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Mechanically-Induced Resistive Switching in Ferroelectric Tunnel Junctions

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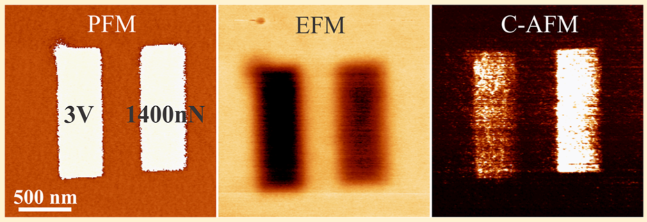

ABSTRACT: Recent advances in atomic-precision processing of oxide ferroelectrics—materials with a stable polarization that can be switched by an external electric field—have generated considerable interest due to rich physics associated with their fundamental properties and high potential for application in devices with enhanced functionality. One of the particularly promising phenomena is the tunneling electroresistance (TER) effect—polarization-dependent bistable resistance behavior of ferroelectric tunnel junctions (FTJ). Conventionally, the application of an electric field above the coercive field of the ferroelectric barrier is required to observe this phenomenon. Here, we report a mechanically induced TER effect in ultrathin ferroelectric films of $BaTiO_3$ facilitated by a large strain gradient induced by a tip of a scanning probe microscope (SPM). The obtained results represent a new paradigm for voltage-free control of electronic properties of nanoscale ferroelectrics and, more generally, complex oxide materials.

KEYWORDS: *Resistive switching, flexoelectric effect, ferroelectric, tunnel junction*

Most of the nanoscale studies of the resistive switching phenomena including the TER effect[1] are based on electrical control of polarization using scanning probe microscopy (SPM).[2−8] For experiments involving electrical poling by an SPM tip in ambient environment, there is always a concern that electrically induced changes in surface conditions, for example, due to redox chemical reactions or charge deposition, may significantly affect resistive switching measurements. Charge injection during switching pulse application may also take place[9] affecting the potential profile inside the ferroelectric barrier. This has raised questions regarding whether this surface modification is in fact the primary mechanism for the reported resistive switching effect as opposed to the mechanism based on the polarization-related change in energy barrier between top and bottom electrodes. For example, redox reactions and associated band bending at the interfaces have been recently proposed as possible mechanisms for the TER effect in ultrathin ferroelectric films.[10] The main purpose of this paper is to demonstrate that the nonvolatile TER effect in ultrathin (several nanometer-thick) ferroelectric films can be induced by purely mechanical means and to show that this effect can be realized without any involvement of surface electrochemical processes commonly expected in SPM poling of oxide films. A comparison between electrically and mechanically induced TER effects allows the assessment of the surface charge influence on resistive switching.

A mechanically induced TER effect is facilitated by the recently discovered flexoelectric switching of ferroelectric polarization[11] resulting from application of a local mechanical load to an ultrathin ferroelectric film via an SPM tip. It has been found that the tip-generated strain gradient in the film can produce a flexoelectric field that is strong enough to switch polarization in a way similar to an external electric field. To explore the mechanically induced TER effect, we have used epitaxial single-crystalline ultrathin (12-unit-cell-thick or ∼4.8 nm) $BaTiO_3$ films grown by pulsed laser deposition on atomically smooth TiO_2-terminated (001)-$SrTiO_3$ substrate with $SrRuO_3$ as a bottom electrode.[12,13] (Details on sample preparation can be found elsewhere[14]). It has been shown previously[14] that compressively strained $BaTiO_3$ films on $SrTiO_3$ substrates possess only out-of-plain polarization. Polarization imaging and local switching spectroscopy have been performed using a resonant-enhanced piezoresponse force microscopy (PFM) mode. Nanoscale electrical transport measurements have been performed in the conductive atomic force microscopy (C-AFM) mode.

Preliminary testing of the samples by PFM shows that the as-grown $BaTiO_3$ films are in a single-domain state with the upward (away from the substrate) polarization direction. These initial conditions turn out to be suitable for our studies as the tip-induced mechanical load can switch the polarization only from upward to downward direction.[11] Figure 1 parts a and b show the PFM amplitude and phase images, respectively, of two downward-oriented domains written in as-grown film: the left domain has been written with an electrically biased tip (+3 V)

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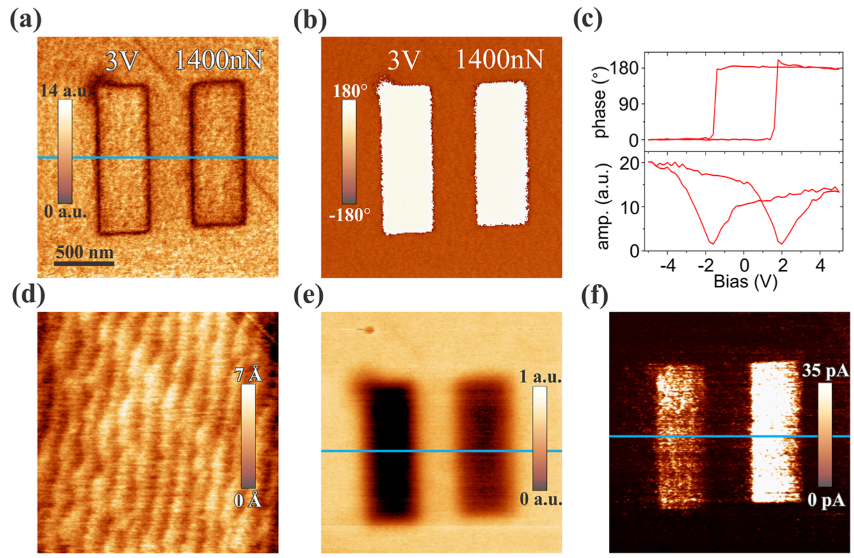

Figure 1. SPM data illustrating the mechanically and electrically induced TER effects. (a, b) PFM amplitude (a) and phase (b) images of the 4.8-nm-thick $BaTiO_3$ film after the generation of the downward-oriented domains by electrical poling (left) and mechanical loading force (right). A saturated amplitude signal indicates fully polarized states. (c) Local PFM hysteresis loops measured in the same $BaTiO_3$ film (top: phase signal, bottom: amplitude signal). (d) Topographic image of the same area acquired after mechanical writing showing that the film surface was not affected by the writing process. (e) EFM image taken at the same location as the PFM images. The EFM image was acquired with a dc read voltage of +2 V. Regions of dark contrast represent downward oriented domains and correspond to a positive surface screening charge. (f) Tunneling current map acquired in the C-AFM mode with a dc read bias 0.3 V at the same location as the PFM and EFM images. The bright contrast corresponds to a higher conductivity. The scan size is the same for all SPM images.

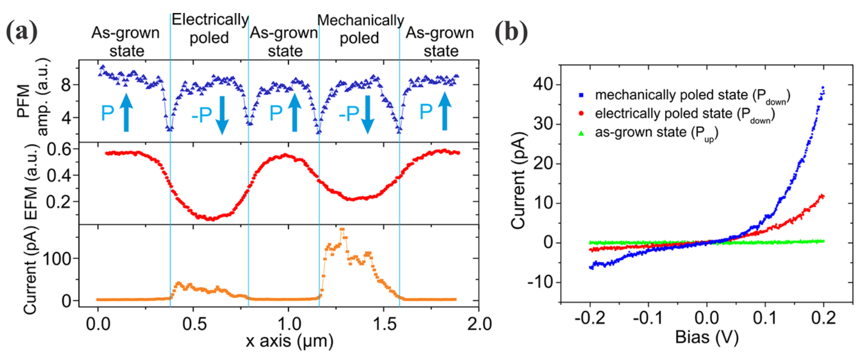

Figure 2. Comparative analysis of the mechanically and electrically induced TER effects. (a) Cross sections through the lines shown in the PFM amplitude, EFM, and current maps (Figures 1a, e, and f, respectively). (b) Local $I-V$ curves measured for the as-grown film area with upward polarization (green), electrically downward-switched domain (red), and mechanically downward-switched domain (blue).

and a load of 20 nN (which is a typical value for the PFM operation mode), whereas the right domain has been produced by scanning the film surface with a grounded tip while applying a mechanical load of 1400 nN. (Although it is difficult to precisely convert the applied mechanical load to equivalent potential, it had been shown earlier[11] that the load of 1000 nN generated a voltage comparable with the coercive bias; thus it is natural to expect complete polarization reversal at a higher load of 1400 nN). After writing, PFM imaging of the resulting domain pattern has been carried out with the same tip at a contact loading force of 20 nN. Both domains exhibit a saturated PFM amplitude signal and 180° phase inversion, indicating a fully switched single domain state. Switchable polarization behavior is confirmed by the local PFM spectroscopic measurements (Figure 1c), which show rather symmetric piezoelectric hysteresis loops with a coercive voltage of ~2.0 V (or coercive field of ~4 MV/cm). The topographic image of the film surface acquired after writing (Figure 1d) does not show any sign of plastic surface deformation. No PFM signal relaxation several days after mechanical writing has been detected, suggesting strong polarization retention. A noteworthy feature of the mechanically written domain is that it is electrically erasable.[11]

Additional analysis of the written domain pattern has been performed using electrostatic force microscopy (EFM; Figure 1d). Note that EFM is sensitive to the presence of the surface charge and thus can be used to assess the difference between surface charge density of electrically and mechanically produced domains. In the EFM imaging conditions used in our study, the dark contrast of the written domains corresponds to a positive surface charge. This is opposite to the negative bound polarization charge of the domains, suggesting that the signal detected by EFM is due to a surface charge that screens polarization of the downward-oriented domains. There is a clear disparity of the EFM signal between electrically written and mechanically written domains. A much darker contrast for the electrically produced domain indicates a higher screening charge density. This effect could be due to the field-induced redox reaction resulting in deposition of extra charge in addition to the adsorption of ionic species from ambient.[15]

The resistive switching behavior has been studied by simultaneous imaging of the electrically and mechanically written domains in the C-AFM mode. Figure 1e shows a current map where contrast variations correspond to changes in conductivity. It can be seen that both electrically and mechanically poled domains with downward polarization have higher conductivity in comparison to the as-grown $BaTiO_3$ film with upward polarization, which is indicative of the resistive switching effect. As no plastic surface deformation due to the tip-induced pressure has been observed, we can exclude a change in film thickness as a root cause for the observed TER. It can be concluded then that it is the change in the energy barrier height due to polarization reversal that lead to the electroresistance effect.[16] Also, the fact that the TER effect can be induced by mechanical pressure without any electrical bias application indicates that the electrochemical surface modification or charge injection as the main mechanisms of resistive switching in ferroelectrics can be ruled out.

Figure 2a summarizes the obtained results in the form of cross-section analysis of the PFM amplitude and EFM and C-AFM images: there is no discernible difference between the PFM images of electrically and mechanically written domains, while the EFM signal shows a clear difference, indicating a surface charge modification as a result of electric voltage application. As for the resistance change, it is interesting that mechanically induced TER is larger than the electrically induced TER. This observation is supported by local spectroscopic measurements (Figure 2b): the resistance changes by 2300% for electrically poled domain versus 7300% resistance change for the mechanically written domain. Note that similar results have been obtained for mechanical writing carried out under open and short circuit boundary conditions using insulating and grounded conductive tips, respectively. It should be also noted that scanning the surface with a tip under an increased load may result in partial removal of surface adsorbate layer, thereby affecting the comparison between conductivity of mechanically and electrically written domains. To address this issue, we first mechanically wrote a downward domain and then electrically switched it upward. This procedure created a domain with the same polarization as in the virgin film but with a cleaner surface. After that mechanical and electrical writing of the downward domains has been performed again as described above. It has been found that in this case mechanically written domain still exhibits a significantly stronger TER than the electrically poled domain, although the difference becomes smaller.

Our earlier studies[6] demonstrated that the significant enhancement of conductance with reversal of ferroelectric polarization from upward to downward state is largely due to the electrostatic modulation of the potential step at the tip/BTO interface resulting in the change of the energy barrier across the $BaTiO_3$ layer. Figure 3 illustrates the band alignment associated with polarization reversal. It can be seen that switching of the polarization direction toward the substrate pushes the conduction band up with respect to the Fermi energy thereby *increasing* conductance (Figures 3a and b). This behavior is due to the decay constant associated with the evanescent state responsible for tunneling in $BaTiO_3$, which increases with energy.[17,18] A difference in conductance between electrically and mechanically written downward domains can be understood from the following consideration. Ferroelectric polarization screening of as-grown BTO film is realized through adsorption of charged species and dipolar molecules on the ferroelectric surface after it has been exposed to air.[19] Ferroelectric polarization reversal from upward to downward alters the screening charge on the surface of the newly written domains as confirmed by our EFM measurements. The higher screening charge density in the case of electrically written domain implies that there is a positive extra charge injected into the adsorbate layer, which likely "overscreens" the polarization charge. This extra charge may result from redox reactions driven by the electrical bias applied to the SPM tip. Accumulation of the additional positive charge on the ferroelectric surface pushes the conduction band of $BaTiO_3$ down altering the band alignment as shown in Figure 3c. This results in the reduced conductance of the electrically written domains in comparison with the domain produced by mechanical means.

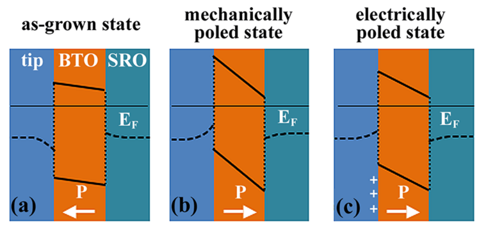

Figure 3. Schematic band diagrams of the FTJ formed by the $BaTiO_3$ (BTO) film sandwiched between the bottom $SrRuO_3$ (SRO) electrode and a conductive SPM tip: (a) for the as-grown upward polarization (toward the tip), (b,c) for the mechanically and electrically poled downward polarization (toward the bottom electrode), respectively. The dashed lines in the electrodes and tip regions indicate schematically a variation in the electrostatic potential. For the downward polarization the Fermi energy (solid horizontal line) lies farther from the conduction band of $BaTiO_3$, resulting in the enhanced conductance due to the decay constant increase with energy. Accumulation of an additional positive charge on the top surface when the polarization is switched electrically pushes the conduction band of $BaTiO_3$ down, resulting in the conductance decrease.

In summary, we have experimentally demonstrated a mechanically induced tunneling electroresistance effect in ultrathin ferroelectric films. This effect is facilitated by flexoelectric switching of polarization due to the strain gradient developed under the SPM tip pressed against the film surface. Strain-mediated voltage-free generation of a stable, fully reversible and reproducible TER effect represents an important breakthrough on both conceptual and practical levels. From the conceptual point of view, it demonstrates mechanical control of electronic properties of ferroelectrics, which can be extended to other functional oxide materials. From the practical point of view, it opens the possibility for application in low-energy archive data storage devices with mechanical writing and electrical reading of data.

Samples and Methods. Epitaxial single-crystalline $BaTiO_3$ films with the thickness of 12 u.c. have been grown using multitarget pulsed laser deposition system on atomically smooth TiO_2-terminated (001)-$SrTiO_3$ substrate with epitaxial $SrRuO_3$ as a bottom electrode. The layer-by-layer growth and the $BaTiO_3$ thickness have been confirmed with in situ high-pressure reflection high-energy electron diffraction monitoring. Before deposition, low angle miscut (<0.1°) $SrTiO_3$ substrates were etched using buffered HF acid for 60 s to produce Ti-termination and then were annealed in oxygen at 1000 °C for 6 h to create atomically smooth surfaces with single-unit-cell-

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height steps. During deposition of all of the layers, the substrate temperature was maintained at 680 °C with chamber oxygen pressure kept at 90 mTorr. The samples have been annealed at growth temperature and 1 atm oxygen pressure for 30 min and then cooled down to room temperature. The resulting surface of the $BaTiO_3$ layer was atomically smooth with single unit cell height steps.

PFM measurements have been carried out using a commercial atomic force microscope (MFP-3D, Asylum Research). Conductive cantilevers (DPE18/Pt, Mikromasch) have been used in PFM measurements. PFM hysteresis loops were obtained at fixed locations on the $BaTiO_3$ film as a function of a dc switching pulses (25 ms) superimposed on ac modulation bias with amplitude of 0.8 $V_{p\text{-}p}$ at 320 kHz. Tip contact forces have been calibrated by measuring force–distance curves. Local current–voltage (I–V) characteristics were measured by positioning a conductive diamond tip (CDT-NCHR, Nanosensors) at a selected point on the film surface and by sweeping a dc voltage. Current maps were obtained simultaneously with the topographic data by scanning the surface with the tip held under a constant dc bias of 0.3 V and measuring current at each pixel point of the scanned area. The typical imaging scan rate was 0.8 Hz. All of the measurements have been performed at room temperature.

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Notes

The authors declare no competing financial interest.

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