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Bipolar Resistance Switching in Transparent ITO/$LaAlO_3$/$SrTiO_3$ Memristors

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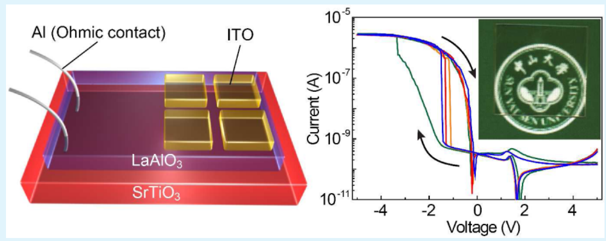
ABSTRACT: We report reversible bipolar resistance switching behaviors in transparent indium−tin oxide (ITO)/$LaAlO_3$/$SrTiO_3$ memristors at room temperature. The memristors exhibit high optical transparency, long retention, and excellent antifatigue characteristics. The high performances are promising for employing ITO/$LaAlO_3$/$SrTiO_3$ memristors in nonvolatile transparent memory and logic devices. The nonvolatile resistance switching behaviors could be attributed to the migration of positively charged oxygen vacancies from the $SrTiO_3$ substrate to the $LaAlO_3$ film, resulting in Poole−Frenkel emission for the low resistance state and thermionic emission for the high resistance state.



KEYWORDS: *$LaAlO_3$/$SrTiO_3$ heterostructure, transparent memristor, nonvolatile resistance switching, Poole−Frenkel emission, thermionic emission*

1. INTRODUCTION

Transparent electronics are very important because of their potential application in next-generation electronic circuitry and optoelectronic devices,[1] like information displayed on an automobile windshield or glass. In particular, transparent resistance random access memory or memristor has stimulated great interest because of the combination of the advantages of invisible electronics and memristor.[2−4] To date, the memristor with a metal/oxide/metal configuration is considered to be next-generation memory to replace the traditional flash memory because of superior characteristics, such as long retention, good endurance, high operation speed, high storage density, and low power consumption.[5−11] The logic ON and OFF states of a memristor can be reversibly switched between low and high resistance by an electric field.[12−14] To construct a high-performance transparent memristor, optically transparent and electrically switchable oxide materials are necessary. Seo et al.[2] proposed a transparent memristor with a ZnO thin film sandwiched by indium−tin oxide (ITO) electrodes, exhibiting unipolar switching characteristics. Afterward, extensive efforts have been focused on the investigation of resistance switching properties of transparent memristors with wide-band-gap magnesium-doped ZnO,[15] Gd_2O_3,[16] HfO_x,[4] and (La,Sr)-MnO_3[17] thin films. In our previous work,[14] platinum/$LaAlO_3$/$SrTiO_3$ (Pt/LAO/STO) heterostructures with several unit cells of LAO thin films showed high-performance resistance switching characteristics, where two-dimensional electron gas (2DEG) at the LAO/STO interface served as the bottom electrode and the LAO film as the memory material. In 2004, Ohtomo and Hwang[18] found high-mobility 2DEG at the interface of two insulating oxides, LAO (band gap E_g = 5.6 eV) and TiO_2-terminated STO (band gap E_g = 3.2 eV).[19] Because the LAO and STO are optically transparent[20] and a resistance switching effect could take place in the LAO film, it is possible to obtain LAO/STO heterostructure-based transparent memristors if a transparent top electrode could be prepared on the LAO surface. In this paper, we report the bipolar resistance switching characteristics of transparent ITO/LAO/STO memristors, which show promising optical transparency, a high resistance switching ratio, good endurance, and long retention of logic states.

2. FILM GROWTH AND DEVICE PREPARATION

The LAO thin films with thicknesses of approximately 4 nm were grown on TiO_2-terminated (001) STO substrates by pulsed-laser deposition using a KrF laser at 800 °C in an oxygen atmosphere of 2×10^{-3} mbar. The energy fluence of the KrF excimer laser (λ = 248 nm) at the single-crystal LAO target was about 1.2 J/cm^2. After growth, the samples were cooled to room temperature at a rate of 5 °C/min in an oxygen pressure of 400 mbar. Figure 1a shows the reflected high-energy electron diffraction (RHEED) pattern after LAO film growth. The streaky RHEED pattern indicates that the films were grown layer by layer, demonstrating high-quality single-crystal LAO films. ITO electrodes with areas of 300 μm × 300 μm were deposited on the LAO surface by electron beam evaporation through a shadow mask at room temperature and then annealed at 200 °C for 6 h at 1 atm of oxygen pressure. To investigate the transparency of ITO/LAO/STO memristors, another sample with a size of 10 mm × 10 mm with the ITO

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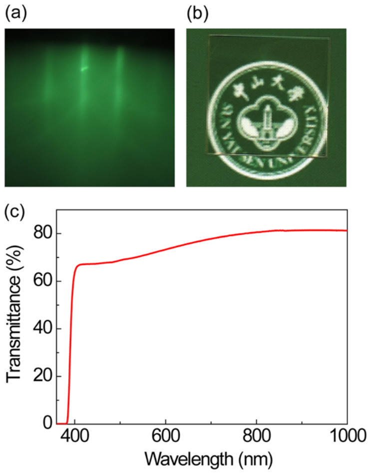

Figure 1. (a) Streaky RHEED pattern indicating that the LAO film was grown layer by layer, demonstrating a high-quality single-crystal LAO film. (b) Image on the bottom seen clearly through the ITO/LAO/STO memristor without any distortion or refraction. (c) Transmittance of the ITO/LAO/STO memristor including the STO substrate in the visible region of approximately 76% and the maximum value of up to around 82%.

film completely covering the LAO surface was prepared. An image on the bottom can be seen clearly through the sample without any distortion or refraction, as shown in Figure 1b. To quantitatively evaluate the transparency of the ITO/LAO/STO memristors, we measured the transmittance of the memristor including the STO substrate in the 200−1000 nm region, as shown in Figure 1c. The average transmittance in the visible region (400−800 nm in wavelength) is approximately 76%, and the maximum value is up to around 82%. The promising optical transparency together with high-quality single-crystal LAO films renders the all-oxide device prospective memory capability and optical transmittance for future applications of the transparent memristor.

3. RESULTS AND DISCUSSION

3.1. Nonvolatile Bipolar Resistance Switching of the ITO/LAO/STO Memristors. To investigate the resistance switching characteristics of transparent ITO/LAO/STO memristors, aluminum electrodes were directly contacted with the electron gas by an aluminum wirebonder and grounded, as shown in Figure 2a. A Keithley 4200 SCS semiconductor characterization system was employed to perform the switching measurement at room temperature. The memory behaviors of the ITO/LAO/STO memristors are demonstrated by the current−voltage ($I-V$) characteristics measured by the sweeping voltage (in volts) in the sequence of +5 → 0 → −5 → 0 → +5, as shown in Figure 2b, revealing a stable bipolar resistance switching. For the first switching cycle (forming process), with a voltage sweeping from zero to a threshold value of −3.3 V, the devices suddenly switch from an initial high resistance state (HRS) to a low resistance state (LRS). In the following switching cycles, the resistance switching $I-V$ characteristics tend to stabilize and the voltage to switch the device from HRS to LRS (set process or write) is lowered to around −1.5 V. The LRS can be reset to the initial HRS (reset process or erase) through a voltage sweeping of 0 → +5 → 0 V cycling. It should be noted that the devices could be switched to HRS if the amplitude of positive voltage is larger than 1 V and the resistance value of HRS is independent of the amplitude of positive voltage beyond the value.

To address the reliability, we investigated the distribution of the switching voltage and resistance at different states, endurance, and retention. Figure 2c shows the distribution of reset and set voltages for the bipolar switching of ITO/LAO/STO devices. The reset voltages are distributed in a narrow range from −1.3 to −1.6 V, while application of a reset voltage of +5 V can invariably switch from LRS to HRS. Figure 2d displays the concentrated distribution of resistance in LRS and HRS. The LRS and HRS are read out at −0.5 V, and the corresponding average resistances are about 1×10^7 and 2×10^9 Ω, respectively. The results indicate that the devices exhibit uniform switching characteristics. The LRS/HRS or write/erase can be reversibly and reproducibly obtained by applying voltage pulses of −5 V/+5 V. The write and erase operations exhibit good endurance and consistent performance during more than 2000 operation cycles, as shown in Figure 2e. Furthermore, both the LRS and HRS can be retained with a HRS/LRS resistance switching ratio of 100 for more than 4×10^4 s (Figure 2f). Simple extrapolation reveals that retention of the bistable resistance states can be extended to more than 10 years with minor variation of the switching ratio. The demonstrated good retention and endurance characteristics are essential for next-generation memory application.

3.2. Switching Mechanism. In the ITO/LAO/STO memristors, the conduction of HRS after the reset process is almost the same as that of the initial resistance state. It is noteworthy that the ITO/LAO/STO memristors show rectifying behavior with a ratio of up to 10^5 at 2 V. The high rectifying ratio could be significant for high-density storage with a passive array (e.g., one diode one resistor), which could be better than that of an active array (e.g., one transistor one resistor) from the point of view of the process and storage density.[7,8] The rectifying characteristic is attributed from the Schottky barrier between the metal and oxide film. We suggest that variation of the barrier height due to migration of the oxygen vacancies under an electric field could contribute to the resistance switching effect. It should be noted that a sudden current change occurs at a reset voltage of approximately −1.5 V but not at a set voltage, as shown in Figure 2b. This result indicates that the bipolar switching behavior could originate from some variations in the LAO films. We could exclude the possibility of a filamentary model because the formation and rupture of the filament could be related to a sudden current change at both the set and reset voltages.[21] To shed light on the origin of the switching effect of ITO/LAO/STO memristors, we carried out theoretical calculation to the transport characteristic in different states, as shown in Figure 3a. For HRS, the conduction follows the thermionic emission theory:[22]

$$J = A^* T^2 \exp(-q\phi_B/k_B T) \exp(qv/nk_B T) \qquad (1)$$

where J is the current density, A^* is the effective Richardson constant, T is the absolute temperature, ϕ_B is the effective barrier height, q is the electron charge, n is the ideality factor, and k_B is the Boltzmann constant. The fitting calculation shows a barrier height of 0.81 eV. On the other hand, the conduction behavior of LRS is dominated by Poole−Frenkel (P−F) emission:[23]

$$J = qN_C \mu E \exp\left(\frac{-q(\phi_B - \sqrt{qE/\pi\varepsilon_0\varepsilon_r})}{k_B T}\right) \qquad (2)$$

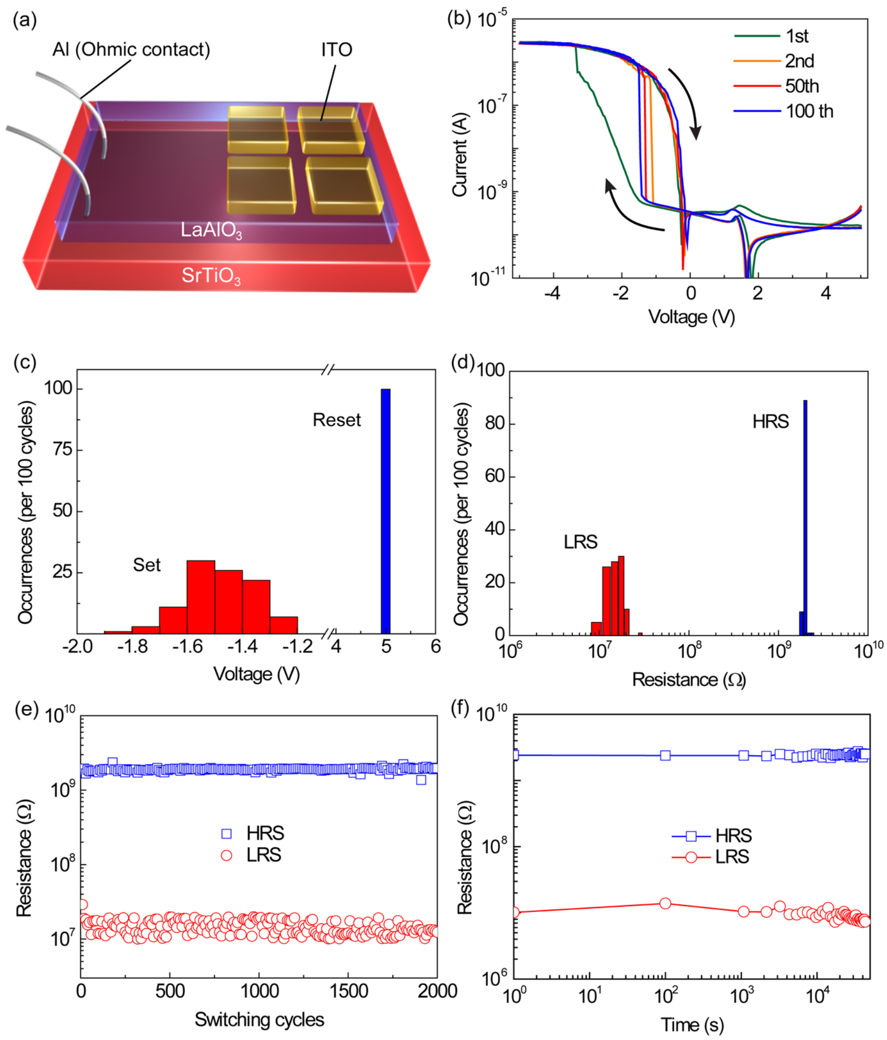

Figure 2. (a) Schematic diagram of the transparent ITO/LAO/STO memristor. (b) Nonvolatile resistance switching demonstrated by the pronounced hysteretic $I-V$ curve. (c) Distributions of the set and reset voltages. (d) Concentrated distributions of resistance in LRS and HRS. (e) Over 2000 write/erase cycles, a stable resistance switching behavior, without detectable signs of deterioration. (f) Nonvolatile property without a significant reduction in the switching ratio of 100 more than 4×10^4 s.

where N_C is the density of states in the conduction band, μ is the carrier mobility, ε_0 is the permittivity of free space, ε_r is the dynamic dielectric constant, and E is the electric field, as shown in Figure 3b. The barrier height for the LRS is calculated to be 0.32 eV. The P−F emission theory involves the consecutive hopping of charges between defect or trap centers, and ionization of the trap charges can be electrically activated.[24] In the LRS of the ITO/LAO/STO memristor, the electrons could consecutively hop between positively charged oxygen vacancies, which can be treated as trap centers in the LAO film. There is a general consensus that migration of the positively charged oxygen vacancies under an electric field plays an essential role in the resistance switching effect of oxide materials.[13] The oxygen vacancies could be generated in the STO substrates during LAO film growth. In our previous work,[14] we suggested that the STO substrate is a reservoir for oxygen vacancies, and migration of the oxygen vacancies across the LAO/STO interface enables the switching operations. In the ITO/LAO/STO devices, after application of a negative voltage to the memristor, a great amount of oxygen vacancies could be driven from the STO substrate to the LAO film and could form a channel for electron hopping. Once the channel in the LAO film connects the ITO electrode, the electrons could easily hop along the channel, leading to a sudden increase of the current and thereby completion of the LRS under a negative voltage, as shown in Figure 3b. From the viewpoint of band theory, the electrons could transport through the defect states in the LAO film to the conduction band. The channel for electron hopping should be different from the conductive filament. As the filament is formed, the conduction behavior in LRS should follow ohmic law.[21,25,26] On the other hand, when a positive voltage is applied, the oxygen vacancies could migrate back to the STO substrate. The Shottky barrier in the LAO film could be recovered to the pristine state. Consequently, the high barrier in LAO films could prevent electrons from going through the LAO films. The electrons have to tunnel through the Shottky barrier in the LAO film by thermionic emission, corresponding to HRS, as illustrated in Figure 3c. Therefore, we suggest that the resistance switching effect is attributed to variation of the barrier height in the LAO film due to migration of the positively charged oxygen vacancies under an electric field.

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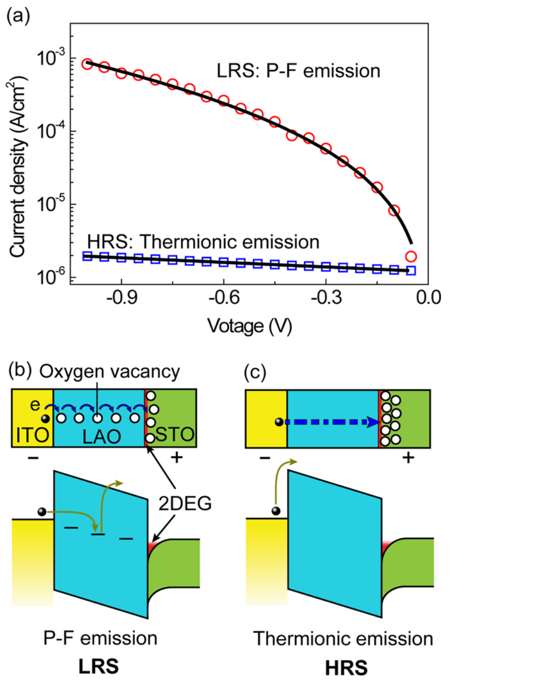

Figure 3. (a) For the LRS, the conduction behavior is dominated by P−F emission, while for the HRS, the conduction behavior follows thermionic emission. (b) A great amount of the oxygen vacancies from the STO substrate could migrate to the LAO film under an electric field and form a channel for electron hopping (upper panel). Accordingly, the electrons could transport through the defect energy levels as a result of generation of the oxygen vacancies in the LAO film to the conduction band, corresponding to completion of the LRS under a negative voltage (lower panel). (c) Oxygen vacancies in the LAO film could migrate back to the STO substrate, resulting in the recovery of the Schottky barrier in the LAO film (upper panel). The electrons have to tunnel through the LAO films by thermionic emission, corresponding to the HRS (lower panel).

4. CONCLUSIONS

In summary, we have demonstrated nonvolatile bipolar resistance switching behaviors of transparent ITO/LAO/STO memristors. The promising optical transparency, high resistance switching ratio, good endurance, and long retention of logic states qualify the LAO/STO heterostructure-based device as a transparent memristive device. The resistance switching could have originated from variation of the barrier height in the LAO film owing to migration of the positively charged oxygen vacancies under an electric field. For the LRS, the conduction behavior is dominated by P−F emission, which is related to electron hopping through the defect energy levels in the LAO film to the conduction band, while for the HRS, the conduction behavior follows thermionic emission when the Schottky barrier in the LAO film is recovered because of return of the oxygen vacancies to the STO substrate under positive voltage.

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Notes

The authors declare no competing financial interest.

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