Controlling Resistance Switching Polarities of Epitaxial BaTiO$_3$ Films by Mediation of Ferroelectricity and Oxygen Vacancies

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1. Introduction

BaTiO$_3$ (BTO) is an important ferroelectric, dielectric, and semiconducting perovskite oxide material.$^{[1–3]}$ It has been widely studied for various application potentials such as ferroelectric memories,$^{[4]}$ multilayer capacitors,$^{[5]}$ and positive temperature coefficient resistors,$^{[6]}$ etc. Recently, resistive random access memory (ReRAM) has been suggested as one of the promising candidates for next-generation nonvolatile memory applications.$^{[7,8]}$ Attention has particularly been paid to BTO films for the applications in ReRAM devices and encouraging results have been reported.$^{[9–17]}$ Correspondingly, various microscopic mechanisms were proposed to explain the resistance switching effects of BTO films. One representative mechanism is the ferroelectric polarization induced interfacial charge coupling (variations of interfacial barrier height and width). The substantial roles of this mechanism in ferroelectric tunnel junctions, where the resistance switching originates mainly from a polarization modulation of the height and width of tunnel barrier, have been addressed.$^{[9,10,12,14]}$ Another mechanism is based on defects (ionic or electronic) mediated phenomena, in which formation/rupture of conductive filaments are believed to be responsible for the resistance switching in BTO films.$^{[11,13]}$ and the formation/rupture of conductive filaments is closely related to the density and migration behaviors of oxygen vacancies ($V_O$) or other defects.$^{[11,13]}$ In addition to the above mentioned mechanisms, other mechanisms were proposed. For example, Wang et al. reported clear resistance switching behaviors for TiN/BTO/TiN structure fabricated by RF sputtering and claimed that the thin TiO$_x$ as interfacial layer between BTO and TiN could cause the resistance switching.$^{[15]}$ Au et al. reported significant resistive switching effects in Ag nanoparticles-embedded BTO films and they claimed that the resistance switching is due to the Ag charge storage.$^{[17]}$

Although excellent electrical properties such as high on/off resistance ratio, good retention, and high endurance etc., have been reported in the above mentioned literature, the resistive switching mechanisms in BTO-like ferroelectric oxide films are
still ambiguous and under dispute. Especially, for leaky ferroelectric semiconducting films, the roles of the ferroelectricity and $V_O$ in modulating the RS behaviors are far from clarified. For example, in the works of Yan et al.\cite{11} and Li et al.\cite{13} only conductive filaments formed by the $V_O$ migration are considered, and the effect of ferroelectricity on the RS behaviors in BTO films was ignored. In the work by Wang et al.\cite{18} the RS effects in semiconducting ferroelectric BiFeO$_3$ (BFO) films are attributed to the modulation of the Schottky-like barriers at both of the top/bottom interfaces due to the accumulation/depletion of $V_O$ in the BFO films induced by the polarization switching. For the same semiconducting ferroelectric BFO system, the RS effects are attributed only to the barrier variation of the bottom BFO/Nb-SrTiO$_3$ (STO) interface.\cite{19} The barrier variation originates from the accumulation/depletion of the free carriers in the Nb-doped STO substrates rather than the accumulation/depletion of oxygen vacancies inside the BFO films.

It is well known that oxygen pressure during the oxide film deposition will greatly affect the film crystal structure, ferroelectricity, conductivity, and charge transport properties.\cite{20,21} In this work, we shall prepare a series of BTO films with different ferroelectric states and electrical conductivities by carefully controlling the oxygen pressure during the film growth using pulsed laser deposition (PLD). Three typical types of resistive switching behaviors will be observed. Our major concern is to manipulate the ferroelectric polarization and $V_O$ concentration, so that the polarization modulated consequence and $V_O$-induced mechanism coexist and compete with each other. Along this line, one can expect a transition of the RS behavior from one to another, for example, the RS polarity reversal. Up to now, attention has been rarely paid to the RS polarity of the devices, while clarifying the intrinsic resistance switching mechanisms remains critical and challenging. We will investigate the RS polarity variation in the BTO thin films prepared under different conditions. Based on the characterizations of their crystal structures, ferroelectric polarizations, and electrical conductivities, the microscopic RS mechanisms responsible for the different RS polarities will be discussed. Additional energy band models will be proposed to explain these RS polarities.

2. Results

Figure 1a shows the X-ray diffraction (XRD) $2\theta$-\(\Omega\) measurements of the six BTO films deposited under different oxygen pressures ranging from $3.3 \times 10^{-6}$ mbar to $3.3 \times 10^{-1}$ mbar on the 20-nm thick La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO)-covered (001) STO substrates. For the convenience of expression, samples with BTO films deposited in the oxygen pressures of $3.3 \times 10^{-1}$, $3.3 \times 10^{-2}$, $3.3 \times 10^{-3}$, $3.3 \times 10^{-4}$, $3.3 \times 10^{-5}$, and $3.3 \times 10^{-6}$ mbar are nominated as P-1, P-2, P-3, P-4, P-5, and P-6, respectively. The thickness of the BTO films is $\approx$300 nm. The (00m) peaks from the

![Figure 1](www.MaterialsViews.com)
STO substrates and (m00)/(00m) peaks of the BTO films reveal the good epitaxial BTO growth on the cube-on-cube orientation. Since the LSMO layers are very thin (only ≈20 nm), the peak from the LSMO layers is not detectable. The peaks labeled with stars originate from the substrates due to the remaining Cu Kβ radiation. A more detailed analysis is carried out for the (003) peaks, as shown in Figure 1b. For samples P-1 and P-2, the (300)/(003) peaks split into two groups of peaks of (003) and (300), implying that the a-domains and c-domains coexist in the two BTO films. When the oxygen pressure decreases down to 3.3 × 10^{-3} mbar, only the c-domains [(003) peak] can be identified and the a-domains [(300) peak] disappear. The (003) diffraction peaks shift toward the high angle with reduced oxygen pressure, indicating the out-of-plane lattice contraction. The reciprocal space mapping (RSM) measurements around the (103) pseudo-cubic reflection of the BTO/LSMO/STO structure were also performed for all the samples so that their crystal structures and lattice constants can be evaluated. Figure 1c is a typical RSM pattern for sample P-3. The calculated lattice parameters from the RSM results are shown in Figure 1d. The large c/a ratios for the samples deposited in the intermediate oxygen pressures (P-3, P-4, and P-5) are evaluated, demonstrating the tetragonal crystal structures. It is well known that a paraelectric BTO phase is cubic and tetragonal BTO corresponds to a ferroelectric phase. The XRD results reveal that the samples P-3, P-4, and P-5 have good ferroelectric properties and the others may not.

Atomic force microscope surface morphology measurements were also done to check the film quality, as seen in Figure S1 (Supporting Information). Except for sample P-1, all other samples exhibit smooth surfaces. Terrace growth patterns in the samples P-3 and P-4 can be identified by careful observation. Usually, it is difficult to preserve the initial vicinal structure on the top surface of such thick films; therefore, this observation confirms the high quality of the BTO films used in the present study.

The resistive switching properties of the Au/BTO/LSMO device structures were investigated. The schematic diagram of the measurement setup is shown in the inset of Figure 2a. The small devices with area of 60 × 60 µm^2 were used for electrical characterization to avoid the effect of the film nonuniformity. Positive and negative biases were applied to the top electrode while the LSMO bottom electrodes were always grounded. To reduce the effects from the transient current as small as possible, a small voltage step of 5 mV and long current integration time (PLC 20 in the current integration time of B1500A) were adopted during all the current–voltage (I–V) measurements (The experimental results for transient current measurements on the sample P-3 are shown in Figure S2 (Supporting Information). It should be noted that the resistances of the LSMO bottom electrodes in all these samples should be less influenced by the different oxygen ambient pressures for the BTO thin-film deposition, as identified by earlier work,\cite{22} because the conductivity of LSMO is dominated by the Mn^{3+}–Mn^{4+} double-exchange mechanism. This allows a safe exclusion of the variation in electrical conductivity for LSMO bottom electrodes.

Figure 2 shows the typical I–V characteristics of all the samples. Three types of RS behaviors can be observed. For the sample P-6, clear bipolar RS effects are exhibited. During the positive voltage scanning
cycle $0 \rightarrow +3 \rightarrow 0$ V), the sample changes from a LRS state to a HRS state, whereas it changes from a HRS to a LRS during the negative voltage scanning cycle $0 \rightarrow -3 \rightarrow 0$ V, as shown in Figure 2a. We assign this kind of RS behavior as type “A” RS behavior. Similarly, the samples P-5 and P-4 also exhibit clear bipolar RS effects, as shown in Figure 2b,c. However, the resistance changes from a HRS to a LRS during the $0 \rightarrow +3 \rightarrow 0$ V cycle, and from a LRS to a HRS during the $0 \rightarrow -3 \rightarrow 0$ V cycle, whose hysteresis direction is completely opposite to that of the type “A” RS behavior. We assign it as type “B” RS behavior. The two types of RS modes exhibit opposite RS polarities, implying that the mechanisms for them should be different. The samples P-3, P-2, and P-1 show almost identical I–V features, as shown in Figure 2d–f. Comparing the RS behaviors of type “A” and type “B” modes, they suggest the following different features: (1) Unlike the large resistance ratio of more than $10^3$ shown in type “A” and type “B” samples, only weak RS effects can be observed. (2) The weak RS effect exhibits a unipolar behavior, while the bipolar RS behaviors are observed in the type “A” and “B” samples. (3) The I–V hysteresis characteristics are almost symmetrical and the magnitude of current at $\pm 3$ V decreases several orders of magnitude down to only pico-ampere scale, implying that the BTO film changes from a good conductor to a good insulator. The RS characteristics observed in the samples P-3, P-2, and P-1 are classified into the type “C” RS behavior.

The huge differences of the RS behaviors in these samples suggest different underlying microscopic mechanisms, which are assumed to be closely related to the differences in their crystal structures and electrical properties due to different growth oxygen pressures. To elucidate the origin for the huge RS differences, the ferroelectricity of all the samples was first investigated by macroscopic polarization-voltage (P-V) measurements. At room temperature, saturated hysteresis loop can be observed only for the samples P-3 and P-2. For the sample P-1, the P-V curve is linear-like, demonstrating very weak or nearly no ferroelectricity. The samples grown in oxygen pressure lower than $3.3 \times 10^{-3}$ mbar are too leaky to obtain macroscopic P-V characteristics at room temperature. Nevertheless, the P-V measurements performed at 80 K revealed well saturated ferroelectric hysteresis for the sample P-4. However, we still cannot observe normal macroscopic P-V hysteresis for the samples P-5 and P-6 even at low temperatures due to very leaky films. Figure 3a,b shows the macroscopic P-V measurements results (The leaky P-V curves for the samples P-5 and P-6 are not shown here). To further check the ferroelectricity of the leaky BTO films, piezoresponse force microscopy (PFM) measurements were carried out for the samples P-5 and P-6. Under the same polarizing and reading conditions, the PFM phase exhibits clear ferroelectric switching features for the sample P-5, but no evidence of ferroelectricity can be observed for the sample P-6, as shown in Figure 3c,d. Based on the macroscopic P-V and nanoscale PFM measurement results, it can be concluded that the samples, P-6 and P-1 have no ferroelectricity; the samples P-3 and P-2 have comparatively good ferroelectricity, and only weak ferroelectric performances for the samples P-4 and P-5 can be revealed. These results are consistent
with the crystal structure analysis by XRD results shown in Figure 1.

In parallel to the ferroelectricity characterizations, the electrical conductivity of the BTO films was also measured. It is known that the conduction of the nondoped BTO films is contributed from the free electrons provided by V\text{O}\text{.}[23] Experimentally, using aberration-corrected annular-bright-field scanning transmission electron microscopy, Xu et al. proved that the V\text{O} concentration increases with reduced oxygen pressure during the deposition.[23] In Zhao's work,[21] Rutherford backscattering spectrometry measurements on the BTO films deposited in the oxygen pressure ranging from 2.2 × 10^{-7} to 2.2 × 10^{-4} mbar also confirmed the same relationship between the V\text{O} concentration and deposition oxygen pressure. In the present work, the V\text{O} concentration in the BTO films is higher at lower oxygen pressure during the PLD. Since it is very difficult to accurately measure the concentration of light elements, such as oxygen, we have a rough comparison on the V\text{O} concentrations of the samples P-6, P-4, and P-3 from the point of view of conductivity. The temperature dependent resistances of the Au/BTO/LSMO structures were measured at a constant voltage of 2 V with the same capacitor size. As shown in Figure S3 (Supporting Information), the three samples exhibit huge resistance differences, which indirectly imply the significant V\text{O} density difference inside them. The sample P-3 exhibits the largest resistance and the sample P-6 the smallest resistance. The negative Hall coefficient obtained by the Hall measurement (results not shown here) shows that the major carrier is electron. The present resistance and Hall measurements indicated that the free carriers (electrons) provided by the doping of V\text{O} have been greatly reduced in the samples P-4 and P-3. The significant increase of the resistance indirectly proved that the V\text{O} concentration has been greatly reduced in the samples P-4 and P-3. The sample P-3 can be nearly dealt as a good insulator, and most probably there are no oxygen vacancies in the BTO film.

3. Discussion

Based on the above analysis on the ferroelectricity and electrical conductivity of the BTO films, the big differences of the RS behaviors of the BTO samples should be attributed to the different ferroelectric properties and V\text{O} concentrations. To interpret the three different types of RS behaviors, we propose the following microscopic RS mechanisms.

As mentioned above, the sample P-6 has nearly no ferroelectricity. Thus, the RS effect is unlikely due to ferroelectric switching. In addition, the features of RS behaviors shown in Figure 2a are also not likely due to the conductive filament mechanism, whose RS behaviors are usually unipolar. We propose that the RS effects are ascribed to the local migration of V\text{O} driven by external electric field. To construct the energy band model, the charge transport characteristics of the interfaces between the Au/BTO and BTO/LSMO have been investigated. As shown in Figure S4a (Supporting Information), the linear I–V characteristics of the in-plane LSMO/BTO (P-6)/LSMO device demonstrate the ohmic contact of the BTO/LSMO interface. On the contrary, the I–V characteristics of the in-plane Au/BTO (P-6)/Au device exhibit the typical Schottky diode behavior, as shown in Figure S4b (Supporting Information), indicating clearly the Schottky contact at the Au/BTO interface. Therefore, the charge transport in the sample P-6 is dominated only by the Schottky barrier at the Au/BTO top interface. When a positive voltage is applied to the top electrode, the oxygen vacancies will be repelled away from the top Au/BTO interface.[24–26]

Then the width and height of the Schottky barrier will increase, as shown in Figure 4a (point “a” in the I–V curve). After scanning the voltage from point “a” to point “b”, the V\text{O} concentration on the top interface will be continuously reduced with the continuous positive voltage stress. Consequently, the width and height of the Schottky barrier at the top interface will be further increased, as shown in Figure 4b. Comparing points “a” and “b” at the same bias voltage, the BTO film will change from a LRS in point “a” to a HRS in point “b” due to the increased height and width of the Schottky barrier at the Au/BTO top interface. When a negative bias voltage is applied to the Au electrode, the oxygen vacancies will move toward the Au/BTO top interface. In point “c”, a small number of V\text{O} accumulated at the Au/BTO interface lowers the Schottky barrier height in comparison with its virgin state (see Figure 4c). After the negative bias voltage sweeps from c → −3 V → d, the oxygen vacancies are intensively accumulated at the top interface. Then the barrier (height and width) at the top interface will be further weakened (see Figure 4d). Therefore, the BTO film switches from the HRS in point “c” to the LRS in point “d”, due to the decrease of the barrier in height and width at the Au/BTO interface. To further confirm this V\text{O} migration model, we carried out current stress measurements under different temperatures. When the sample P-6 is biased at a constant voltage of ±2V, we observe that: (1) The stress current decreases/increases with the increase of the stress time, which further confirms the model that the positive/negative voltages will repel/attract oxygen vacancies from the interface and result in the increase/decrease of the resistance. (2) The stress current decreases/increases faster at a higher temperature, also confirming the model in which the oxygen vacancies have higher mobility at higher temperatures. The corresponding results are shown in Figure S5 (Supporting Information).

For the samples grown with oxygen pressures higher than 3.3 × 10^{-6} mbar, their RS behaviors (type “B” and type “C”) are completely different from that of type ‘A’. In this case, the V\text{O} migration model cannot be used to explain the type “B” and type “C” RS behaviors. A number of theoretical[27] and experimental works[28–30] showed that the charge transport across the metal/ferroelectrics/conductive oxide device is controlled by the ferroelectric polarization switching induced Schottky barrier variation at the top/bottom interface. The ferroelectric polarization controls the accumulation or depletion of electron charges at the interface, and the associated bending of the n-BTO conduction band determines the transport regime across the interface. According to the investigation on ferroelectricity, the samples with type “B” RS behaviors (samples P-5 and P-4) have strong or weak ferroelectricity at room temperature. Therefore, the ferroelectricity should play an important role in inducing the type “B” RS behaviors. To confirm this assumption, we calculate the ferroelectric polarization-induced interface barrier changes of the sample P-4 using the theoretical model proposed by Pintilie et al.[31,32], as shown in Table 1. It shows that the ferroelectric switching does
modulate the barrier height at the top/bottom interface. The bottom BTO/LSMO interface is no longer of the ohmic contact. Furthermore, the potential change across the BTO/LSMO interface is more significant than that of the Au/BTO interface, which may be due to the much larger screen length of LSMO (2.0 Å) than that of Au (0.3 Å). Therefore, charge transport behaviors across the two back to back metal-semiconductor Schottky contacts are dominated by the bottom BTO/LSMO interface. Based on the above analysis, we propose the following model to explain the RS behaviors shown in the type “B” samples (P-5 and P-4), as shown in Figure 5. When a positive voltage is applied onto the top Au electrode (Figure 5 a), the depletion layer width and barrier height at the top interface will increase due to the downward polarization, while they are decreased at the bottom BTO/LSMO interface. When the positive voltage scans from voltage point “a” to point “b” (Figure 5b), the downward polarization will continuously increase, therefore the energy band at the bottom interface will keep bending-down, leading to the decrease of the resistance in point “b”. On the contrary, a negative voltage applied onto the top electrode will produce an upward polarization, which will result in the decrease/increase of the barrier height and width at the top interface/bottom interface (Figure 5c). When the negative voltage scans from point “c” to point “d” (Figure 5d), the upward polarization will continuously increase. The energy band at the bottom interface will keep bending-up, leading to the increase of the resistance in point “d”.

For the sample P-3, we also estimate the barrier changes by ferroelectric polarization switching using the same methods for the sample P-4, where only the parameters used in the calculation are somewhat different. Since the sample P-3 has better ferroelectricity, a higher $P_r$ value of 4.5 $\mu$C cm$^{-2}$ is adopted, and different virgin values of the barrier height at the interface are used considering the better insulating properties (different positions for the conduction band). The estimated barrier height of the top Au/BTO interface will change from 1.84 to 1.92 eV (downward polarization) or 1.76 eV (upward polarization). The barrier height at the bottom BTO/LSMO interface will change from 1.64 to 1.22 eV (downward polarization) or 2.06 eV (upward polarization). Although significant barrier height changes can be observed, the RS effects of sample P-3 are rather weak, as

### Table 1. The barrier height changes with and without polarization switching of sample P-4.

| Barrier height     | Virgin value [eV] | Polarization down [eV] | Polarization up [eV]| a) |
|--------------------|------------------|------------------------|----------------------|
| Top interface (Au/BTO) | 1.65             | 1.71                   | 1.59                 |
| Bottom interface (BTO/LSMO) | 1.45             | 1.17                   | 1.73                 |

a) The following parameters are used for the calculation of the barrier height: $P = 3 \mu$C/cm$^2$, $\varepsilon_{\text{static}} = 60$, $I_1 = 0.3 \AA$, $\varepsilon_{\text{M1}} = 1.5$, $L_1 = 2.0 \AA$, $\varepsilon_{\text{M2}} = 2$. The $P$ and $\varepsilon_{\text{static}}$ values are taken from the data adopted by Daniel et al. in Ref. [32]. The $I_1$ and $\varepsilon_{\text{M1}}$ values are estimated from the Cu values used in Ref. [32], since they are rarely reported. The $L_1$ and $\varepsilon_{\text{M2}}$ values are from the experimental results by X. Hong et al. (Appl. Phys. Lett. 86, 142501(2005)) and by Mistrik et al. (J. Appl. Phys. 99, 08Q317(2006)). The real parameters may have some deviation to the presently used for calculation. The calculated results are enough to demonstrate the change of the barrier height with ferroelectric switching.

Figure 4. The schematic energy band diagrams for sample P-6 (3.3 × 10$^{-6}$ mbar) under different bias voltage conditions, which indicate that the bipolar RS polarities are dominated by $V_O$ migration under external electric field. a) positive voltage in position “a”, $V_O$ slightly depleted at the top interface; b) positive voltage in position “b”, $V_O$ deeply depleted at the top interface; c) negative voltage in position “c”, $V_O$ slightly accumulated at the top interface; d) negative voltage in position “d”, $V_O$ deeply accumulated at the top interface.
shown in Figure 2d. As already known from the results in
Figure 3a, the sample P-1 doesn’t have ferroelectricity and
the sample P-2 has weaker ferroelectricity than the sample
P-3. They have different ferroelectricity. However, all of them
exhibit nearly the same current–voltage behaviors, as shown in
Figure 2d–f. The present results suggest that the ferroelectric
polarization cannot necessarily induce the RS effect in insulating
ferroelectric film without sufficient free carriers (electrons cre-
ated by $V_O$ in the present case). It should be pointed out that
remarkable RS effect is possible for ferroelectric tunnel diode
based on very thin BTO film, in which the charge transport is
dominated by the direct tunneling process of electrons.\[9\] For
the present metal (Au)-insulator (300 nm BTO)-metal (LSMO)
(MIM) structures, the weak $I–V$ hysteresis loops as observed
in the samples P-3, P-2, and P-1 are believed to be mostly due
to the dielectric relaxation current. As also shown in Figure S2
(Supporting Information), the current–voltage behaviors of the
sample P-3 are closely related to the voltage sweeping speeds,
which implies that the $I–V$ hysteresis shown in Figure S2 (Sup-
porting Information) is not from the steady transport current.
Our present results demonstrate that ferroelectric switching
can induce significant RS effects for thick BTO films, but it only
works on the semiconductor-type BTO films (P-5 and P-4), which
further demonstrates that the free carriers (electrons) is critical
for the thick ferroelectric film to obtain remarkable RS effects.

### 4. Conclusion

In conclusion, we have carried out a comprehensive study on
the resistive switching behaviors of epitaxial BTO thin films
deposited on LSMO-covered STO substrates. We have demon-
strated that the RS behaviors of BTO films are due to the com-
petition between ferroelectric polarization and $V_O$ migration.

It has been revealed that the free carriers are crucial to obtain
the polarization switching induced large RS effects in thick fer-
roelectric films. Especially, we have observed two completely
opposite RS switching polarities for the BTO films deposited in
different oxygen pressures, and have clarified the microscopic
mechanisms responsible for the different RS polarities from
the viewpoints of the ferroelectricity and electrical conductivity.

The present work clarifies the intrinsic relationship between
the complex RS behaviors and their embedded mechanisms for
BTO-like ferroelectric semiconducting oxide films, and provides
beneficial insights in the accurate design and control of the RS
behaviors in the high performance ReRAM devices.

### 5. Experimental Section

The BTO/LSMO oxide heterostructures were epitaxially grown on
(001)-oriented SrTiO$_3$ single crystal substrate by PLD. The LSMO
bottom electrodes were grown at a substrate temperature of 600 °C
and 0.21 mbar oxygen pressure. After the growth of 50 nm LSMO
layers, the BTO films with thickness of 300 nm were deposited at a
substrate temperature of 650 °C. The laser fluency and laser frequency
were fixed to be 0.6 J cm$^{-2}$ and 3 Hz for the deposition of all the BTO
films. The BTO films were deposited by only varying the deposition
oxygen pressure while keeping other processing parameters completely
identical. The gold top electrodes were evaporated to fabricate the Au/
BTO/LSMO/STO RS devices. The crystal structure was examined by
X-ray diffraction measurement using a Philips X’pert MRD meter. The
$2\theta$-scan was carried out to check the crystal phase and preferred
orientation. The crystal structure and the strain status of the BTO films
on STO substrates were further investigated by RSM, from which the
lattice constants were calculated. The surface morphologies of substrates
and deposited films were studied by atomic force microscopy (Digital
Instruments 5000) working in tapping mode. The ferroelectricity of the
leaky BTO films was investigated by piezoresponse force microscopy
(Cypher, Asylum Research). The resistance-temperature properties

![Figure 5. The schematic energy band diagrams for sample P-4 (3.3 x 10^{-4} mbar) under different bias voltage conditions a) positive voltage in position “a”; b) positive voltage in position “b”; c) negative voltage in position “c”; d) negative voltage in position “d”. “δ” means the dead layer width between the metal/ferroelectric; “W1” and “W2” mean the depletion layer width in the top and bottom interface. The inset of the figure shows the positions “a”, “b”, “c”, and “d” in the IV hysteresis loop.](image-url)
of the BTO films were measured by a Keithley 6430 sub-femtoampere sourcemeter with a variable temperature vacuum probe station (Jannis). Ferroelectric and resistive switching characteristics were investigated by a Radiant ferroelectric tester Premier II and an Agilent B1500A high precision semiconductor product analyzer, respectively.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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