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Citation: *Appl. Phys. Lett.* **111**, 062901 (2017); doi: 10.1063/1.4997412

View online: <http://dx.doi.org/10.1063/1.4997412>

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Electric field modulated conduction mechanism in Al/BaTiO₃/La_{0.67}Sr_{0.33}MnO₃ heterostructures

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(Received 19 May 2017; accepted 20 July 2017; published online 8 August 2017)

Mediating a metastable state is a promising way to achieve a giant modulation of physical properties in artificial heterostructures. A metastable state La_{0.67}Sr_{0.33}MnO₃ (LSMO) layer suffering tensile strain was grown on MgO substrates. Incorporating with the ferroelectric BaTiO₃ (BTO) layer, an accumulation or depletion state controlled by electric fields can be formed at the BTO/LSMO interface, which drives a switching of the conduction mechanism between space charge limited conduction and Poole-Frenkel emission, corresponding to the low and high resistance states. Our results lighten an effective way for electric-field modulated resistance states in multiferroic magnetoelectric devices. *Published by AIP Publishing.*

[<http://dx.doi.org/10.1063/1.4997412>]

Heterostructures with the structure of metal/ferroelectric/semiconductor (M/F/S) are considered to be the most promising candidates for future universal memory devices.^{1–4} In these kinds of structures, the binary data can be stored with respect to the two opposite polarization states which have different resistance states. Based on such a mechanism, the M/F/S memory cells have the following advantages. First, the resistance states are non-volatile, which allows the data to be retained when they are not powered.⁵ Second, they exhibit the ultrafast write/read speed as the ferroelectric switching is usually on the nanosecond scale.^{5,6} Most importantly, unlike the magnetic random access memories of which the size of memory cells is limited by the leakage magnetic field, the write/read processes of M/F/S memory cells are based on the electric field which would make it as small as possible. However, most of the ferroelectrics are insulating wide bandgap semiconductors at room temperature, which hinder the stable detection of the memory status as the maximum diode current is limited to the order of $\approx 20 \text{ mA cm}^{-2}$.^{7–9}

In the above mentioned structure, a considerable diode current can, in fact, only be detected in the structure with a nanometer thick ferroelectric barrier by quantum tunneling.¹⁰ When the thickness of the ferroelectric layer was only a few nanometers, many problems such as polarization instability, depolarization field, and leakage current enhancement may occur. To overcome the above disadvantages, increasing the thickness of the insulating ferroelectric layer and introducing extra defects have been suggested.⁹ With the increasing thickness of the ferroelectric layer, the leakage current can be greatly suppressed and the conduction current can be sustained by the thermal assisted emission conductivity mechanism with traps, namely, the Poole-Frenkel (PF) emission.^{11,12}

BaTiO₃ (BTO) as a typical ferroelectric material with strong room temperature ferroelectricity, low leakage current, and stable polarization has been widely studied in tunnel junctions^{2,3,13} and heterostructures.^{14–16} Incorporating it with the metastable state La_{0.67}Sr_{0.33}MnO₃ (LSMO) grown on tensile strain substrates, an orbital reconstruction will be brought to the LSMO layer, which can benefit the achievement of giant electric field modulated physical properties.^{17,18} In this work, a ferroelectric polarization modulated resistance state with a high ON/OFF ratio and switchable and retainable properties was achieved in the metastable state Al/BTO/LSMO heterostructures. Our work shows that the transition of the resistance state is related to the large thickness (60 nm) of the BTO layer, which makes it different from the usual ferroelectric tunnel junctions. The conduction mechanism can be modulated by electric fields and lead to retainable and switchable resistance states.

The 20-nm-thick LSMO acting as the bottom electrode was first deposited on the (001) oriented MgO single crystal substrates by facing-target sputtering. During the deposition, the Ar/O₂ ratio was kept at 10:7 with the total pressure of 0.93 Pa and the temperature was held at 630 °C. After the deposition, it was annealed at 630 °C in a pure oxygen atmosphere with the pressure of 260 Pa. Then, the ferroelectric BTO layer with the thickness of 60 nm was deposited on the LSMO layer by radio-frequency magnetron sputtering. The corresponding parameters were 3:1, 1.4 Pa, and 630 °C. After the deposition, it was annealed in the deposition atmosphere with a mixture of Ar and O₂. Finally, the Al top electrode with the diameter of $\sim 40 \mu\text{m}$ was directly bonded on the surface of BTO by using a wire bonder. The lattice structures (Fig. S1, [supplementary material](#)) were analyzed by high-resolution synchrotron x-ray diffraction (SXRD) measurements in the Beijing Synchrotron Radiation Facility (1W1A beamline, China). The surface morphology, local ferroelectric properties and surface charge states were measured using

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a Bruker Multimode 8 and Dimension Icon with Kelvin probe force microscopy (KPFM) module. The I - V characteristics and resistance switching properties of the heterostructures were measured by using a Keithley 2400 Sourceme-ter.

Figure 1(a) shows the surface topography of the LSMO layer which exhibits a terrace structure with the surface undulation less than 8 Å. The step height of the terrace is close to a unit cell (~ 4 Å), indicating the high quality of the film. Moreover, in Fig. 1(b), the BTO grown on the LSMO layer also shows a terrace structure with the step heights close to a few unit cells. Piezoresponse force microscopy (PFM) hysteresis loops shown in Fig. 1(c) indicate the intrinsic ferroelectric properties of the BTO layer. The coercive voltages indicated by the minimum value of amplitude are about -2.0 and 3.0 V. Figures 1(d) and 1(e) show the out-of-plane PFM phase and amplitude writing on the BTO layer. Sample bias with $+6$ V was first applied to switch the ferroelectric polarization upward in the $5 \times 5 \mu\text{m}$ area indicated by the blue dashed line. Then, a sample bias with -6 V was applied to switch the ferroelectric polarization downward in the inner area as indicated by the red dashed line. The outer ring shows the original state of the domain. Clearly, phase and amplitude contrast represents the inherent ferroelectric properties of the films.

We carried out a further study on the polarization modulated electrical transport properties of the heterostructures. As shown in Fig. 2(a), the resistance versus voltage pulse (R - V) curves exhibit hysteresis loops, demonstrating bipolar non-volatile resistive switching. The measurement process is demonstrated in the inset of Fig. 2(a); first, a writing voltage pulse with the duration of ~ 300 ms was applied, and then, the resistance was measured by applying a -1 V read voltage (~ 100 ms) after a 3 s interval. With the increasing value of voltage pulses, the heterostructure was gradually set to a high resistance state. This phenomenon strongly indicates that the positive voltage pulses which make the polarization point to the top Al electrode set the heterostructure to a high resistance state. The heterostructure keeps the high resistance

state even though the voltage pulses decreased to -1.5 V, implying good retention properties of the heterostructure. With the increase in negative voltage pulses, the resistance decreases with a sharp drop at -2.8 V. This is consistent with the coercive voltage observed in the PFM hysteresis loops, indicating ferroelectric polarization modulated resistance states in the heterostructure. Moreover, we run the measurement loops for several times, and the R - V hysteresis loops maintain high stability with the ON/OFF ratio of ~ 10 .

The corresponding current-voltage (I - V) curves on a log scale are also shown in Fig. 2(b). The numbers in the figure denote the sequences of voltage sweeps. Distinct reproducible hysteresis characteristics were observed, indicating a typical non-volatile resistive switching behavior. Moreover, a sharp drop at -2.8 V was also observed, which is consistent with the R - V curves and the PFM hysteresis loop measurements [Fig. 1(c)]. The left inset of Fig. 2(b) shows the corresponding I - V curves on a linear scale, and we can observe a clear diode effect.

To gain further insight into the resistive switching at the Al/BTO/LSMO heterostructures, we performed a detailed analysis on the conduction mechanism and we found that it could be modulated by the voltage pulses. The four I - V branches in Fig. 2(b) were fitted by different conduction mechanisms as shown in Fig. 3. For the first branch of the I - V curves, it shows a linear relation when it was fitted by the log I -log V relation with the voltage pulses smaller than 5.4 V. This result suggests that the space-charged-limited conduction (SCLC) dominates in our sample with the increasing voltage pulses.¹⁹ However, it should also be noted that the I - V curves show a linear relation between $\log(I/V)$ and $V^{-1/2}$ when the voltage pulse is higher than 1.8 V [the inset of Fig. 3(a)], which suggests the Poole-Frenkel emission (PF) mechanism.^{11,12} From the PFM characterization, we know that the negative coercive voltage of this heterostructure is close to -2.0 V, consistent with 1.8 V for I - V curve fitting as the direction of the electric field applied in the PFM characterization and I - V curve measurement is just

FIG. 1. Morphology and ferroelectricity of the BTO/LSMO heterostructure. (a) and (b) Morphology of a 20 nm LSMO surface on the MgO substrate and 60 nm BTO on the LSMO layer. (c) Local PFM ramp curves (phase and amplitude) for the 60 nm BTO. Out-of-plane PFM phase (d) and amplitude (e) images of $7 \times 7 \mu\text{m}$ area measured after positive (6 V) and negative (-6 V) probe bias switching of the BTO layer.

FIG. 2. (a) Resistance as a function of writing voltage pulse amplitude at $V_{\text{read}} = -1$ V; the inset shows the schematic of the relationship between the writing (W) pulses and reading (R) voltage. (b) The corresponding I - V curves are shown on a log scale, the left inset shows the I - V curves on a linear scale, and the right inset shows the schematic of the devices.

on the contrary. The gradual change in the conduction mechanisms from SCLC to PF emission is consistent with these results. With the application of positive voltage pulses, the heterostructure was set to the high resistance state, and the dominant conduction mechanism is the PF emission as shown in Fig. 3(b). The PF emission conduction mechanism is further confirmed by the performance of temperature dependent I - V characteristics (supplementary material, Figs. S5 and S6). The linear relationship of $\log(I/V)$ vs $V^{1/2}$ and $\log(I/V)$ vs $1/T$ confirms the PF emission conduction mechanism.²⁰ In Fig. 3(c), the transport properties show a transition from PF emission below -2.8 V to SCLC above -2.8 V, corresponding to the transition of high and low resistance states modulated by voltage pulses. The SCLC dominates the transport properties and the heterostructure remains in the low resistance state although the pulses were decreased from -7.0 to 0 V in Fig. 3(d). The conduction mechanisms for the corresponding voltage pulse area are shown in the inset of Fig. 3(d), where the blue and red colors denote the SCLC and the PF emission conduction mechanisms, respectively. A voltage pulse modulated conduction mechanism can be clearly seen.

How could the conduction mechanisms be modulated by voltage pulses? We reveal the physical picture combined

with the KPFM analysis. KPFM is highly sensitive to the electrical variations induced by surface screening charges and remnant polarization and thus can be used to determine the charge states of the heterostructures.^{21–23} In Fig. 4(a), a distinct difference between the original, 6 V and -6 V can be observed clearly, and the sign of the surface potential is the same as the poled voltage pulse as shown in Fig. 4(b). This effect is induced by the accumulation of charge at the surface as the surface potential of the polarized area is the sum of what the surface charge generates and the dipoles in the area contribute.²³ When a 6 V bias was applied to the heterostructure, the ferroelectric polarization of the BTO points downward, and the bound charge of the remnant polarization is negative as indicated by the inset of Fig. 4(b). Thus, the accumulated charge would be positive at the surface for positive bias and negative for negative bias.

The physical image behind the electric field modulated resistance is the ferroelectric polarization influenced charge state, which has a strong effect on the band structure at the LSMO/BTO interface.^{24–26} In this work, the conduction mechanism for the high resistance state is the PF emission, which is a kind of thermal assisted conduction based on traps.^{11,12} Unlike the Fowler-Nordheim tunnel conduction

FIG. 3. Replots of the four I - V branches in Fig. 2(b) along with fittings to different conduction mechanisms: (a) branch 1, (b) branch 2, (c) branch 3, and (d) branch 4. The left top panel of (c) shows the 3rd I - V branch, and the other panels show the fitting of the conduction mechanism labeled I, II, and III in the left top panel. The inset of 3(a) shows the fitting of PF emission in the area indicated by the green line. The inset of 3(d) shows the corresponding conduction mechanism for the R - V curve.

FIG. 4. (a) KPFM surface potential and (b) the corresponding surface potential profile indicated by the red line in (a); the inset of (b) is the schematic of local poling of the heterostructure by a conductive tip. Schematic of (c) and (d) charge distribution and (e) and (f) energy-band diagrams of the heterostructure in the low resistance state and the high resistance state.

mechanism²⁷ in which the current directly tunnels through the barrier, the PF emission exhibits conductive behavior based on the trap barriers. In contrast to the easy volatilization of Bi in BiFeO₃²⁸ and Pb in PbTiO₃,²⁹ both Ba and Ti are stable in BTO, and thus, the oxygen vacancies can be easily formed and serve as the traps in the PF emission.¹² The electrons can pass through the thick BTO layer by jumping the traps one by one as shown in Fig. 4(e). When the ferroelectric polarization of BTO points the LSMO layer, the positive bound charges at the interface will cause an accumulation of the negative majority electron carriers in the LSMO layer through the ferroelectric field effect,^{30,31} resulting in a lowered energy barrier, and the conduction property is dominated by the SCLC mechanism. In contrast, switching the ferroelectric polarization away from the LSMO layer, the negative bound charges appeared at the BTO/LSMO interface, which repel the negative majority carriers and form a depletion area as shown in Fig. 4(f). Thus, an increased energy barrier is formed and the dominant conduction mechanism switches to the PF emission.

In conclusion, a pulse electric field modulated conduction mechanism was achieved in the metastable Al/BTO/LSMO heterostructures. Combined with the KPFM analysis, we show

that the modulated conduction mechanism is due to the ferroelectric field effect which drives the formation of the accumulation or depletion area in the LSMO layer and results in the increased or decreased energy barrier. Thus, the SCLC mechanism dominates the low resistance state, while the PF emission dominates the high resistance state. The transition of the conduction mechanism modulated by voltage pulses shows great potential in bistable resistive devices with promising applications in data storage and sensors.

See [supplementary material](#) for the characterization of structure and electrical transport properties of the heterostructures.

This work was supported by the National Natural Science Foundation of China (51272174 and 11434006). The authors thank S. Wu and L. Y. Xu for PFM and KPFM performance. This work was supported by Beijing Synchrotron Radiation Facility (BSRF).

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