Reversible Chemical Switching of a Ferroelectric Film

R. V. Wang,[1,2,*] D. D. Fong,[1] F. Jiang,[1,†] M. J. Highland,[1] P. H. Fuoss,[1] Carol Thompson,[3] A. M. Kolpak,[4,‡] J. A. Eastman,[1] S. K. Streiffer,[2] A. M. Rappe,[4] and G. B. Stephenson[1,2]

[1]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[3]*Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, USA*
[4]*The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA*

(Received 19 July 2008; revised manuscript received 25 September 2008; published 26 January 2009)

According to recent experiments and predictions, the orientation of the polarization at the surface of a ferroelectric material can affect its surface chemistry. Here we demonstrate the converse effect: the chemical environment can control the polarization orientation in a ferroelectric film. *In situ* synchrotron x-ray scattering measurements show that high or low oxygen partial pressure induces outward or inward polarization, respectively, in an ultrathin $PbTiO_3$ film. *Ab initio* calculations provide insight into surface structure changes observed during chemical switching.

DOI: 10.1103/PhysRevLett.102.047601 PACS numbers: 77.80.Fm, 68.43.−h, 68.47.Gh, 77.84.Dy

Ferroelectric materials are fascinating and useful because the spontaneous polarization which appears below the Curie temperature T_C is strongly coupled to long-range electric and stress fields, leading to outstanding properties such as piezoelectricity and electrically switchable structure [1,2]. Understanding the behavior of ultrathin ferroelectric films, for which interfacial effects begin to dominate over the physics of the film interior, has been an area of major progress recently [3–18]. One of the most important interfacial effects is the screening of the intrinsic surface charge of the polar phase [19], since this bound charge produces an electric field opposing the bulk polarization. The energy of this depolarizing field can be reduced by stripe domain formation [3–10] or by compensation via free charge at the interfaces [8,11–17]. In both cases, incomplete screening leads to a depression of T_C for thinner films and a critical thickness below which the polar phase is not stable. While electronic charge in metallic electrodes provides screening adequate to stabilize the polar phase down to nanometer dimensions [8,11,12,17], similar small critical thicknesses have been observed for films without surface electrodes [2,13,15,16]. *Ab initio* calculations [15,16] have indicated that extra ions or point defects could be providing charge compensation at these surfaces. Such ionic compensation of ferroelectric surfaces has also been inferred from electric force microscopy measurements [20]. The electronic or ionic nature of the compensating charge at interfaces has become a subject of debate for polar oxides in general [19,21,22].

Because of this evidence that ions can provide surface charge compensation for ferroelectrics, potentially giving new device functionality, several recent studies have focused on the interaction between the chemistry of the environment and the polarization orientation. Experiments have shown that ferroelectric surfaces with opposite polarity have different properties for adsorbing molecules [23,24]. *Ab initio* calculations have found that catalytic activity [25] and equilibrium surface stoichiometry [26] depend upon polarization orientation. In this work, we demonstrate the converse effect—that the chemical environment can control the polarization of a ferroelectric film by determining the ionic compensation at its surface. In particular, the polarity of an ultrathin $PbTiO_3$ film can be reversibly switched by changing the chemical potential of oxygen over its surface. By following the behavior *in situ*, we see that chemical potential affects ferroelectric film polarization in the same way as electric potential. In combination with *ab initio* based modeling, these experiments show that the chemical environment can play a dominant role in the behavior of nanoscale ferroelectrics.

Experimental methods.—We use *in situ* synchrotron x-ray scattering to investigate changes in the polarization of a $PbTiO_3$ film induced by varying the partial pressure of oxygen (pO_2) in equilibrium with its surface at elevated temperatures. While x-ray scattering is not sensitive to the interfacial charge from polarization, it is very sensitive to the atomic positions in the crystal structure of the ferroelectric film that determine its polarization. The samples consist of $PbTiO_3$ films grown on $SrRuO_3$ films on $SrTiO_3$ (001) substrates [27]. Both epitaxial films are coherently strained to the $SrTiO_3$ in-plane lattice parameter, forcing the polarization to be perpendicular to the film plane [28]. The conductive $SrRuO_3$ layer provides electronic compensation of the bottom interface of the $PbTiO_3$, while the top surface is exposed to a controlled vapor ambient. Previous work [15] has shown that the equilibrium $PbTiO_3$ structure in an oxidizing environment is a monodomain state with positive polarization, i.e., with polarization vector pointing out of the surface. Studies were carried out on samples with $PbTiO_3$ thicknesses of 2 to 21 nm at temperatures of 550 to

950 K by exposing them to various pO_2 levels in a flowing nitrogen ambient, while monitoring film and surface structure [27].

Experimental results.—Figure 1 shows hysteresis in the ferroelectric film structure as a function of pO_2 indicating polarization switching. The state reached at a given pO_2 depends on whether pO_2 is decreased from a high value, Fig. 1(a), or increased from a low value, Fig. 1(b). The most intense (red) feature is the $PbTiO_3$ Bragg peak. The variation in the L (out-of-plane) peak position plotted in Fig. 1(c) indicates change in the c lattice parameter, which is proportional to the square of the local polarization magnitude $|P|^2$ to a good approximation [27]. The behavior is comparable to the standard "butterfly loop" which

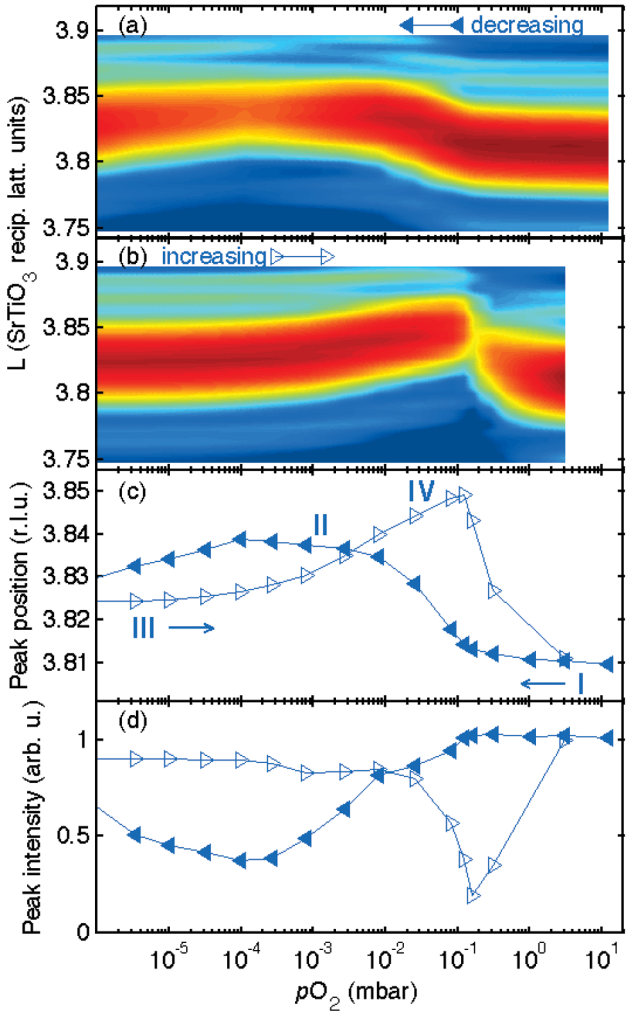

FIG. 1 (color). Hysteresis in L scans through the 304 Bragg peak of a 10 nm $PbTiO_3$ film at 644 K, at various oxygen partial pressures pO_2. Plots (a) and (b) are for pO_2 decreasing from a high value and increasing from a low value, respectively. Redder hues indicate higher intensity (log scale). Plots (c) and (d) show peak position and intensity; closed and open symbols are for decreasing and increasing pO_2, respectively. To fully switch the sample at low pO_2 (not shown), oxygen flow was set to zero, resulting in $pO_2 < 10^{-7}$ mbar.

occurs when the polarization of a ferroelectric film is switched using an external voltage applied across electrodes [1]. The peak position change from I to II is due to piezoelectric compression of the positively polarized film by an increasingly negative field, while the change from II to III reflects switching via nucleation and growth of negatively polarized domains. In the second half cycle, the change from III to IV shows piezoelectric compression of the negatively polarized film under increasingly positive field; finally, from IV to I the film switches back to positive polarization. Here the oxygen chemical potential produces the electric field across the film, as evidenced by these piezo and switching responses. The butterfly loop shape of Fig. 1(c) is characteristic of polarization switching [1], since the sign of the piezoelectric effect depends on whether the film surface has been equilibrated at high or low pO_2, indicating a reversal of polarization. Other possible explanations for changes in lattice parameter, such as a change in the oxygen vacancy concentration in the film interior, would be expected to produce a monotonic variation with pO_2, unlike our observations.

The intensity of the $PbTiO_3$ Bragg peak and the interference fringe pattern are sensitive to the polarization structure of the film [29,30]. As shown in Fig. 1(d), the Bragg peak intensity goes through minima at the points in the cycle where polarization switching is occurring. This is a signature of a process in which domains of the opposite sign nucleate and coalesce, resulting in domains of both polarities being present simultaneously during switching, since destructive interference between scattering from domains of opposite polarity reduces the Bragg intensity. For the atomic displacements in epitaxially strained $PbTiO_3$ on $SrTiO_3$ at temperatures near 700 K, oppositely polarized domains scatter nearly 180° out of phase at reciprocal space positions with relatively large Miller index L (e.g., $L = 4$) [31]. This produces the especially deep intensity minima shown in Fig. 1. Simultaneously, with these decreases in the Bragg intensity, we observe increases in diffuse scattering in the HK plane surrounding the Bragg peak [27], consistent with the presence of a mixed-domain state during switching. At the switching points we also observe an inversion in the contrast of the narrow fringes from the $SrRuO_3$ film that modulate the broader fringes from the thinner $PbTiO_3$ [27]. Since scattering from the $PbTiO_3$ and $SrRuO_3$ adds coherently in our high quality heterostructures, this inversion provides direct interferometric confirmation of the atomic displacements in the $PbTiO_3$ that constitute polarization reversal. Finally, the x-ray intensities from oppositely polarized monodomain states differ somewhat due to resonant scattering effects. At the x-ray energy used (28.3 keV), the $PbTiO_3$ 304 intensity from the positive (outward) polarization state is calculated to be 11% larger than that from the negative state. We observe that the intensity from the high pO_2 state is $12 \pm 1\%$ higher than that from the low pO_2 state, showing that switching occurs and that we have correctly identified the polarization directions.

Figure 2(a) shows the c lattice parameter as a function of pO_2 for a 10 nm film at three temperatures. Butterfly loops are observed at 644 and 737 K, with smaller c values at higher temperature as expected as the T_C for this film thickness (920 K [15]) is approached and polarization decreases. There is no butterfly loop at $T = 950$ K, since the film is in the paraelectric phase, and the value of c is almost constant at the calculated zero-polarization value [27]. This strongly supports the interpretation of the observations as polarization switching, since alternative explanations such as bulk oxygen vacancy concentration changes or film decomposition would produce larger, rather than smaller, effects at higher temperature. We have measured the response of several films with thicknesses ranging from 2 to 21 nm. All show butterfly loops at $T < T_C$, with smaller lattice parameter changes at larger film thicknesses. We observe that the bistable behavior is repeatable, provided that the excursions in pO_2 are large enough to fully switch the sample. For small changes in pO_2 in the nonswitching regions (x_{pos} near unity or zero), the measured lattice parameter remains on one of the two branches of the loop with little or no hysteresis.

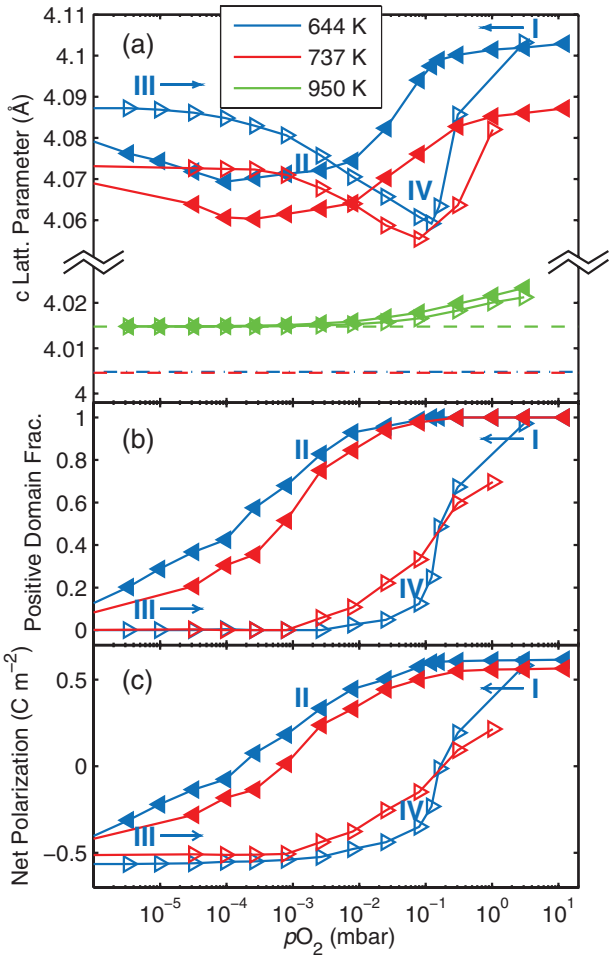

FIG. 2 (color). Analysis of scattering data for a 10 nm $PbTiO_3$ film, showing ferroelectric response to ambient oxygen concentration. Closed and open symbols are for decreasing and increasing pO_2, respectively. (a) $PbTiO_3$ c lattice parameter for three temperatures. Note that for 950 K, response to pO_2 is minimal because T is greater than T_C. Dashed lines are the zero-polarization values of c for each T. (b),(c) Results of a structural model fit to L scans for the 644 and 737 K data, deducing the fraction of positively polarized domains and the net polarization.

We can quantitatively fit the observed L scans to a structural model based on switching by domain nucleation and growth, similar to that used previously [15,27,29], to extract the fraction x_{pos} of positive domains in the $PbTiO_3$ film. Figures 2(b) and 2(c) show the positive domain fraction x_{pos} obtained from the fits, and the calculated net polarization $\langle P \rangle = |P|(2x_{pos} - 1)$. These results indicate that the ferroelectric film can be fully and reversibly switched between monodomain states with positive and negative polarization orientations by varying the pO_2 of the ambient.

Ab initio calculations and surface structure.—To investigate the mechanism by which the chemical environment controls the film polarization, we have modeled surface reactions of vapor species with the ferroelectric film. Significant surface charge density is required to compensate the observed polarization of about 0.5 C/m^2, which corresponds to 0.5 electronic charges per unit cell area. Previous density functional theory calculations [15] have shown that negative ions bonded to the surface such as O^{2-} or OH^- could be responsible for compensating the surface of positively polarized films under high pO_2 conditions. Using the same methods, we have performed additional calculations showing that one missing oxygen per four unit cells in the PbO surface layer (arranged in a 4×1 symmetry) will stabilize negative polarization in a 3-unit-cell-thick $PbTiO_3$ film on a 3-unit-cell-thick $SrRuO_3$ electrode [27]. While the ground state polarization magnitude is only 35% that of bulk $PbTiO_3$, it will be larger in thicker films such as those studied experimentally. Table. I gives the ground state energy ΔE_{DFT} at $T = 0$ K and the estimated enthalpy and free energies at $T = 644$ K. These are differences between the system with a missing surface oxygen plus a free oxygen atom, relative to that with no missing surface oxygen (which we found to have an unpolarized ground state). The free energy $\Delta G = \Delta G^\circ - \theta kT \ln pO$ has been calculated using an O coverage $\theta = -0.25$ and an O atom pressure $pO = 2.7 \times 10^{-22}$ bar, corresponding to $pO_2 = 1 \times 10^{-6}$ mbar at $T = 644$ K [27]. The stabilization of negatively polarized domains by a 4×1 missing oxygen surface structure agrees with a simple charge balance. If each oxygen ion carries $-2e$ charge, then this structure provides $+0.5e$ per unit cell area surface charge, just that needed to compensate the observed polarization. Experimentally, we indeed observe that a surface reconstruction with 4×1 symmetry forms at low pO_2 [27]. Its intensity scales with the fraction of negative domains, indicating that this reconstruction may be formed by an ordering of the missing oxygen that compensates the surface.

TABLE I. Calculated polarization and per-unit-cell-area energy ΔE_{DFT} at $T = 0$ K, standard enthalpy ΔH° and free energy ΔG° at $T = 644$ K, and free energy ΔG at $pO_2 = 1 \times 10^{-6}$ mbar, for a $PbTiO_3$ on $SrRuO_3$ system with one missing surface oxygen per four 1×1 unit cells. The change in sign from ΔG° to ΔG indicates that the system with missing oxygen is energetically favored relative to the stoichiometric system at low pO_2.

Compensation	$P/\lvert P_{\mathrm{bulk}}\rvert$	ΔE_{DFT} [eV]	ΔH° [eV]	ΔG° [eV]	ΔG [eV]
Missing O 4×1	-0.35	0.42	0.43	0.18	-0.51

Conclusions—.The multiple types of x-ray measurements described above, together with *ab initio* calculations showing that ionic compensation of the surface can control the ground state polarization, demonstrate that simple variations in oxygen chemical potential at the surface give effects directly analogous to applied voltage and can reversibly switch the polarization of a ferroelectric film. Thus the chemistry of the environment must be taken into account when studying polarization in ultrathin films without a top electrode. Compared with interfaces of fixed-polarity materials [19,21,22], ferroelectric surfaces give an especially rich set of behavior for understanding charge compensation of polar discontinuities, since the surface is free to structurally reconstruct and can be chemically equilibrated with a controlled environment, and the polarization in the bulk can vary in response to surface compensation. It should be possible to use chemical processes as a new method to create domain structures in ferroelectric films, including patterning through a lithographically produced mask.

These observations of chemical control of polarization also provide insight into the mechanism by which the polarization orientation of a ferroelectric film can modify surface chemical reactions. The ability to electrically switch the reactivity of a surface could form the basis for new classes of thin-film chemical actuators [23,24] and catalysts [25], offering dynamical control of reactivity and selectivity over a wide range in a single system. Further understanding of the interactions of ambients with polarization at ferroelectric surfaces promises to provide a new means for manipulating both ferroelectricity and surface chemistry.

We thank K. J. Choi, D. M. Kim, and C. B. Eom for growing the $SrRuO_3$ bottom electrode films. X-ray studies were performed at the Advanced Photon Source beam line 12ID-D. Work was supported under Contract No. DE-AC02-06CH11357 between UChicago Argonne LLC and the Department of Energy. A. M. K. and A. M. R. acknowledge the support of the Department of Energy under Grant DE-FG02-07ER15920, the Air Force Office of Scientific Research under Grant FA9550-07-1-0397, and a Challenge Grant from the HPCMO of the Department of Defense.

*Present address: Numonyx Corp., Santa Clara, CA 95054, USA.

†Present address: Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA.

‡Present address: Department of Applied Physics, Yale University, New Haven, CT 06520, USA.

[1] D. Damjanovic, Rep. Prog. Phys. **61**, 1267 (1998).
[2] C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science **303**, 488 (2004).
[3] S. K. Streiffer *et al.*, Phys. Rev. Lett. **89**, 067601 (2002).
[4] D. D. Fong *et al.*, Science **304**, 1650 (2004).
[5] D. D. Fong and C. Thompson, Annu. Rev. Mater. Res. **36**, 431 (2006).
[6] B. K. Lai *et al.*, Phys. Rev. Lett. **96**, 137602 (2006).
[7] M. Sepliarsky, M. G. Stachiotti, and R. L. Migoni, Phys. Rev. Lett. **96**, 137603 (2006).
[8] J. Paul *et al.*, Phys. Rev. Lett. **99**, 077601 (2007).
[9] R. Takahashi *et al.*, Appl. Phys. Lett. **92**, 112901 (2008).
[10] P. Aguado-Puente and J. Junquera, Phys. Rev. Lett. **100**, 177601 (2008).
[11] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).
[12] D. J. Kim *et al.*, Phys. Rev. Lett. **95**, 237602 (2005).
[13] C. Lichtensteiger *et al.*, Phys. Rev. Lett. **94**, 047603 (2005).
[14] M. Stengel and N. A. Spaldin, Nature (London) **443**, 679 (2006).
[15] D. D. Fong *et al.*, Phys. Rev. Lett. **96**, 127601 (2006).
[16] J. E. Spanier *et al.*, Nano Lett. **6**, 735 (2006).
[17] G. Gerra, A. K. Tagantsev, and N. Setter, Phys. Rev. Lett. **98**, 207601 (2007).
[18] E. Bousquet *et al.*, Nature (London) **452**, 732 (2008).
[19] J. Goniakowski, F. Finocchii, and C. Noguera, Rep. Prog. Phys. **71**, 016501 (2008).
[20] S. V. Kalinin and D. A. Bonnell, Phys. Rev. B **63**, 125411 (2001).
[21] N. Reyren *et al.*, Science **317**, 1196 (2007).
[22] W. Siemons *et al.*, Phys. Rev. Lett. **98**, 196802 (2007).
[23] Y. Yun and E. I. Altman, J. Am. Chem. Soc. **129**, 15 684 (2007).
[24] D. Li *et al.*, Nature Mater. **7**, 473 (2008).
[25] A. M. Kolpak, I. Grinberg, and A. M. Rappe, Phys. Rev. Lett. **98**, 166101 (2007).
[26] S. V. Levchenko and A. M. Rappe, Phys. Rev. Lett. **100**, 256101 (2008).
[27] See EPAPS Document No. E-PRLTAO-102-063903 for methods and supplemental data. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[28] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[29] C. Thompson *et al.*, Appl. Phys. Lett. **71**, 3516 (1997).
[30] C. Thompson *et al.*, Appl. Phys. Lett. **78**, 3511 (2001).
[31] G. B. Stephenson *et al.*, Physica (Amsterdam) **336B**, 81 (2003).