Flexible polarization rotation at the ferroelectric/metal interface as a seed for domain nucleation

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Ferroelectric materials are promising candidates to serve as commercial memories because of their faster accessing time, lower energy consumption, and potentially lower cost. Recently, the realization of ultrahigh-density ferroelectric nanocapacitor arrays [1,2], at the Tbit in−2 level, makes this aim much closer to a practical application. However, its widespread application of low-dimensional ferroelectric heterostructures. Employing quantitative atom-resolved (scanning) transmission electron microscopy and first-principles calculations, we report that structural and chemical reconstruction universally lowers symmetry of the ferroelectric-metal interface. Irrespective of structural and strain mismatch, chemical termination and diffusion, polar catastrophe, and electrode type, the polarization screening is executed by a flexible polarization rotation at several-unit-cell-thick interfaces. By combining nanoscale and atomic-scale microscopy investigations, our ex situ electric-field biasing experiments reveal that the monoclinically distorted interfaces may act as seeds to nucleate new domains during the polarization switching process. These findings suggest that the long-standing fatigue issue is expected to be overcome by interface modification engineering at the monolayer scale.

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The absence of a realistic polarization screening scenario at the pivotal ferroelectric-metal interface impedes the widespread application of low-dimensional ferroelectric heterostructures. Employing quantitative atom-resolved (scanning) transmission electron microscopy and first-principles calculations, we report that structural and chemical reconstruction universally lowers symmetry of the ferroelectric-metal interface. Irrespective of structural and strain mismatch, chemical termination and diffusion, polar catastrophe, and electrode type, the polarization screening is executed by a flexible polarization rotation at several-unit-cell-thick interfaces. By combining nanoscale and atomic-scale microscopy investigations, our ex situ electric-field biasing experiments reveal that the monoclinically distorted interfaces may act as seeds to nucleate new domains during the polarization switching process. These findings suggest that the long-standing fatigue issue is expected to be overcome by interface modification engineering at the monolayer scale.

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As the PZT film is grown on a DyScO$_3$ substrate, tensile strain ($\sim$0.9%) leads to the formation of a ferroelastic $c/a$/$c$/$a$ domain array [29] (see Supplemental Material Fig. S1 [30]). In order to unravel the details of these mismatches, $[\bar{1}10]$$_T$/$[010]$$_O$ oriented ($x = 0.9$) PZT/SrRuO$_3$ specimens are prepared for the TEM study. Figure 1(c) shows an atomically resolved TEM image of a PZT/SrRuO$_3$ interface. As evidenced by the simulated image [the inset in Fig. 1(c)], all atomic columns are clearly resolved, in which the Pb-O1 shows a single column of Pb/O1 due to their small interatomic separation and exhibits a weak contrast at this sample thickness ($\sim$5.4 nm). The vertical shifts of the oxygen columns (red circles) in opposite directions with respect to the neighboring Zr/Ti columns (green circles) mark two domains in this image area: domain I, with larger downward shifts of O2, and domain II, with smaller upward shifts. These two domains form a tail-to-tail 180° charged domain wall (CDW) with the walls planes normal to the polarization directions and bridged by a unit-cell step in the middle region. Below domain II, the brighter atom columns well define that the interface is terminated by SrO-Zr/TiO$_2$ atomic planes. Furthermore, buckling of the O2-Zr/Ti atomic planes clearly displays the in-phase octahedral rotation of SrRuO$_3$ along the $[010]$$_O$ direction.

In order to unravel the polarization compensation mechanism, an image-simulation-based quantitative TEM study was performed to determine the atomic positions near the interface and the CDW [41]. By removing artifacts affecting the intensity peak positions in the experimental image, e.g., specimen tilting away from the Laue orientation, residual lens aberrations, and the interfacial element diffusion (see Supplemental Material Fig. S2 [30]), measurements of individual atomic shifts with picometer precision become possible.

Figure 2(a) shows the lattice parameter changes as a function of distance normal to the interface. Compared with the nearly constant pseudocubic ($p$) $a_p$ axis ($a_p = \sqrt{2}a_0/2$ for SrRuO$_3$ and $a_p \approx a_T$ for PZT), $\sim$0.3913 nm, pronounced changes are observed along the $c$-axis direction. Via a smooth reduction in domain I ($c = 0.4160$ nm, $c/a = 1.063$), the $c$ axis measured from Pb atoms (blue squares) steeply increases to 0.4246 nm ($c/a = 1.085$) near the CDW. A stepwise decrease is then observed in the middle of domain II ($c/a \approx 1.042$) and near the interface ($c/a = 1.025$). The $c$ axes measured from Zr/Ti atoms (pink squares) show smaller values, which diverge from the larger values determined from the Pb atoms. On the SrRuO$_3$ side, nevertheless, a reversed tendency
(\(c_{p,\text{Sr}} < c_{p,\text{Ru}}\)) is observed in \(~3\) pseudocubic unit cells near the interface.

These divergent behaviors, reflecting a rearrangement of atomic positions inside the unit cells, can be attributed to lattice responses to polarization screening at both interfaces. For the horizontal O2-Ru-O2 atomic planes of SrRuO3 [Fig. 1(c)], the in-phase octahedral rotation results in alternate up and down shifts of O2 atoms around the Ru positions. On approaching the interface, the displacements decrease in magnitude and penetrate into the PZT layer by 2 unit cells [Fig. 2(b)]. Meanwhile, the polar displacements of O2 atoms (\(\delta_{z_{\text{O2},\text{Zr/Ti}}}\)) in PZT also propagate into the SrRuO3 electrode by \(1\)–\(2\) pseudocubic unit cells. As a result of interface bonding [13,42] and polarization screening, the antiferrodistortive order then couples with the polar displacements of O2 atoms (\(\delta_{z_{\text{O2},\text{Zr/Ti}}}\)) in the SrRuO3 electrode.

The formation of the polar catastrophe, oxygen-octahedral rotation results in alternate up and down shifts of O2 atoms around the Ru positions. On approaching the interface, the displacements decrease in magnitude and penetrate into the PZT layer by 2 unit cells [Fig. 2(b)]. Meanwhile, the polar displacements of O2 atoms (\(\delta_{z_{\text{O2},\text{Zr/Ti}}}\)) in PZT also propagate into the SrRuO3 electrode by \(1\)–\(2\) pseudocubic unit cells. As a result of interface bonding [13,42] and polarization screening, the antiferrodistortive order then couples with the polar displacements of O2 atoms (\(\delta_{z_{\text{O2},\text{Zr/Ti}}}\)) in the SrRuO3 electrode.

FLEXIBLE POLARIZATION ROTATION AT THE … PHYSICAL REVIEW B 98, 020102(R) (2018)

FIG. 3. (a) Atomically resolved high-angle annular dark field (HAADF)-STEM image of the \((x = 0.9)\) PZT/SrRuO3 interface (arrow oroses) recorded along the \([100]_T\) direction. Atomic column types: Pb (yellow), Zr/Ti (green), Sr (dark yellow), Ru (blue). (b)-(e) EDS maps for Pb, Sr, Ti, and Ru, respectively. (f) Averaged atomic percentage profiles for the heavy atoms across the SrO-Zr/TiO2 terminated interface. (g) First-principles calculated \((\text{Pb}_{0.75}\text{Sr}_{0.25})\text{(Ti}_{0.75}\text{Ru}_{0.25})\text{O}_3\) supercell (space group \(Cm\)) viewed along the \([110]_T\) direction.

To quantify the interfacial chemical diffusion, atomic-resolution energy-dispersive x-ray spectroscopy (EDS) was performed on the \((x = 0.9)\) PZT/SrRuO3 interface areas [Fig. 3(a)]. For \(A\)-site elements, the Sr atom is found to diffuse strongly into the PZT layer over one atomic layer [Figs. 3(b) and 3(c)], while for \(B\)-site elements, the Ti atom reversely diffuses into the SrRuO3 electrode over one atomic layer [Figs. 3(d) and 3(e)]. The elemental profiles reveal the asymmetric chemical diffusion and the SrO-Zr/TiO2-plane terminated interface [Fig. 3(f)]. The composition of the first interfacial unit cell is approximately \((\text{Pb}_{0.2}\text{Sr}_{0.8})(\text{Zr}_{0.75}\text{Ti}_{0.25})\text{O}_3\) on the PZT side and \((\text{Sr}_{0.75}\text{Pb}_{0.25})(\text{Ru}_{0.5}\text{Ti}_{0.5})\text{O}_3\) on the SrRuO3 side.

These results highlight that, driven by structural and chemical reconstruction, the SrO-Zr/TiO2 terminated PZT/SrRuO3 interface is characteristic of monoclinic lattice distortion and flexible polarization rotation. Specifically, the incorporation of Sr into the PZT layer [46,47] reduces the interfacial lattice tetragonality and the magnitude of \(P_{\text{SZ}}\). At the same time, a metal-to-insulator transition, which takes place at \(x = 0.5\) in \(\text{Sr}(\text{Ru}_{1-x}\text{Ti}_x)\text{O}_3\) [48], suppresses the interface conductivity and results in a penetration of polarization into the SrRuO3 electrode. Together with the structural reconstruction, the monoclinic lattice distortion therefore facilitates the development of in-plane polarization at the interface.

This screening scenario is supported by our first-principles calculations of Sr and Ru codoped PbTiO3 and a report of polarized SrO planes at SrRuO3/BaTiO3 interfaces [49]. By averaging the composition of the second-to-fourth unit cells in domain II, a supercell of \((\text{Pb}_{0.75}\text{Sr}_{0.25})\text{(Ti}_{0.75}\text{Ru}_{0.25})\text{O}_3\) was constructed for the calculation (see Supplemental Material Fig. S3 [30]). Our result shows that the supercell with monoclinic symmetry (space group \(Cm\)) has the lowest energy and the polarization is allowed to rotate freely within the confined \((110)_T\) plane. By fixing the in-plane lattice constant to a bulk value of \(\text{SrRuO}_3\), the out-of-plane and in-plane polarizations are \(P_{\text{SZ}} = 66.2 \mu \text{C cm}^{-2}\) and \(P_{\text{SX}} = 13.2 \mu \text{C cm}^{-2}\) for the supercell, which are close to the experimental values presented in Figs. 2(c) and 2(f). Meanwhile, the inert displacements of Ru atoms along the \([001]_T\) direction manifest their passive contribution to polarization penetration into the SrRuO3 electrode [Fig. 3(g)]. Apart from the ionic screening, the decreased oxygen octahedral rotation [50,51] also provides evidence for impaired electronic screening on approaching the interface, as denoted by the yellow shadow in Fig. 2. Therefore, an \(\text{in situ}\) screening scenario is suggested at the oxide heterointerface [13–15].

In order to verify the validity and universality of the screening mechanism, a more complex BiFeO3/SrRuO3 interface, involving polar catastrophe, oxygen-octahedral rotation mismatch, strain mismatch, and chemical diffusion, was
FIG. 4. (a) Atom-resolved HAADF-STEM image of the BiFeO$_3$/SrRuO$_3$ interface, involving polar catastrophe, oxygen-octahedral rotation mismatch ($\phi \approx 12^\circ$ for BiFeO$_3$ and $\phi \approx 6^\circ$ for SrRuO$_3$), and chemical diffusion, recorded along the [100]$_T$ direction. The yellow, orange, and blue arrows denote the polar displacement vectors compiled from (c), SrO-FeO$_2$ termination, and CDW, respectively. Atomic column types: Bi (green), Fe (pink), Sr (dark yellow), Ru (blue). (b), (c) Lattice parameter and polar displacement changes measured across the interface and the CDW (blue dashed lines) and plotted as a function of distance normal to the interface.

examined by high-angle annular dark field (HAADF)-STEM (Supplemental Material Fig. S4 [30]). In the BiFeO$_3$ layer, the lower-left-hand and upper-left-hand displacements of Fe clearly identify a tail-to-tail $71^\circ$ or $109^\circ$ CDW with the domain polarization pointing along the projected $(00\bar{1})_T$ direction [Fig. 4(a)]. Similarly, the epitaxial growth relationship yields a constant $a_p$ axis ($\approx 0.3980$ nm) and the CDW leads to lattice expansion ($c/a \approx 1.042$) with respect to the domains ($c/a \approx 1.024$) [Fig. 4(b)]. Nevertheless, the $c_p$ axis is found to reduce abruptly from 0.4209 nm ($c/a \approx 1.057$) to 0.3926 nm ($c/a \approx 0.986$) as passing across the interface, which is accompanied with a decrease/increase in out-of-plane/in-plane displacements ($\delta z_{Fe-Bi}/\delta x_{Fe-Bi}$) on the BiFeO$_3$ side, and dominance of the in-plane displacements ($\delta z_{Ru-Sr} \approx 8.9$ pm) on the SrRuO$_3$ side [Fig. 4(c)]. These structural changes provide evidence for a monocliniclike lattice distortion at the BiFeO$_3$/SrRuO$_3$ interface ($\sim 6$ unit cells thick) and the CDW, thereby enabling the polarization to rotate flexibly within the symmetry-permitted planes [Fig. 4(a)].

Apart from the SrO-BO$_2$ termination, the PZT/SrRuO$_3$ interfaces terminated by RuO$_2$-PbO atomic planes were also investigated (Supplemental Material Fig. S5 [30]). The impact of interface termination type on internal built-in field is discussed with respect to the measured hysteresis loops (Supplemental Material Fig. S6 [30]). In contrast to the SrO-BO$_2$ termination, the RuO$_2$-PbO termination results in a downward orientation of $P_3$ (towards the interface) in the entire c domain. According to density-functional theory calculation [52], the worse/better screening capability of a SrRuO$_3$ electrode with SrO/RuO$_2$ termination may therefore explain the presence/absence of the interfacial CDWs inside the c domains [30]. More importantly, the interface reconstruction enabled flexible polarization rotation is also verified at the RuO$_2$-PbO terminated interfaces, independent of the change in oxygen partial pressure (0.1–1 mbar) during sample growth (Supplemental Material Fig. S7 [30]). In analogy to oxide electrodes, Au and Pt electrodes also lead to flexible polarization rotation at the metal-electrode/PZT interfaces, which are about 3 unit cells (Supplemental Material Fig. S8 [30]). The observed universality of the screening mechanism suggests that the ferroelectric-metal interfaces may act as seeds to nucleate new domains during the polarization switching process. Considering the distinct switching dynamics of ferroelastic domains [53,54], the model system Pt/($x = 0.6$)PZT/SrRuO$_3$/SrTiO$_3$, with a monodomain ferroelectric state, was selected to confirm this argument by means of ex situ biasing and TEM/STEM investigations (Supplemental Material Fig. S9 [30]).

By switching the Pt-electrode covered regions, an array of $180^\circ$ domains, with the DWs lying in the $(100)_T$ plane, was achieved in the Pt patterned square area [Figs. 5(a) and 5(b)]. A nonuniform piezoresponse force microscopy (PFM) phase image suggests that the polarization in the targeted regions was not fully switched. Manifested by bright-contrast spots, cross-sectional dark-field TEM imaging shows that incomplete domain switching leads to preferential nucleation of nanodomains (diameter at 3–14 nm) near the PZT/SrRuO$_3$ and Pt/PZT interfaces [Fig. 5(c)]. This is confirmed by atom-resolved HAADF-STEM observations on the written DW area. The newly created nanodomains near the interfaces, which are surrounded by the initial-state domain with an upward $P_3$ orientation, are found to possess a reversed $P_3$ orientation along with in-plane atomic displacements [Fig. 5(d)].
result confirms that the low-symmetric ferroelectric-metal interfaces indeed induce the nucleation of new domains during the polarization switching process. The seed effect of the ferroelectric-metal interface is further supported by the observation of polarization curling and flux closure structures in multiferroic Co/PbTiO$_3$/La, SrMnO$_3$ tunnel junctions [55], in which flexible polarization rotation is identified near both interfaces. Since the in-plane polarization component does not contribute to the interface capacitance, it therefore plays a deleterious role in practical ferroelectric devices [56]. In addition, a photoemission and x-ray absorption study reveals that Ti remains tetravalent in the Sr(Ru$_{1−x}$Tix)$_3$O$_9$ ($0 \leq x \leq 1$) films [57], suggesting that oxygen vacancies, which may be generated in the operating devices, are not a necessary ingredient for the compensation of ferroelectric polarization at the initial-state interfaces.

In fact, the screening scenario deciphered at the ferroelectric-metal heterointerfaces is analogous to the behavior at interfacial CDWs. Driven by a polarization discontinuity, monocliniclike lattice distortion associated with atomic rearrangement enables the development of in-plane polarization. As a result, flexible polarization rotation leads to a cycloidal polarization configuration at the CDWs [Figs. 1(d) and 4(c)], which is different from the reported charged 180° and 90° DWs [43,44], suggesting that oxygen vacancies, which may be generated in the operating devices, are not a necessary ingredient for the compensation of ferroelectric polarization at the initial-state interfaces.

In summary, driven by structural and chemical mismatches, the ferroelectric-metal interfaces universally adopt low-symmetry monoclinic structures via breaking of the parent lattice symmetries [60–62]. As a consequence, the polarization screening is implemented by flexible polarization rotation at the heterogeneous interfaces, which are responsible for the nucleation of new domains during the polarization switching process. In order to overcome the degradation of the ferroelectric devices [3], our findings suggest that interface engineering, e.g., conductivity modification by inserting alien atomic monolayers [63,64], is expected to revive the screening effectiveness of the electrodes. It is hoped that such measures may overcome the long-standing fatigue issue and that applications of ferroelectric-based devices will become widespread in the future.

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See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.98.020102 for details on experimental methods, domain configurations, surface and interface information for the (x = 0.9, 0.6) PZT and BiFeO3 films, quantitative atom-resolved (S)TEM studies, identification of interface termination, first-principles calculations, effects of polar catastrophe, RuO2–PbO termination, oxygen partial pressure, polarization orientation and strain mismatch on polarization screening, effect of interface termination on internal built-in fields, and implementation of ex situ biasing experiments, which includes Refs. [31–40].