**Ferroelectric field effect tuned giant electroresistance
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Ferroelectric Field Effect Tuned Giant Electroresistance in
La_{0.67}Sr_{0.33}MnO₃/BaTiO₃ Heterostructures

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4 **ABSTRACT**
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7 The mediation of metastable state has been approved to be a promising tool to achieve
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9 giant modulations of the physical properties in artificial structures. In this work, the
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11 metastable state $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) films with the coexistence of two phases were
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13 fabricated on the tensile ferroelectric BaTiO_3 (BTO) substrates. Upon application of pulse
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15 electric fields to the BTO substrates, the oxygen vacancies and charge redistribute and
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17 result in giant and volatile electroresistance (~230%) and normal and nonvolatile
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19 electroresistance (~5%) in the LSMO films, respectively. The observation of binary
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21 resistance states is very interesting and totally un-expected, since only a normal
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23 electroresistance has been reported in the similar LSMO/piezoelectric structures
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25 previously. Here, we attribute the binary state performance to the model of oxygen
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27 redistribution and charge accumulation/depletion modulated by the ferroelectric field
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29 effect. The oxygen redistribution strongly affects the double exchange interaction in the
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31 LSMO layer, which leads to the giant and volatile electroresistance. This work indicates
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33 that the mediation of metastable states by electric field is a promising way to enrich the
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35 physical properties in artificial structures.
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53 **Keywords:** Metastable state, Oxygen vacancies, Ferroelectric field effect,
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Electroresistance, Multiferroic heterostructures

INTRODUCTION

A metastable state is not a thermodynamically equilibrium state (i.e. stable state) that has a higher free energy than that of the stable state. The free energy of a metastable state is one of the minima in the free-energy–landscape of the system that is separated by a certain energy barrier from other minima, particularly from the absolute energy minimum of the stable state. The typical metastable states can be described by different physical order parameters, such as the coexistence of antiferromagnetic and ferromagnetic phases, metallic and insulating phases, uniform and non-uniform compositions, etc.^{1, 2} More interestingly, in the metastable state, the free energies of each phase are comparable, and thus, phase transformations among them can be triggered by even subtle excitations, such as magnetic field, electric field, photo illumination, or thermal perturbation³. Since the physical properties of a material depend critically on the material’s structure and composition, the mediation of metastable states, therefore, becomes a promising strategy to achieve a large modulation of the physical properties in artificial heterostructures^{4, 5}. To realize a large modulation of the physical properties, one should first fabricate a material composed of multi-phases (metastable states), then apply a particular strain, an electric field, a magnetic field, or other external stimulations to

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4 induce the phase transformations in the selected system. Consequently, the physical
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7 properties will be tuned significantly following the phase transformation. Based on above
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10 discussions, the strongly correlated perovskite manganite should be a proper candidate,
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13 because its physical properties (magnetic and electric transport properties) strongly
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16 depend on the lattice distortion or strain caused by doping.⁶ All of these modulations of
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19 the physical properties are closely correlated to four degrees of freedom, namely, the spin,
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22 charge, orbit, and lattice orders in perovskites. The physical properties can be easily
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25 modulated if one or more degrees of freedom are changed⁵. By combining a perovskite
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28 with a ferroelectric material, a prototype device of non-volatile, ferroelectric field effect
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31 transistor was successfully demonstrated⁷.

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33 The strongly correlated perovskite structure compound $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is a fascinating
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36 material due to its colossal magnetoresistance^{8, 9}, room temperature ferromagnetism,¹⁰
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39 and half-metallicity⁹. Many investigations focus on its coupling with ferroelectric
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42 materials, such as interfacial coupling influenced exchange bias effect in
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45 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{TbMnO}_3$ bilayers and superlattices^{11, 12}, the strain and ferroelectric field
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48 effect co-modulated exchange bias¹³ and polarization charge affected redistribution of
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51 oxygen vacancies in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{BiFeO}_3$ heterostructures¹⁴, the lattice strain dominated
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54 modulation of magnetization in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ heterostructures¹⁵, the
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ferroelectric polarization induced phase transition that enhances the tunnel electroresistance (ER) in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BaTiO}_3/\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ heterostructures¹⁶, the polarization induced charge transfer at the $\text{Sm}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ interfaces¹⁷ and the dynamic strain affected ER in $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/0.7\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3-0.3\text{PbTiO}_3$ heterostructures¹⁸. For the strain dominated ER, however, the ratio of high/low resistance is usually very small, within only a few percents¹⁸, which cannot be used in ferroelectric field effect transistors.

To overcome this disadvantage, in this work, we employed the metastable state strategy and observed an ER as large as 230% in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{BaTiO}_3$ heterostructures. To achieve the metastable states, a tensile strained LSMO (lattice constant of 3.87 Å) film of 5 nm was grown on BTO (lattice constant of 4.01 Å) substrates using facing target magnetron sputtering method. With such a small thickness, the interfacial effect will significantly alter the magnetic and electrical properties of LSMO layer^{19, 20} due to the coexistence of multi phases in the film.

EXPERIMENT DETAILS

The LSMO thin films were grown on 0.5-mm-thick BTO (110) single crystal

substrates by the facing targets magnetron sputtering method with a base pressure of 2×10^{-5} Pa. During the deposition, the substrate temperature was kept at 650 °C, and the Ar to O₂ ratio was kept at 10:7, with a total pressure of 0.8 Pa. After the deposition, the LSMO layer was annealed in a pure oxygen atmosphere of 200 Pa at 650 °C. The crystal structures of the films were analyzed using the high-resolution synchrotron X-ray diffraction (SXRD) measurements in the Beijing Synchrotron Radiation Facility (1W1A beamline, China). The ferroelectric performance of the heterostructures was characterized using Bruker Multimode 8 atom force microscopy (AFM). We also used the monochromatic Cs-corrected high-resolution scanning transmission electron microscopy (STEM, Titan 80-300, FEI) to characterize the interfacial structure of the samples by imaging their cross-sections. The electric field modulated ER was measured by a physical properties measurement system (PPMS, Quantum Design) combined with a Keithely 2400 sourcemeter, 6220 current source, and 2182 voltage meter.

RESULTS AND DISCUSSION

The ferroelectric performance and crystal structure of the heterostructures are shown in Fig. 1. The PFM phase image in Fig. 1(a) shows the original out-of-plane ferroelectric

domain structure of the BTO substrates, indicating that the “up” and “down” ferroelectric domains distribute rather randomly in the sample. By applying a -10 V voltage bias on the tip of the AFM, the ferroelectric polarization is switched to the downward orientation in scanned area of $3 \times 3 \mu\text{m}^2$ enclosed by the cyan dashed line (Fig. 1(b)). Then, a tip bias with 10 V was applied to switch the ferroelectric polarization to the upward orientation within the square previously scanned by a voltage of -10 V bias. As indicated by the red dashed line (Fig. 1(b)), the ferroelectric polarization in this small square area was switched upward by the positive voltage. Piezoresponse force microscopy (PFM) hysteresis loops, shown in Figs. 1(c, d), indicate the intrinsic switchable ferroelectric properties of the heterostructures. Clearly, phase and amplitude contrast represent the inherent switching of the ferroelectric polarization in the heterostructures. A tensile strain of ~ 150 ppm in Fig. 1(e) is observed in the in-plane direction of the BTO substrates, which is much smaller than ~ 1500 ppm found in the $0.7\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3\text{-}0.3\text{PbTiO}_3$ substrates¹⁶. The coercivity of the BTO substrates can be determined to be ~ 0.8 kV/cm, which is consistent with the results reported by Christen *et al.*³

The crystal structure of the LSMO layers was characterized by X-ray diffraction method. As shown in Fig. 1(f), only the (110) X-ray diffraction peak of the substrate can be seen, which is induced by the thin thickness of the LSMO (5 nm) layer and tensile

strain. However, when the thickness was increased to 30 nm, the satellite peaks emerge in company with the (110) diffraction peak of LSMO (Fig. S1), suggesting the high-quality growth of the samples. In addition to the crystal structure characterized by X-ray diffraction method, the occurring of metal-insulator-transition is another symbol of LSMO. Fig. S2(a) shows the temperature dependent resistance of LSMO(30 nm)/BTO heterostructures. It shows a metal-insulator transition behavior with the transition temperature of ~ 283 K. With the decreasing of temperature, it also shows an abrupt change of resistance around 190 K and 275 K, corresponding to the phase transition temperature of BTO. The phase transition shows a hysteresis behavior during the heating and cooling processes. When we reduced the thickness of the LSMO to 5 nm (Fig. S2(b)), the resistance of LSMO layer increases with the decrease of temperature, reflecting a semiconducting transport behavior. The transition of conducting mechanism from metallic to semiconducting with the decreasing thickness of LSMO layers indicates that the tensile strain plays a key role in determining the physical properties of the LSMO layers. The strain plays a role on preferential orbital occupation of the $3d$ electrons^{21, 22}. The anisotropy of the d orbitals influences the electron correlation effects, giving rise to the anisotropy of the electron transfer and eventually destroying the double exchange interaction, which leads to the coexistence of the metallic and insulating phase in the

LSMO layer.^{19, 20}

The interfacial structure was further confirmed by the STEM measurements, which reveals high crystallinity and atomically sharp interfaces as shown in Fig. 2 (a). However, due to the tensile effect during growth, the growth mechanism may be the island growth mode, thus the thin film (5 nm) is not fully continuous, and the holes with size of ~10 nm can be seen in the AFM and cross-section STEM images (insets of Fig. 2(a)). The tensile strain also leads to the mixed phases A and B in the LSMO layer. Figures 2(b) and 2(c) show the high-resolution images of the areas enclosed by the dashed rectangles indicated in Fig. 2(a). In phase A, shown in Fig. 2(b), a defect at the interfacial area can be clearly seen, which strongly affects the growth of LSMO, and leads to the distorted arrangement of the atoms. In Fig. 2(c), although the atoms arranged orderly without defect in phase B, they suffered tensile strain. The in-plane distance of two closest La/Sr atoms is 5.67 Å, which is much larger than that of 5.33 Å for the interlayer distance as indicated in Fig. 2(c). Since the physical properties of LSMO strongly depend on the Mn-O-Mn bond angle and the strain, the distorted structure of phase A and the tensile strain in phase B will lead to the completely different physical properties of the LSMO layer^{20, 23, 24}, which can be thought as a metastable state. To further characterize the strain influenced growth of the LSMO layer, the in-plane distance of closest La/Sr atoms along ($\bar{1}10$) orientation is

shown in Fig. 2(d). For phase A, the defected phase, the in-plane distance increases with the increasing layer number (denoted in the area between the Figs. 2(b) and 2(c)). While for phase B, the defect free phase, the in-plane distance decreases with the increasing layer number and shows a value larger than that of the bulk. That indicates a tensile strain influence on the LSMO layer from the substrate, which refers to a tensile strain dominated growth. In addition, the energy dispersive spectroscopy (EDS, Fig. 2(e)) taken at the interfacial area also confirms that the interface is chemically sharp.

Now, let us explore the effect of the ferroelectric field of the BTO substrate on the metastable state of LSMO layer. The resistance of the LSMO layer was measured with current source mode under different bias fields (voltages applied perpendicularly to the sample plane) using a field effect transport device, as shown in the inset of Fig. 1(f)^{25, 26}. The size of the sample is 7*3 mm² with four Pt electrodes on the surface of the LSMO layer, and the distance between each electrode is about 1 mm. Figure 3 shows the resistance of the LSMO/BTO heterostructure as a function of time under different pulse electric fields. Before collecting the resistance data, a pulse electric field with a width of 100 ms was applied to pre-pole the device. The time dependent resistance was collected continually for 100 times with a time interval of 2.5 s. Then, a new pulse electric field was applied in opposite direction and resistance was measured for another 100 times with

a time interval of 2.5 s. The schematic of the pulse electric field is shown in the bottom of Fig. 3(a). The time dependent resistance measurements were repeated for several times with opposite pulse electric fields of different field strength (from 0.6 kV/cm to 4.2 kV/cm), and four resistance states denoting R_I , R_{II} , R_{III} and R_{IV} are discovered. When the positive pulse is removed, the resistance of the LSMO layer is greatly reduced and a platform (R_I) (indicated by the green filled scatters) is formed by the pulse electric field. However, this modulation is not robust; it keeps the platform (R_I) for a short period and then increases slowly to a consistent value (R_{II}), as shown in Fig. 3(b). With the application of a negative pulse, the resistance is greatly enhanced and a high resistance platform (R_{III}) is formed. Similar to the result of the positive pulse, it keeps the platform for a short while and then gently returns to the R_{IV} state. We denoted the R_I , R_{III} as volatile resistance states, and the R_{II} , R_{IV} as the nonvolatile resistance states. The discussion on the volatile and nonvolatile resistance will be given later.

In addition to the four resistance states, an asymmetry manifested as the difference of the duration of the platforms and the values of the volatile ER is also discovered. As shown in Fig. 3 (b), the duration of the platform increases from 0 s at 0.6 kV/cm to ~20 s at 4.2 kV/cm under negative pulse electric field, while for the positive pulse electric field, it increases from ~30 s to ~70 s with the same amplitude of the pulse electric field.

Meanwhile, in Fig. 3(c), we can also see that the amplitude of the ER increases rapidly with the increasing negative pulse electric field, while for the positive pulse electric field case, the ER just increases gently. They reach a maximum of $\sim 23\%$ ($|R_I - R_{II}|/R_{II} * 100\%$) and $\sim 230\%$ ($|R_{III} - R_{II}|/R_{II} * 100\%$) by applying positive and negative 4.2 kV/cm pulse electric fields, respectively. This asymmetry indicates a strong ferroelectric polarization related effect on resistance modulation rather than the strain related effect, which normally gives a symmetric behavior.

There are three factors that may contribute to the observed ER: the capacitor effect, the dynamic strain effect^{18, 27, 28} and the ferroelectric field effect. For the capacitor effect, it attracts and repels the majority carriers in the semiconductor layer in metal-oxide-semiconductor structure to realize ON/OFF states. However, it needs a consistent voltage to sustain these states because the majority carriers will be released if the voltage is removed. Because of this, the capacitor effect does not account for the non-volatile ER. This result is further evidenced by the disappearance of ER in the LSMO(5 nm)/SrTiO₃ structure shown in Fig. 3(d). We can see that after applying a pulse electric field, the resistance of the structure is modulated but returns to its original value quickly, no matter if the pulse electric field is positive or negative. For the dynamic strain effect affected ER, it is usually not sensitive to the thickness of the LSMO layer. In Fig.

S4, for the heterostructure with LSMO thickness of 30 nm, the ER is only ~0.3%, which is much smaller than that of ~5% for the 5 nm case, indicating that the ER is an interfacial effect rather than strain effect.

We ascribe the origin of the non-volatile and volatile ER to ferroelectric field effect induced charge reconstruction and oxygen vacancy redistribution. The LSMO belongs to the class of strongly correlated materials; its physical properties are strongly related to the Sr content, temperature and strain²¹⁻²⁴. When the polarization is switched to the LSMO layer (upward direction), the ferroelectric field effect will induce the accumulation of electrons in the LSMO layer, which will have an influence on the LSMO layer and lead to a low resistance state. Switching the polarization to the opposite position causes an accumulation of holes, and a high resistance state can be achieved. It should be noted that the modulation induced by the accumulation/depression of charge is quite weak, where the value is only ~3%, but it is persistent.

The giant and volatile ER is related to the redistribution of the oxygen vacancies. As shown in Fig. 2(a), the thin LSMO layer on BTO substrate suffers tensile strain and exhibits mixed phases. It is a metastable state under a critical condition and the physical properties can be easily tuned by external stimulation. Moreover, in LSMO, there is a strong double exchange coupling between two next-to-nearest neighbor magnetic cations

through a non-magnetic oxygen ion^{29, 30}, so the redistribution of oxygen vacancies strongly affects the physical properties of LSMO. As shown in Fig. 4(a), the upward ferroelectric polarization not only induces the accumulation of electrons at the interfacial LSMO but also leads to the migration of oxygen vacancies. The low resistance state originates from the following two factors: (1) the injection of electrons greatly reduces the amount of oxygen vacancies, and (2) the positive bond charge drives the oxygen vacancies away from the interface area. These two factors favor the formation of O²⁻ anions in the LSMO, which enhances the double exchange interaction and leads to the low resistance state. On the contrary, the downward ferroelectric polarization favors the formation of oxygen vacancies, as shown in Fig. 4(b). Without O²⁻ anions, the double exchange interaction is strongly suppressed, leading to the high resistance state. In addition, the asymmetry of the durations of the high and low resistance states is related to the stability of the oxygen vacancies. The stability of the oxygen vacancies depends on the strain related influence, which could increase the unit cell volume in the oxides during the growth^{31, 32}. For the LSMO grown on the tensile BTO substrates, it is in a metastable state in which the amount of oxygen vacancies is in a balance state. Any further increasement of the oxygen vacancies is not favored due to the following two points: (1) it will lead to the distortion of the LSMO layer, which is not an energy favorable state; (2)

the increasement will further expand the unit cell volume. For the state with reduced oxygen vacancies, although still energy unfavorable, it is more stable than the previous mentioned vacancies surplus model as it would not further distort the structure. Due to the ferroelectric field effect, the upward polarization can reduce the amount of oxygen vacancies via shift of oxygen center, while the downward polarization will increase the amount of oxygen vacancies. The increment of oxygen vacancies by downward polarization is more energy cost; thus, receiving a worse stability than upward polarization case. That is the reason of the longer duration of the low resistance state than that of the high resistance state.

The volatile and giant ER dominated by oxygen redistribution is further confirmed by the comparison of the R - t curves annealed at oxygen atmosphere with the pressure of 3000 and 200 Pa. When the sample is annealed in a high oxygen atmosphere, the oxygen vacancies could be greatly reduced, thus the redistribution of oxygen vacancies is weakened, leading to the disappearing of the platform behavior (Fig. S5).

To further confirm this result, the R - V curves of the heterostructures was measured. Like the measurement of the R - t curves, the device is pre-poled by a pulsed electric field perpendicular to the plane before collecting the resistance data. The resistance was collected every 8 seconds for 20 points immediately after the application of the poling

pulse electric field, and the applied poling electric field varied from 4.2 kV/cm to -4.2 kV/cm and then back to 4.2 kV/cm. The R - V curves collected after 1 second, 81 seconds, and 153 seconds are shown in Figs. 5(a-c).

Fig. 5(a) shows the R - V curve collected after 1 second. The ER is defined as $ER = (R - R_0)/R_0 * 100\%$, where R_0 is the zero-field resistance when the electric field decreases from positive to zero. It keeps a constant value around -20%, with the electric field decreasing from 4.2 kV/cm to ~0.5 kV/cm. Further decreasing the electric field to ~-0.7 kV/cm, the ER drops linearly, indicating the volatile behavior. Then it exhibits a sudden jump when the electric field is lower than ~-0.7 kV/cm. This sudden jump is related to the switching of the ferroelectric polarization at the coercive field of ~0.8 kV/cm, as shown in Fig. 1(c). The change of bond charge from positive to negative strongly affects the distribution of oxygen vacancies and leads to the high resistance state. With a further decrease of the electric field (lower than ~-3.2 kV/cm), the ER shows a sudden drop. This effect can be understood as the full switching of ferroelectric polarization. The bond charge does not change with the further reduction of electric field, and thus, the ER remains constant.

For the mixed-state shown in Fig. 5(b), the ER keeps a constant value of ~0% with the electric field decreasing from 4.2 kV/cm to -3.0 kV/cm. The reverse of the electric

field does not change the ER, reflecting a non-volatile ER. When the electric field went below -3.0 kV/cm, the ER shows an obvious jump. The value of $\sim 30\%$ is much larger than that of the nonvolatile ER of $\sim 0\%$ (with electric field from 4.2 to -3.0 kV/cm), indicating the existence of the volatile and giant ER. It decreases with the increasing electric field and disappears until the electric field reaches -1.8 kV/cm. In Fig. 5(c), the ER shows a hysteresis loop, quite similar to the Phase-Voltage curve shown in Fig. 1(d), demonstrating a bipolar non-volatile ER. The ER collected after 153 s at 300 K (the inset of Fig. 5(c)) also shows a hysteresis loop. This further confirms that the ER results from the ferroelectric field effect rather than from the strain effect which would have yielded a butterfly shape^{33, 34}. The time dependent R - V curves are shown in Fig. 5(d). The ER keeps a constant value initially and then decreases with the decreasing electric field, and the onset of the decrease is time dependent. At 1 second, the onset electric field is ~ 0.5 kV/cm, while it is ~ 4.0 kV/cm at 49 seconds. The enhancement of onset electric field with increasing time is related to the redistribution of oxygen vacancies, which is consistent with the results from the R - t curves.

Unlike the strain or charge dominated ER effect in ferroelectric field effect devices, a giant and volatile ER is achieved here. The duration of the giant ER is related to the electric field, temperature, and strain as well as the density of oxygen vacancies. It would

be meaningful if the duration could be elongated, which would benefit the design of next generation field effect devices.

CONCLUSION

In conclusion, a giant and volatile ER has been achieved in the metastable state LSMO/BTO ferroelectric field effect structures. This ER stems from ferroelectric field effect induced redistribution of oxygen vacancies in the LSMO layer. The stability of the oxygen vacancies further leads to a time dependent behavior of the ER. In addition, the non-volatile ER was also discovered, which related to the accumulation and depletion of charge at the interfacial area. Our results show that adjusting the related parameters, which would be helpful for the development of next generation ferroelectric-based storage devices, can effectively modulate the giant ER.

Figure captions

Figure 1. Ferroelectricity and the structure of the LSMO/BTO heterostructures. (a) Out-of-plane PFM phase image of the original ferroelectric domain structure, (b) the PFM phase image after applying a -10 V probe bias in a $3\times3\text{ }\mu\text{m}^2$ area (indicated by the cyan dashed line) and a 10 V probe bias in a $1\times1\text{ }\mu\text{m}^2$ area (indicated by the red dashed line). Local PFM ramp curves of amplitude (c) and phase (d). (e) Strain versus electric field curve measured by a strain gauge, (f) XRD θ - 2θ scan pattern of the LSMO/BTO heterostructure. The inset shows the schematic of the device structure.

Figure 2. STEM images of the LSMO/BTO structure. (a) Interface of the structure. The top inset shows the whole view of the structure and the bottom inset shows the surface morphology of the LSMO layer, the yellow triangle in the top inset show the holes in LSMO layer. (b) and (c) show the high-resolution images of the corresponding areas indicated by the dash rectangles in (a). The numbers 1–9 between (b) and (c) indicate the first atomic layer (1) to the ninth atomic layer (9) of LSMO from the interface. The bright and dark dots indicated by cyan and yellow roundel are the La/Sr and Mn atoms respectively. (d) The in-plane interatom distance of closest La/Sr atoms of phase A and B. (e) Energy dispersive spectroscopy maps of Ba, O and La at the interface.

Figure 3. (a) Electric field dependent R - t curves measured at 240 K, where the electric field formed platform is indicated by the green filled scatters; the inset is an enlarged view of the area indicated by the red dashed line. (b) Giant and volatile ER with different electric fields. (c) Non-volatile and volatile ER under different electric fields. (d) R - t curves of LSMO(5 nm)/STO measured under 4.2 kV/cm electric field at 300 K.

Figure 4. Schematic of the charge and oxygen vacancies redistribution with upward (a) and downward (b) ferroelectric polarizations.

Figure 5. *R-V* curves of the LSMO/BTO heterostructure at 240 K collected after removing the electric field for 1 second (a), 81 seconds (b) and 153 seconds (c). The inset of Fig. 4(c) shows the *R-V* curve at 300 K collected after 153 seconds. (d) Time dependent *R-V* curves with the electric field ranging from 4.2 to 0 kV/cm.

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Author Contributions

D. Z. and J. Z. have contributed equally to this work. D.Z. and H.B. designed the outline of the manuscript and wrote the main manuscript text. J.Z. and X.Z. performed the STEM investigation. Y.W., Z.W., W.Z., D.L., L.Z. C.J., and P.L. contributed detailed discussions and revisions. All authors reviewed the manuscript.

Notes

The authors declare no competing financial interest

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