Color online) (a) Resistance switching of a typical Pt/LaAlO₃/Nb:SrTiO₃ device. With increasing reverse bias, the switching hysteresis becomes more pronounced in the forward direction. (b) Data retention of the device. Inset shows that the $R_{\text{OFF}}/R_{\text{ON}}$ ratio increases with the reverse bias.

device into a low resistance state (LRS or ON), while a forward sweeping drives it back to the high resistance state (HRS or OFF). As the reverse bias increases, the switching hysteresis in positive bias region becomes more pronounced. Accordingly, the $R_{\text{OFF}}/R_{\text{ON}}$ ratio read at +0.5 V increases as shown in the inset of Fig. 2(b), and it is 2×10^5 when voltage pulses of ± 8 V are applied to reset/set the devices. To evaluate the device stability, data retention was characterized at a reading voltage of +0.5 V. As shown in Fig. 2(b), both HRS and LRS can be retained for more than 12 h without obvious deterioration.

This resistance switching behavior appears to be related to the bias modified interfacial Schottky barrier;^{14,17,18} an applied electrical field can drive the migration of oxygen vacancies in LAO, which then modulates the depletion layer width, resulting in the resistance change. It is well known that the capacitance is inversely proportional to the depletion layer width in Schottky junctions. Therefore, when the device is in different resistance states, its capacitance might change accordingly. In order to test this scenario, we carried out capacitance-voltage (C - V) measurements at 100 kHz between -6 and $+6$ V. Figure 3(a) shows the C - V curve of the Pt/LAO/Nb:SrTiO₃ device before the forming process which exhibits the typical characteristic of a Schottky junction with a weak hysteresis. However, after forming, a

FIG. 3. (Color online) C - V curves taken on a typical Pt/LaAlO₃/Nb:SrTiO₃ device (a) before and (b) after the forming process. (c) HCS and LCS switched over 2000 cycles. Inset is a blowup of five switching events. (d) Retention of both capacitance states for 12 h.

FIG. 4. (Color online) (a) Electrode area dependence of the HRS and LRS. (b) Oxygen partial pressure dependence of the forming voltage and the $R_{\text{OFF}}/R_{\text{ON}}$ ratio. (c) Temperature dependence of the HRS and LRS resistances. (d) Film thickness dependence of the forming voltage and the $R_{\text{OFF}}/R_{\text{ON}}$ ratio.

prominent hysteresis was observed in the positive voltage region as shown in Fig. 3(b). A reverse bias scan to -6 V drives the device to a high capacitance state (HCS) and a subsequent forward bias scan to $+6$ V switches the device to a low capacitance state (LCS). As demonstrated in the inset of Fig. 3(c), the capacitance at a bias voltage of $+1$ V can be reproducibly switched between LCS and HCS by voltage pulses. Figure 3(c) shows that the devices can be switched over 2000 cycles without degradation, indicating a good endurance. The nonvolatile retention performance of the devices was also measured; as shown in Fig. 3(d), both capacitance states can be retained for more than 12 h.

The concurrent resistance and capacitance switching behaviors can be explained by considering the migration of oxygen vacancies at the Pt/LAO interface. In n -type oxide semiconductors like LAO, oxygen vacancies often act as donors, and the variation in their population in Schottky junctions can modify the depletion layer.¹⁴ When a sufficient reverse bias is applied to the Schottky barrier, the positively charged oxygen vacancies migrate to the Pt/LAO interface, resulting in the net reduction in charges in the depletion region. This makes the barrier narrower and lower, leading to LRS and HCS. On the other hand, when a sufficient forward bias is applied and drives away the oxygen vacancies from the interface, the electrons are detrapped at the Pt/LAO interface, which leads to a wider and higher barrier, corresponding to HRS and LCS.

In most interface dominated resistance switching, the resistance of ON and OFF states changes inversely with the electrode area due to the lateral homogenous conduction at interface.¹⁹ In our case, however, the HRS and LRS resistance is independent of the electrode area as shown in Fig. 4(a), suggesting that the resistance switching in the Pt/LAO/Nb:SrTiO₃ devices involves inhomogeneous conducting filaments.^{20,21} This scenario is consistent with the fact that a large population of oxygen vacancies are readily generated in the Nb:SrTiO₃ substrate in the oxygen poor environment during the film growth.²² The Nb:SrTiO₃ substrate can be considered as the oxygen vacancy reservoir and

facilitates the formation of conducting filaments during the resistance switching. Since the oxygen vacancies play an important role in the resistance switching,^{23,24} we tuned its concentration by growing 20 nm LAO thin films under different oxygen partial pressure. Figure 4(b) shows the dependence of forming voltage on the oxygen pressure; with the oxygen partial pressure increasing from 2×10^{-4} to 2 Pa, the forming voltage increases from -13 to -31 V while the $R_{\text{OFF}}/R_{\text{ON}}$ stays unchanged. This indicates that more oxygen vacancies are generated in Nb:SrTiO₃ when the oxygen partial pressure is low, which facilitates the formation of conducting filaments with a lower forming voltage. The critical role of Nb:SrTiO₃ also corroborates the fact that no reliable resistance switching was observed if Nb:SrTiO₃ was replaced by Pt or SrRuO₃.

To further shed light on the nature of conducting filaments, we examined the temperature dependence of the HRS and LRS resistances. As shown in Fig. 4(c), both states show the semiconducting behavior, where the resistance decreases with increasing temperature. This is different from the conventional filamentary conduction picture which often involves metallic conducting channels.²⁵ Therefore, even part of the conducting paths in LAO could be metallic, the dominating contribution to the overall resistance comes from the semiconducting segments and the Schottky junction in series. We also studied in detail the dependence of forming voltage on the LAO thickness while the oxygen pressure was fixed at 2×10^{-4} Pa. As shown in Fig. 4(d), the forming voltage increases almost linearly from -13 to -41 V as the film thickness goes up from 10 to 120 nm, whereas the $R_{\text{OFF}}/R_{\text{ON}}$ ratio is also thickness independent.

In summary, we have demonstrated concurrent resistance and capacitance switching in Pt/LaAlO₃/Nb:SrTiO₃ devices which show good data retention and endurance. Both the modification of Schottky-like Pt/LaAlO₃ interface and the formation of conducting filaments contribute to the switching effects. Our results also suggest that the generation and migration of oxygen vacancies can be controlled by the growth conditions and the electrode selection, which is critical for achieving reliable device performance.

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