Supporting Information

Observation of strong polarization enhancement in ferroelectric tunnel junctions

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Film growth: BiFeO₃ and La_{0.7}Sr_{0.3}MnO₃ films are synthesized by reactive oxide molecular-beam epitaxy in a Veeco GEN10 MBE using distilled ozone as the oxidant species as described previously^{28,29}. The La_{0.7}Sr_{0.3}MnO₃ films are grown at 700 °C using 10% ozone at a background pressure of 9x10⁻⁷ Torr. Films are grown by alternating co-depositing lanthanum and strontium with depositing manganese by shuttering effusion cells. The La/Sr ratio is determined from RHEED oscillations during growth of LaMnO₃ and SrMnO₃ and the A-site to B-cite ratio is determined from RHEED oscillations during growth of a calibration La_{0.7}Sr_{0.3}MnO₃ film.

After electrode growth, the films are cooled in the 10% ozone environment then transferred and stored in vacuum. The substrate and electrode are then transferred back into the growth chamber and heated in a distilled ozone environment. BiFeO₃ films are subsequently grown at a substrate temperature between 650 °C and 680 °C in a background pressure of 5×10^{-6} Torr (mmHg) of distilled O₃ (estimated to be 80% pure O₃). Bismuth and iron are codeposited with an Fe flux of 1.6×10^{13} atoms/(cm² s) determined from x-ray reflectometry thickness analysis of a calibration film and an estimated Bi flux of 8×10^{13} atoms/(cm² s) determined by quartz crystal monitor. Substrate temperatures are measured by an optical pyrometer with a measurement wavelength of 980 nm focused on a platinum layer deposited on the backside of the substrate. The film surface is periodically monitored by RHEED during growth, and the films are cooled in the distilled ozone environment after growth.

Transmission electron microscopy (TEM) and Piezoelectric force microscopy (PFM): TEM specimens were prepared by mechanical polishing followed by argon ion milling. STEM HAADF imaging and EELS experiments were carried out on Nion UltraSTEM 200 equipped with C3/C5 corrector and high-energy resolution monochromated EELS system (HERMES) in Irvine Materials Research Institute at the University of California, Irvine. The microscope was operated at 100 kV with convergence semi-angle of 30 mrad and with a beam current of ~100pA. The inner and outer semi-angles of the ADF detector were approximately 70 and 200 mrad, respectively. A dispersion of 0.3 eV/channel was used and the dwell time was 0.5 s/pixel for acquisition of EELS spectrum. The pre-edge background in each EELS spectrum was removed by power-law function in commercial software package DigitalMicrograph. PFM experiments were carried out on a commercial Asylum Research MFP-3D scanning probe microscope by using Nanosensors PPP-EFM cantilevers..

Phase-field simulations: The phase-field simulation was performed using a FORTRAN program, which evolves the spatial polarization with respect to time, that follows the time-dependent Ginzburg-Landau equation:

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)}, i = 1,2,3$$

in which P is polarization, the primary order parameter, F is the total free energy, and L is a kinetic parameter related to domain wall mobility. The total free energy is a integral of the energy density from multiple contributions, including landau, elastic, electrostatic, and gradient energies.

$$F = \int_{V} [f_{Landau}(P_i) + f_{Elastic}(P_i, \epsilon_{ij}) + f_{Electric}(P_i, E_i) + f_{Gradient}(P_{i,j})] dV$$

We performed a 2D simulation in the x-z plane with a system size of 5 nm × 20 nm, where the thickness of the substrate was 5 nm and film was 10 nm. The landau, elastic, and electrostrictive coefficients used are listed in Table S1. The elastic boundary condition was chosen to be traction free on film surface, and zero displacement at the substrate (bottom of the simulation region). Since in experiment, there was no bottom electrode, we chose to use the open circuit electric boundary condition, for which the electric displacement was fixed at 0 at the film/substrate interface and film surface. We employed an isotropic gradient energy coefficient of $g_{11} = 0.6$ and an isotropic dielectric constant of $\epsilon_{ii} = 50$. Two groups of simulations were setup, one with initial polarization equals (0.5, 0.5, -0.5) C/m², and the other with initial polarization equals to (0.5, 0.5, 0.5) C/m². The interfacial oxygen deficient region was set to be 2nm thick, from the film/substrate interface to 2nm into the BFO thin film. For each group of simulations, we vary the defect charge amount from -1.3×10^9 C/m³ to -1.04×10^{10} C/m³ every -1.3×10^9 C/m³, and consider a corresponding positive charge layer at the interface in the bottom electrode region to keep the overall charge in the system to be zero.

Discussion on PFM results

In addition to STEM imaging, we also performed piezoelectric force microscopy (PFM) measurements on the 2.4-nm-thick and 10-nm-thick BiFeO₃ films. The characteristics of polarization structures in both films revealed by PFM in Fig. S7 are in good consistence with the results of STEM imaging. First, in the 2.4-nm-thick film (Fig. S7a), the amplitudes of the piezoresponse generated by a constant AC voltage applied at the PFM probe are different across three different domains (*i.e.*, an as-grown domain with polarization mostly pointing downward, a written domain with uniform downward polarization switched by a 4 V voltage on the probe, and a written domain with uniform upward polarization switched by a -4 V voltage on the probe). This indicates the polarization magnitudes of these three domains are different, since the out-of-plane piezoresponse is in principle proportional to the out-of-plane polarization strength. In particular, the polarization strength in the downward-polarized written domain is much larger than in the upward-polarized one, which matches our STEM observation in Fig. 4. And the downward polarization strength in the as-grown one is reduced compared to the written one, which suggests the as-grown downward-polarized domain may also contain nanoscale regions with polarization rotated up and to in-plane directions. In contrast, the amplitudes of the piezoresponse across two written domains with reversed polarization in the 10-nm-thick film are more symmetric (Fig. S7d), indicating their out-of-plane polarizations are more similar in strength.

Second, a comparison of the out-of-plane polarization strength in the 2.4-nm-thick and 10-nm-thick BiFeO₃ films can be made with the assumption of a simple relationship between the applied electric field (E_z) and the induced out-of-plane piezoelectric strain (u_z):

$$u_z \propto h E_z \varepsilon_{33} \varepsilon_0 Q_{11} P_z,$$

where *h* is the film thickness, P_z is the out-of-plane polarization strength, and ε_{33} and Q_{11} are the components of the dielectric and electrostrictive tensors, respectively⁹. This equation can be also be rewritten as:

$$\Delta u_z \propto V \varepsilon_{33} \varepsilon_0 Q_{11}(P_z(up) + P_z(down)),$$

where Δu_z is the change of u_z when the out-of-plane polarization is reversed, and V is the averaged applied voltage across the film thickness during the polarization switching. Since we applied same voltage sweeps (-5V to 5V) to reversibly switch the polarization in both films, the change of out-of-plane polarization strength (($P_z(up) + P_z(down)$)) in the two films can be directly compared through comparing Δu_z , which are 2.34 and 3.13 pm for the 2.4-nm-thick and 10-nm-thick films, as shown in Fig. S7c and f, respectively. Given that in the 2.4-nm-thick film the upward polarization is strongly attenuated (Fig. 4 and Fig. S7a), the measured Δu_z (2.34 pm) should be mostly induced by the downward polarization. In contrast, the measured Δu_z (3.13 pm) in the 10-nm-thick film is caused by both upward and downward polarization that are almost equal in strength. Therefore, the half of Δu_z (1.57 pm) should be corresponding the downward polarization strength in the 10-nm-thick film. We thus conclude the downward polarization strength in the 2.4-nm-thick film is considerably enhanced as compared to the 10-nm-thick film, according to PFM measurements.
 Table S1. Coefficients used in the phase-field simulation.

| Landau coefficient | Elastic constant | Electrostrictive coefficient |
|---|------------------------------------|---|
| a1= 8.78*10^5*(TEM-1103) (C ⁻² m ² N) | c11=3.02*10^11 (Nm ⁻²) | Q11=0.035 (C ⁻² m ⁴) |
| a11= 4.71*10^8 (C ⁻⁴ m ⁶ N) | c12=1.62*10^11 (Nm ⁻²) | Q12=-0.0175 (C ⁻² m ⁴) |
| a12= 5.74*10^8 (C ⁻⁴ m ⁶ N) | c44=6.8*10^10 (Nm ⁻²) | Q44=0.0403 (C ⁻² m ⁴) |



Figure S1. (a,b) Original (a) and smoothed (b) atomic-resolution energy dispersive x-ray spectroscopy (EDS) maps of element distribution across the BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ interface. (c) Corresponding HAADF STEM image. (d,e) Original (d) and smoothed (e) combined EDS maps.



Figure S2. EELS spectra for the BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ interface with downward polarization in the 10-nm-thick film, corresponding to the blue-colored analysis in Fig. 2i and j. The number here corresponds to the unit-cell number in the x-axis in Fig. 2i and j.



Figure S3. EELS spectra for the BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ interface with upward polarization in the 10-nm-thick film, corresponding to the red-colored analysis in Fig. 2i and j. The number here corresponds to the unit-cell number in the x-axis in Fig. 2i and j.



Figure S4. (a-c) A HAADF STEM image (a) of a downward polarized domain at the interface region of the same 10-nm-thick BiFeO₃ film and corresponding maps of $-D_{FB}$ vectors (b) and out-of-plane lattice parameter over in-plane lattice parameter ratios (c/a ratios) (c) overlaid on the same HAADF STEM image. (d-g) Changes of out-of-plane components of $-D_{FB}$ vectors ($|-D_{FB}|_z$) (d), c/a ratios (e), EELS Fe L₃/L₂ ratios (f), and integrated O K-edge intensities (g) across the BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ (BFO/LSMO) interface. The yellow dashed lines indicate the BFO/LSMO interface. At this interface, accumulation of oxygen vacancies is not observed, according to the EELS results. Correspondingly the polarization structures show different features as compared to Fig. 2



Figure S5. EELS spectra for the $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ interface with downward polarization in the 10-nm-thick film, corresponding to the analysis in Fig. S4f and g. The number here corresponds to the unit-cell number in the x-axis in Fig. S4f and g.



Figure S6. Atomic structures in a 5-nm-thick BiFeO₃ film. (a-c) A HAADF STEM image (a) of an upward polarized domain at the interface region and corresponding maps of $-D_{FB}$ vectors (b) and c/a ratios (c) overlaid on the same HAADF STEM image. (d-f) A HAADF STEM image (d) of a downward polarized domain at the interface region and corresponding maps of $-D_{FB}$ vectors (e) and c/a ratios (f) overlaid on the same HAADF STEM image. (g-h) Changes of out-of-plane components of $-D_{FB}$ vectors (g) and c/a ratios (h) across the BiFeO₃/La_{0.7}Sr_{0.3}MnO₃ (BFO/LSMO) interface. The yellow dashed lines indicate the BFO/LSMO interface.



Figure S7. PFM characterization of the 2.4-nm-thick and 10-nm-thick BiFeO₃ films. (a,b) Amplitude (a) and phase (b) images for as-grown, 4V-switched, and -4V-switched domains in the 2.4-nm-thick film, and corresponding line profiles. (c) PFM switching loops of the 2.4-nm-thick film. (d,e) Amplitude (d) and phase (e) images for 4V-switched and -4V-switched domains in the 10-nm-thick film, and corresponding line profiles. (f) PFM switching loops of the 10-nm-thick film.