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H. W. Lu
Lanzhou Jiaotong University


Chung Wung Bark
Gachon University


Evgeny Tsymbal
University of Nebraska at Lincoln


Alexei Gruverman
University of Nebraska at Lincoln

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Ferroelectric Tunnel Memristor

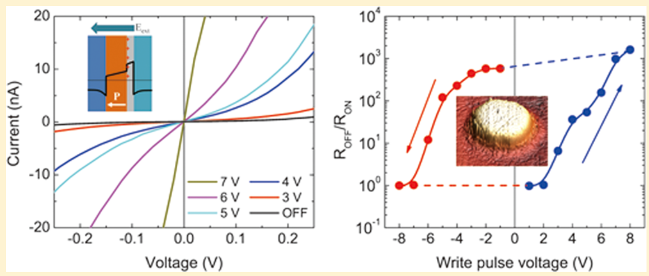
D. J. Kim,[†] H. Lu,[†] S. Ryu,[‡] C.-W. Bark,[‡] C.-B. Eom,[‡] E. Y. Tsymbal,[†] and A. Gruverman*[,†]

[†]Department of Physics and Astronomy & Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, United States

[‡]Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States

S *Supporting Information*

ABSTRACT: Strong interest in resistive switching phenomena is driven by a possibility to develop electronic devices with novel functional properties not available in conventional systems. Bistable resistive devices are characterized by two resistance states that can be switched by an external voltage. Recently, memristors—electric circuit elements with continuously tunable resistive behavior—have emerged as a new paradigm for nonvolatile memories and adaptive electronic circuit elements. Employment of memristors can radically enhance the computational power and energy efficiency of electronic systems. Most of the existing memristor prototypes involve transition metal oxide resistive layers where conductive filaments formation and/or the interface contact resistance control the memristive behavior. In this paper, we demonstrate a new type of memristor that is based on a ferroelectric tunnel junction, where the tunneling conductance can be tuned in an analogous manner by several orders of magnitude by both the amplitude and the duration of the applied voltage. The ferroelectric tunnel memristors exhibit a reversible hysteretic nonvolatile resistive switching with a resistance ratio of up to 10^5 % at room temperature. The observed memristive behavior is attributed to the field-induced charge redistribution at the ferroelectric/electrode interface, resulting in the modulation of the interface barrier height.



KEYWORDS: *Ferroelectric tunnel junction, memristor, resistive switching, polarization retention*

Electrically induced resistive switching has been observed in a number of binary and complex oxide materials. Depending on the specific system, the proposed mechanisms are quite diverse and include, among others, electromigration, crystalline defects, Schottky barrier variations, and electrically induced filament formation.[1−7] Recent reports of the tunneling electroresistance (TER) effect in ferroelectric tunnel junctions[8−10] invoke a change in the potential energy barrier associated with the reversal of ferroelectric polarization.[11] All of these systems, however, irrespective of the physical mechanism of switching, are bistable devices; that is, the application of an external bias voltage switches resistance between *two states*: ON (low resistance) and OFF (high resistance) states.

Another type of the resistive switching behavior, which had been theoretically predicted almost 40 years ago,[12] was recently discovered in the Pt/TiO_2/Pt junctions.[13] It is characterized by a *continuous* change in resistance with the amount of current flown across the device. It is assumed that the physical mechanism of this effect involves coupled motion of electrons and ions within the oxide layer under an applied electric field. When the current is stopped, the device retains its last resistance state and thus may act as a nonvolatile memory element. Due to the nonvolatile nature of the resistance state, such a device was dubbed a "memristor" (as a short form of "memory resistor"). In a more general sense, the term "memristor" implies a resistance dependence on the amplitude and duration of the applied voltage and, thus, on the history of the current flow through the device.[12,13] Integrated circuits that include memristors have the potential to significantly extend circuit functionality in such applications as high-density multilevel nonvolatile memories and adaptive networks that require synapse-like functions.[14]

Memristors based on oxide materials typically require relatively thick oxide layers, ranging from tens to hundreds of nanometers.[1,15−17] As a result, these types of memristors are characterized by relatively large values of resistance and in many cases significant fluctuations in low-resistance states, for example due to the stochastic nature of the filament formation.[1,15] In this Letter, we introduce ferroelectric tunnel memristors (FTM)—ferroelectric tunnel junctions with continuously tunable resistance. A ferroelectric tunnel junction (FTJ) is a device where tunneling current can be toggled between two nonvolatile states through the reorientation of polarization in the ferroelectric barrier with a thickness of just several nanometers.[18,19] A demonstration of stable polarization in ultrathin ferroelectrics[20−23] triggered strong interest in resistive switching in FTJs. Recently, several research groups independently reported observation of the tunneling electroresistance (TER) effect using a combination of piezoresponse

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force microscopy (PFM) and conductive atomic force microscopy (C-AFM) techniques,[8−10,24−26] thus confirming earlier theoretical predictions.[11,27−29] Here, we report observation of the tunable, hysteretic, and nonvolatile resistive switching behavior in the micrometer-size FTJ devices with the OFF/ON resistance ratio reaching 10^5 %. In contrast to the TER effect associated with ferroelectric polarization switching, the observed memristive behavior is not directly linked to the polarization reversal in FTJs. We attribute the observed resistive switching behavior of FTM to the field-induced charge redistribution at the interface resulting in the modulation of the interface barrier height. The ferroelectric polarization promotes charge accumulation and enhances stability of the resistive switching effect.

Results. *Experimental Details.* Resistive switching measurements have been carried out using the Au/Co/$BaTiO_3$/$La_{2/3}Sr_{1/3}MnO_3$/$NdGaO_3$ (Au/Co/BTO/LSMO/NGO) heterostructures shown schematically in Figure 1a. Epitaxial single-crystalline BTO films were grown by pulsed laser deposition on the LSMO(50 nm)/NGO(110) substrates with in situ high-pressure reflection high-energy electron diffraction (RHEED) monitoring.[30] Figure 1b shows RHEED intensity oscillations and RHEED patterns indicating a layer-by-layer growth and epitaxial structure of the BTO films. The BTO thickness ranged from 1.6 to 3.2 nm (4−8 unit cells (u.c.)). Top Au(10 nm)/Co(10 nm) electrodes of 5 μm in diameter were fabricated by sputtering followed by photolithographic patterning (Figure 1c).

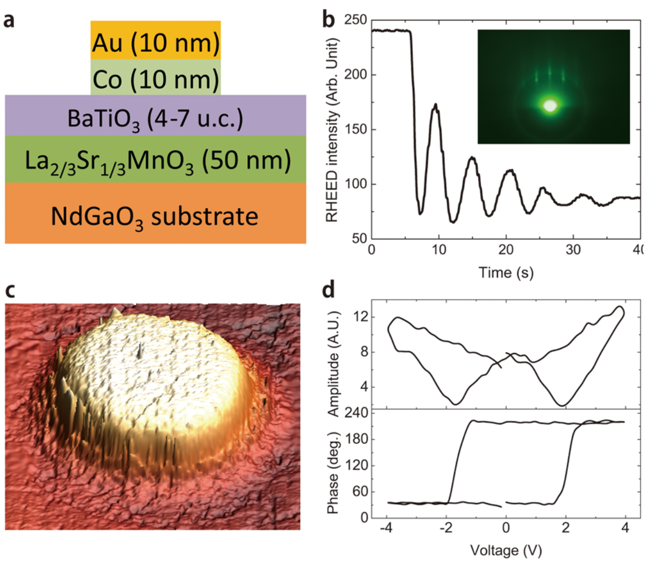

Figure 1. (a) A schematic cross-section of the junction. (b) Reflective high-energy electron diffraction (RHEED) oscillation during the deposition of $BaTiO_3$. The inset is the RHEED pattern of the $BaTiO_3$ surface. (c) Topography of the junction. The nominal diameter of the top electrode is 5 μm. (d) PFM amplitude and phase hysteresis loops measured in the Au/Co/$BaTiO_3$/$La_{2/3}Sr_{1/3}MnO_3$/$NdGaO_3$ junction with the 4-u.c.-thick $BaTiO_3$ barrier.

The ferroelectric and electrical transport properties of the samples have been tested using a commercial AFM (Asylum Research, MFP-3D) by means of resonant-enhanced PFM and C-AFM modes, respectively. All studied heterostructures (down to the thinnest one with the BTO thickness of 4 u.c.) exhibit clear switchable piezoresponse signals, which is indicative of their ferroelectric state (Figure 1d). Further experimental details can be found in the Materials and Methods section.

Retention of the Resistive Switching Effect. A majority of the earlier studies of the TER effect in ferroelectrics have been performed in ultrathin films with a bare surface (without a top electrode), which typically exhibit a high R_{OFF}/R_{ON} value (up to $\sim 10^4$ %) and strong retention (at least several days).[8−10] However, the realization of the stable TER effect in the FTJ device configuration, where the ferroelectric film is sandwiched between two electrodes, typically suffers from quick relaxation of polarization due to an uncompensated depolarizing field.[31,32] This relaxation could be due to the finite screening length in electrodes and formation of the low-k dielectric layer at the film−electrode interface. The solution of this problem is critically important for the employment of FTJ switches in electronic circuits.

First-principle calculations set the critical thickness for polarization instability in a BTO layer sandwiched between $SrRuO_3$ electrodes at 6 u.c., which is equivalent to the thickness of 2.4 nm.[33] However, our recent experimental studies showed that polarization screening by metal oxide electrodes is less effective than predicted, resulting in progressive loss of the net polarization in the BTO junctions as thick as 24 u.c. (9.6 nm).[34] A similar polarization decay has been reported for nanometer-thick Pb(Zr,Ti)O_3 films with $SrRuO_3$ electrodes.[35] We fabricated FTJ heterostructures employing Co as a top electrode to improve ferroelectric polarization stability. However, even in this case, the Au/Co/BTO/LSMO/NGO heterostructures with the Co electrodes fabricated at a high base pressure (HBP) of 10^{-4} Torr exhibit fast polarization decay and instability of resistive switching as shown in Figure 2a. It can be seen that upon application of a −6 V pulse the Au/Co/BTO/LSMO/NGO heterostructure is switched from a high-resistance (R_{OFF}) state to a low-resistance (R_{ON}) state yielding their ratio, R_{OFF}/R_{ON}, of more than 1000%. But it can be also seen that the ON resistance state is not stable and its resistance is quickly increasing with time (left panel in Figure 2a), and within several minutes the difference between R_{OFF} and R_{ON} disappears; that is, the R_{OFF}/R_{ON} value approaches 1 (note that initially the system is in the OFF state which is a stable one (right panel in Figure 2a)).

To obtain a better understanding of the mechanism of resistive switching, we studied the effect of top electrode deposition conditions on the stability of the low-resistance state. Our premise was that the formation of the Co oxide layer at the Co/BTO interface during deposition could lead to less effective screening of the depolarizing field and, hence, to unstable polarization, which in turn affects the retention of the resistive switching effect. Indeed, the Au/Co/BTO/LSMO/NGO heterostructure with the Co electrode deposited at a low base pressure (LBP) of 10^{-6} Torr exhibits a much more stable resistive switching effect with neither ON or OFF states showing any noticeable sign of relaxation (Figure 2b). A comparison of the time-dependent behavior of R_{OFF}/R_{ON} for two types of Au/Co/BTO/LSMO/NGO heterostructures with Co electrodes deposited at HBP and LBP is shown in Figure 2c. There is a clear difference in retention between for the two systems, which illustrates a critical role of the interface properties in resistive switching.

Memristive Behavior. In the LBP-processed Au/Co/BTO/LSMO/NGO heterostructures, both R_{ON} and R_{OFF} exhibit exponential thickness dependence, while R_{OFF}/R_{ON} is almost thickness independent—the resistive switching ratio is about

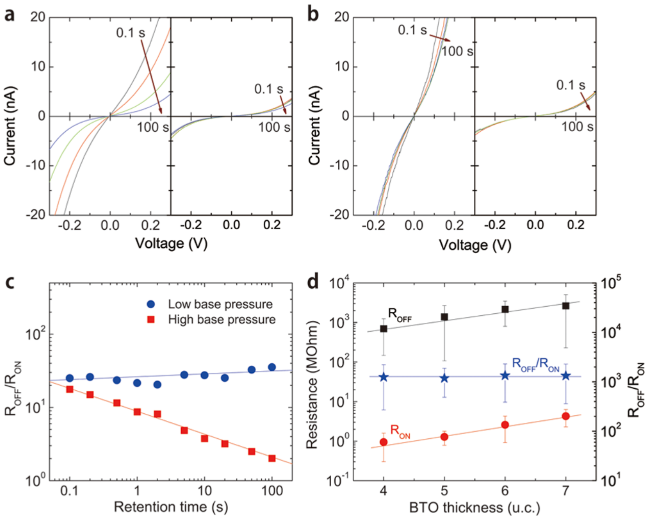

Figure 2. Temporal evolution of the $I-V$ curves measured in the 6-u.c.-thick $BaTiO_3$ junctions with the top Co electrode fabricated under (a) high base pressure and (b) low base pressure. The writing pulse voltage was fixed at ±6 V for both junctions. (c) Differential resistance ratio of OFF and ON states at 0 V of reading voltage sweep, R_{OFF}/R_{ON}, calculated from a and b. The solid lines represent power-law functions fitting the time-dependent behavior. (d) Differential resistance values at 0 V in the OFF and ON states (R_{OFF} and R_{ON}, respectively) and their ratio, R_{OFF}/R_{ON}, as a function of the $BaTiO_3$ barrier thickness in the LBP-processed Au/Co/BTO/LSMO/NGO junctions. The writing pulse was ±8 V and 1 ms for all junctions. The error bars represent the standard deviation measured in more than 20 junctions for each barrier thickness.

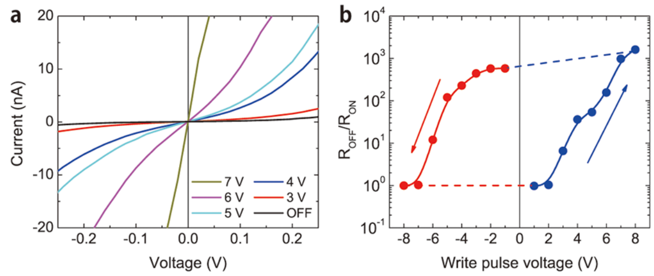

Figure 3. (a) Current−voltage ($I-V$) curves measured in the 4-u.c.-thick $BaTiO_3$ junctions after application of the 1 ms writing pulses with amplitudes varying in the range from 3 to 7 V. (b) R_{OFF}/R_{ON} as a function of the writing pulse amplitude (pulse width is 1 ms) for the 4-u.c.-thick $BaTiO_3$ junctions. The lines are the guides for eyes. The R_{OFF}/R_{ON} value gradually increases with positive writing voltage and gradually decreases with increase in the negative writing voltage. The R_{OFF} value is constant, and only the R_{ON} value varies with the writing voltage.

10^3 (10^5 %) for all of the measured ferroelectric barrier thicknesses (Figure 2d). This observation is in striking contrast to the behavior previously reported for FTJs where R_{OFF}/R_{ON} increased exponentially with ferroelectric barrier thickness,[8] consistent with theoretical predictions for the TER effect.[11] It is notable that the change in resistance due to switching between OFF and ON states is much larger than the respective change in resistance with the BTO thickness (Figure 2d). This fact suggests that the properties of the interface, rather than bulk properties of the ferroelectric barrier, are responsible for the observed resistive switching behavior.

Furthermore, we find that R_{OFF}/R_{ON} can be continuously tuned by several orders of magnitude by varying the writing voltage. Figure 3a shows a set of the $I-V$ curves measured for the Au/Co/BTO(4 u.c.)/LSMO/NGO heterostructure after it had been poled by voltage pulses of various amplitudes. In the OFF state, the resistance of the sample is about 1 GΩ. Applying a voltage pulse above the coercive voltage of 2 V switches the resistance state to the ON state. It can be seen that the higher writing pulse voltage results in higher current (or equivalently, in the lower resistance ON state). The R_{OFF}/R_{ON} value starts increasing as the writing bias exceeds 2 V, which corresponds to the positive coercive voltage of the BTO barrier (Figure 1d), and reaches 10^5 % at the writing bias of 8 V. Similarly, we found that the R_{OFF}/R_{ON} value increases with the writing pulse duration (see Supporting Information, Figure S1). For all values of the writing voltage, we observed strong retention of the resistive switching effect (see Supporting Information, Figure S4). The R_{OFF}/R_{ON} value starts decreasing with the change in the writing voltage polarity at −2 V, which corresponds to a negative coercive voltage of BTO. The difference between the ON and OFF resistance states eventually disappears at −8 V. Figure 3b summarizes the observed resistive behavior: it is tunable, reversible, and hysteretic.

Discussion. The tunable and nonvolatile nature of electrical resistance of the Au/Co/BTO/LSMO/NGO heterostructure allows us to treat it as a memristor. We use the term "memristor" in the same way it has been used in recent experimental papers on observation of the nonvolatile resistance state in the TiO_2 devices that can be changed electrically in an analogous manner.[13] Another reason to use this term is to distinguish the observed behavior from the TER effect in ultrathin ferroelectric films, which is realized in the form of bistable nonvolatile states with fixed resistance values.[10]

The voltage dependence of R_{OFF}/R_{ON}, which at the same time is independent of the thickness of the BTO barrier, implies a mechanism different from the mechanism of the TER effect in FTJs. Given that the resistive switching is very sensitive to the processing conditions of the top electrode, we suggest that charge migration and accumulation at the Co/BTO interface facilitated by its defect structure play an important role in the observed effect.[15,36] Note that Co tends to oxidize, which may lead to the formation of the passive dielectric layer with an increased density of oxygen vacancies at the top BTO interface in the LBP-processed Au/Co/BTO/LSMO/NGO heterostructures. It is suggested that the barrier height associated with this layer is higher in comparison with the barrier of BTO and provides significant contribution to the resistance behavior. Under a positive bias applied to the top electrode, oxygen vacancies accumulate at the CoO_x/BTO interface, effectively reducing the barrier height and decreasing the resistance of the ON state (Figure 4). Decrease in resistance with the writing pulse amplitude and duration is consistent with this mechanism. Enhanced retention of the resistive switching in the LBP-processed Au/Co/BTO/LSMO/NGO heterostructures can be explained by more effective domain pinning by interface defects. A negative bias induces a dissipation of accumulated charges at the interface and/or a reduction of Co oxide at the interface, switching the heterostructure into the high-resistance state.

The importance of the interface can be also invoked from the fitting of the measured conductance $G(V)$ as function of probe voltage V using the Brinkman−Dynes−Rowell (BDR) model for tunneling.[37] Figure 5 shows the normalized conductance curve $G(V)/G(0)$ (where $G(0)$ is conductance at zero bias) for

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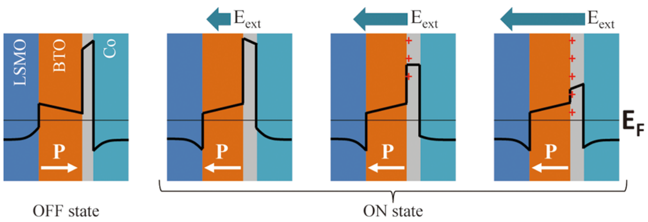

Figure 4. Schematic illustration of the energy barrier diagrams for the OFF and ON states as a function on the external electric field E_{ext}. The gray layer between the Co and BTO layers is the passive dielectric layer of CoO_x.

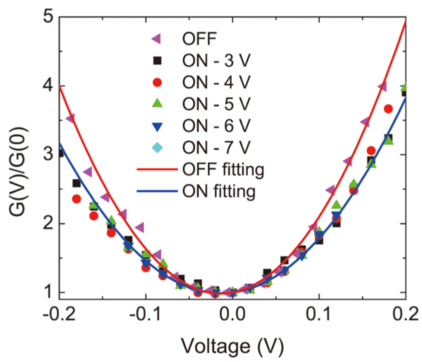

Figure 5. Conductance curves $G(V)/G(0)$ measured in the 4-u.c.-thick $BaTiO_3$ junction after application of the writing pulses with the various amplitudes.

various ON states generated by writing pulses of various amplitudes. (Conductance values were obtained by differentiation of the $I-V$ curves in Figure 3a.) It is seen that for all resistance states, $G(V)/G(0)$ is well-described by the parabolic curves, which is one of the indications of quantum tunneling.[37] Interestingly, all $G(V)/G(0)$ data points for the ON states fit a single curve with some small deviation for $G(V)/G(0)$ in the OFF state. This universal behavior is in contrast to the observed dramatic variations in the conductance $G(0)$ for different resistance states. Qualitatively, this behavior can be understood by the fact that $G(0)$ is largely determined by the interface resistance, whereas the voltage dependence is controlled by tunneling through the ferroelectric barrier. We note that the observed tunable resistance is different from the recently reported TER effect in similar FTJ heterostructures,[26] which is associated solely with the polarization switching in the ferroelectric barrier.

While the tunable resistive switching is determined mainly by the interface, the ferroelectric layer still plays an important role in the resistive behavior of FTM as an electrically switchable barrier for the tunneling current. This is evident from the fact that substituting the $BaTiO_3$ layer with the $SrTiO_3$ layer of the same thickness results in almost complete annihilation of the resistive switching effect (see Supporting Information, Figure S2). Also, an onset of the resistive switching at 2 V (Figure 3b) coincides with the coercive field of the BTO film (Figure 1d),[38] which suggests that polarization in BTO affects the charge accumulation at the interface and determines the hysteretic nature of the resistive switching effect. Specifically, the negative bound polarization charges at Co/BTO interface facilitate accumulation of oxygen vacancies resulting in the reduced energy barrier of the interface and lowering the resistance of the ON state as shown in Figure 4.

In summary, we have demonstrated a ferroelectric tunnel memristor, which exhibits tunable, nonvolatile, hysteretic resistance switching behavior with the OFF/ON resistance ratio reaching 10^5 %. Tunable resistive switching is attributed to the field-induced charge redistribution at the ferroelectric–electrode interface resulting in the modulation of the interface barrier height. A large value of the observed effect, its long-time retention, and the robustness of the resistance state against the read-out process make the ferroelectric tunnel memristor a promising device concept for next-generation of nonvolatile memories and logic neuromorphic circuits.

Materials and Methods. *Sample Preparation.* To achieve a coherent oxide multilayer system, a low miscut (<0.1°) $NdGaO_3$ (110) substrate was treated by a modified buffered HF etch and annealed in oxygen atmosphere at 1050 °C for 12 h to create an atomically smooth surface with single unit cell height steps. Epitaxial single-crystalline $La_{2/3}Sr_{1/3}MnO_3$ films and $BaTiO_3$ films have been grown using a multitarget pulsed laser deposition system. The layer-by-layer growth and the $BaTiO_3$ thickness were confirmed with in situ high-pressure reflection high-energy electron diffraction monitoring. The substrate growth temperature was maintained at 750 °C. The top Au(10 m)/Co(10 nm) electrodes of 5 μm in diameter have been fabricated ex-situ by lift-off and sputtering followed by photolithographic patterning through image reversal lithography. After evacuating the chamber down to base pressure of 10^{-4} Torr or 10^{-6} Torr, Co was sputtered at 10 mTorr, and then, without braking vacuum, the Au capping layer was sputtered at 7 mTorr. The sputtering power was 35 W. Different base pressures of 10^{-4} Torr or 10^{-6} Torr have been used to study the effect of top electrode processing conditions on Co oxidation.

PFM and C-AFM Measurements. During PFM and C-AFM measurements, the driving voltage was applied to the top electrode. A typical frequency range of a modulation voltage during resonance-enhanced PFM studies was ~350 kHz with amplitude of 0.4 V (peak-to-peak). Conductive Pt/Ti-coated and B-doped diamond-coated silicon cantilevers were used for PFM and C-AFM measurements, respectively. Resistance states have been generated by applying square writing voltage pulses with variable duration (from 1 ms up to 10 s) and amplitude (from −8 V up to 8 V). A nondestructive read-out of the resistance states is subsequently performed by measuring the $I-V$ curves using a smaller voltage range (from −0.3 V up to 0.3 V). The $I-V$ curves were obtained by the application of a triangular voltage sweep after application of a rectangular writing pulse. A typical pulse train used for $I-V$ measurements is shown in Supporting Information, Figure S3. The retention of the resistive switching effect was investigated by acquiring the $I-V$ curves at various time intervals after application of the writing pulse. The reproducibility of the electronic properties has tested by measuring more than 50 FTJs for each BTO layer thickness. To obtain the R_{OFF} and R_{ON} values, we took differential resistance from the slope of $I-V$ curves at 0 V of the triangular voltage sweep because the current of the OFF state is extremely low around 0 V. The time required for the acquisition of a single $I-V$ curve was 200 ms.

■ ASSOCIATED CONTENT

Supporting Information

Writing pulse duration dependence of memristive resistive switching behavior, comparison of resistive switching behavior of the junction with $BaTiO_3$ and $SrTiO_3$ barriers, resistance measurements, and retention behaviors of various resistance states. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ REFERENCES

(1) Waser, R.; Aono, M. Nanoionics-based resistive switching memories. *Nat. Mater.* **2007**, *6*, 833−840.
(2) Rossel, C.; Meijer, G. I.; Bremaud, D.; Widmer, D. Electrical current distribution across a metal-insulator-metal structure during bistable switching. *J. Appl. Phys.* **2001**, *90*, 2892−2898.
(3) Sawa, A.; Fujii, T.; Kawasaki, M.; Tokura, Y. Hysteretic current-voltage characteristics and resistance switching at a rectifying Ti/$Pr_{0.7}Ca_{0.3}MnO_3$ interface. *Appl. Phys. Lett.* **2004**, *85*, 4073−4075.
(4) Chudnovskii, F. A.; Odynets, L. L.; Pergament, A. L.; Stefanovich, G. B. Electroforming and switching in oxides of transition metals: The role of metal-insulator transition in the switching mechanism. *J. Solid State Chem.* **1996**, *122*, 95−99.
(5) Szot, K.; Dittmann, R.; Speier, W.; Waser, R. Nanoscale resistive switching in $SrTiO_3$ thin films. *Phys. Status Solidi* **2007**, *1*, R86−R88.
(6) Szot, K.; Speier, W.; Bihlmayer, G.; Waser, R. Switching the electrical resistance of individual dislocations in single-crystalline $SrTiO_3$. *Nat. Mater.* **2006**, *5*, 312−320.
(7) Tsui, S.; Baikalov, A.; Cmaidalka, J.; Sun, Y. Y.; Wang, Y. Q.; Xue, Y. Y.; Chu, C. W.; Chen, L.; Jacobson, A. J. Field-induced resistive switching in metal-oxide interfaces. *Appl. Phys. Lett.* **2004**, *85*, 317−319.
(8) Garcia, V.; Fusil, S.; Bouzehouane, K.; Enouz-Vedrenne, S.; Mather, N. D.; Barthelemy, A.; Bibes, M. Giant tunnel electroresistance for non-destructive readout of ferroelectric states. *Nature* **2009**, *460*, 81−84.
(9) Maksymovych, P.; Jesse, S.; Yu, P.; Ramesh, R.; Baddorf, A. P.; Kalinin, S. V. Polarization control of electron tunneling into ferroelectric surfaces. *Science* **2009**, *324*, 1421−1425.
(10) Gruverman, A.; Wu, D.; Lu, H.; Wang, Y.; Jang, H. W.; Folkman, C. M.; Zhuravlev, M. Y.; Felker, D.; Rzchowski, M.; Eom, C.-B.; Tsymbal, E. Y. Tunneling electroresistance effect in ferroelectric tunnel junctions at the nanoscale. *Nano Lett.* **2009**, *9*, 3539−3543.
(11) Zhuravlev, M. Y.; Sabirianov, R. F.; Jaswal, S. S.; Tsymbal, E. Y. Giant electroresistance in ferroelectric tunnel junctions. *Phys. Rev. Lett.* **2005**, *94*, 246802.
(12) Chua, L. O. Memristor, The missing circuit element. *IEEE Trans. Circuit Theory* **1971**, *18*, 507−519.
(13) Strukov, D. B.; Snider, G. S.; Stewart, D. R.; Williams, R. S. The missing memristor found. *Nature* **2008**, *453*, 80−83.
(14) Ha, S. D.; Ramanathan, S. Adaptive oxide electronics: A review. *J. Appl. Phys.* **2011**, *110*, 071101.
(15) Waser, R.; Dittmann, R.; Staikov, G.; Szot, K. Redox-based resistive switching memories − Nanoionic mechanisms, prospects, and challenges. *Adv. Mater.* **2009**, *21*, 2632−2663.
(16) Chua, L. Resistance switching memories are memristors. *Appl. Phys. A: Mater. Sci. Process.* **2011**, *102*, 765−783.
(17) Krzysteczko, P.; Münchenberger, J.; Schäfers, M.; Reiss, G.; Thomas, A. Memristive magnetic tunnel junction as a nanoscopic synapse-neuron system. *Adv. Mater.* **2012**, *24*, 762−766.
(18) Tsymbal, E. Y.; Kohlstedt, H. Tunneling Across a Ferroelectric. *Science* **2006**, *313*, 181−183.
(19) Tsymbal, E. Y.; Gruverman, A.; Garcia, V.; Bibes, M.; Barthélémy, A. Ferroelectric and multiferroic tunnel junctions. *MRS Bull.* **2012**, *37*, 138−143.
(20) Tybell, T.; Ahn, C. H.; Triscone, J.-M. Ferroelectricity in thin perovskite films. *Appl. Phys. Lett.* **1999**, *75*, 856−858.
(21) Lichtensteiger, C.; Triscone, J.-M.; Junquera, J.; Ghosez, P. Ferroelectricity and tetragonality in ultra-thin $PbTiO_3$ films. *Phys. Rev. Lett.* **2005**, *94*, 047603.
(22) Tenne, D. A.; Bruchhausen, A.; Lanzillotti-Kimura, N. D.; Fainstein, A.; Katiyar, R. S.; Cantarero, A.; Soukiassian, A.; Vaithyanathan, V.; Haeni, J. H.; Tian, W.; Schlom, D. G.; Choi, K. J.; Kim, D. M.; Eom, C. B.; Sun, H. P.; Pan, X. Q.; Li, Y. L.; Chen, L. Q.; Jia, Q. X.; Nakhmanson, S. M.; Rabe, K. M.; Xi, X. X. Probing nanoscale ferroelectricity by ultraviolet Raman spectroscopy. *Science* **2006**, *313*, 1614−1616.
(23) Jia, C. L.; Nagarajan, V.; He, J. Q.; Houben, L.; Zhao, T.; Ramesh, R.; Urban, K.; Waser, R. Unit-cell scale mapping of ferroelectricity and tetragonality in epitaxial ultra-thin ferroelectric films. *Nat. Mater.* **2007**, *6*, 64−69.
(24) Crassous, A.; Garcia, V.; Bouzehouane, K.; Fusil, S.; Vlooswijk, A. H. G.; Rispens, G.; Noheda, B.; Bibes, B.; Barthelemy, A. Giant tunnel electroresistance with $PbTiO_3$ ferroelectric tunnel barriers. *Appl. Phys. Lett.* **2010**, *96*, 042901.
(25) Pantel, D.; Goetze, S.; Hesse, D.; Alexe, M. Room-temperature ferroelectric resistive switching in ultrathin $Pb(Zr_{0.2}Ti_{0.8})O_3$ Films. *ACS Nano* **2011**, *5*, 6032−6038.
(26) Chanthbouala, A.; Crassous, A.; Garcia, V.; Bouzehouane, K.; Fusil, S.; Moya, X.; Allibe, J.; Dlubak, B.; Grollier, J.; Xavier, S.; Deranlot, C.; Moshar, A.; Proksch, R.; Mathur, N. D.; Bibes, M.; Barthélémy, A. Solid-state memories based on ferroelectric tunnel junctions. *Nat. Nanotechnol.* **2012**, *7*, 101−104.
(27) Kohlstedt, H.; Pertsev, N. A.; Rodriguez Contreras, J.; Waser, R. Theoretical current-voltage characteristics of ferroelectric tunnel junctions. *Phys. Rev. B* **2005**, *72*, 125341.
(28) Velev, J. P.; Duan, C.-G.; Belashchenko, K. D.; Jaswal, S. S.; Tsymbal, E. Y. Effect of ferroelectricity on electron transport in Pt/$BaTiO_3$/Pt tunnel junctions. *Phys. Rev. Lett.* **2007**, *98*, 137201.
(29) Velev, J. P.; Duan, C.-G.; Burton, J. D.; Smogunov, A.; Niranjan, M. K.; Tosatti, E.; Jaswal, S. S.; Tsymbal, E. Y. Magnetic Tunnel Junctions with Ferroelectric Barriers: Prediction of Four Resistance States from First Principles. *Nano Lett.* **2009**, *9*, 427−432.
(30) Choi, K. J.; Biegalski, M.; Li, Y. L.; Sharan, A.; Schubert, J.; Uecker, R.; Reiche, P.; Chen, Y. B.; Pan, X. Q.; Gopalan, V.; Chen, L.-Q.; Schlom, D. G.; Eom, C. B. Enhancement of ferroelectricity in strained $BaTiO_3$ thin films. *Science* **2004**, *306*, 1005.
(31) Kim, D. J.; Jo, J. Y.; Kim, Y. S.; Chang, Y. J.; Lee, J. S.; Yoon, J.-G.; Song, T. K.; Noh, T. W. Polarization relaxation induced by a depolarization field in ultrathin ferroelectric $BaTiO_3$ capacitors. *Phys. Rev. Lett.* **2005**, *95*, 237602.
(32) Dawber, M.; Chandra, P.; Littlewood, P. B.; Scott, J. F. Depolarization corrections to the coercive field in thin-film ferroelectrics. *J. Phys.: Condens. Matter* **2003**, *15*, L393−L398.
(33) Junquera, J.; Ghosez, Ph. Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature* **2003**, *422*, 506−509.
(34) Lu, H.; Liu, X.; Burton, J. D.; Bark, C.-W.; Wang, Y.; Zhang, Y.; Kim, D. J.; Stamm, A.; Lukashev, P.; Felker, D. A.; Folkman, C. M.; Gao, P.; Rzchowski, M. S.; Pan, X. Q.; Eom, C.-B.; Tsymbal, E. Y.; Gruverman, A. Enhancement of ferroelectric polarization stability by interface engineering. *Adv. Mater.* **2012**, *24*, 1209−1216.
(35) Nagarajan, V.; Junquera, J.; He, J. Q.; Jia, C. L.; Waser, R.; Lee, K.; Kim, Y. K.; Baik, S.; Zhao, T.; Ramesh, R.; Ghosez, Ph.; Rabe, K. M. Scaling of structure and electrical properties in ultrathin epitaxial ferroelectric heterostructures. *J. Appl. Phys.* **2006**, *100*, 051609.
(36) Yang, J. J.; Pickett, M. D.; Li, X.; Ohlberg, D. A. A.; Stewart, D. R.; Williams, R. S. Memristive switching mechanism for metal/oxide/metal nanodevices. *Nat. Nanotechnol.* **2008**, *3*, 429−433.
(37) Brinkman, W. F.; Dynes, R. C.; Rowell, J. M. Tunneling conductance of asymmetrical barriers. *J. Appl. Phys.* **1970**, *41*, 1915−1921.

(38) Given that the R_{OFF}/R_{ON} value keeps increasing with increase in the writing bias (up to 8 V which is well above the voltage when polarization is completely saturated), we can rule out the gradual change in the switched polarization volume as a reason behind the observed tunable resistive switching effect.

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