



## Polarization Switching without Domain Formation at the Intrinsic Coercive Field in Ultrathin Ferroelectric $\text{PbTiO}_3$

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Polarization switching in ferroelectrics has been thought to occur only through the nucleation and growth of new domains. Here we use *in situ* synchrotron x-ray scattering to monitor switching controlled by applied chemical potential. In sufficiently thin  $\text{PbTiO}_3$  films, nucleation is suppressed and switching occurs by a continuous mechanism, i.e., by uniform decrease and inversion of the polarization without domain formation. The observed lattice parameter shows that the electric field in the film during switching reaches the theoretical intrinsic coercive field.

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Ferroelectrics are a fascinating class of materials both for studies of the fundamentals of phase transitions and for a number of emerging device technologies [1–6]. The key functionality of ferroelectrics arises because their polarization can be switched between different stable orientations by application and removal of an electric field greater than a threshold known as the coercive field  $E_C$ . In principle,  $E_C$  can be no larger than the intrinsic coercive field  $E_{IC}$  at which the initial state becomes unstable and the polarization can continuously evolve to the new orientation with no nucleation barrier. At fields below  $E_{IC}$  the initial state is metastable, so that switching requires thermally activated nucleation of domains of the new orientation. The distinction between nucleated and continuous mechanisms, illustrated in Fig. 1, is a fundamental characteristic of all phase transitions, as originally discussed by Gibbs in his seminal treatment of phase stability [7,8]. However, despite early predictions that the nucleation barrier for ferroelectric switching should be large [9], observed switching behavior has remained an anomaly. The consensus has been that polarization inversion in ferroelectrics occurs only by domain nucleation and growth [6], and a continuous mechanism has never been experimentally demonstrated.

The switching behavior of ferroelectric thin films is an area of continuing interest and controversy [10–25]. Measured values of  $E_C$  are typically larger in films than in bulk systems, and it has been reported that  $E_C$  can reach  $E_{IC}$  in ultrathin polymer films [24]. However, this report has been questioned on several grounds [18,20–22]. External electrical measurement of the internal field in ultrathin films is generally ambiguous because of unknown interfacial voltage offsets and electrode effects [10,18–20,25]. Measured values of  $E_C$  reaching and even apparently exceeding  $E_{IC}$  in ultrathin oxide films have been explained in this way [19]. Analysis of electrical data on polarization decay [17] indicates that such interfacial

voltage offsets indeed contribute strongly to the internal field in ultrathin films. Because of the strain dependence of  $E_{IC}$ , systematic study is also complicated when film strain varies with thickness [19]. Furthermore, modeling has suggested [15] that switching can still occur through domain nucleation even if the internal field reaches  $E_{IC}$ . Piezoresponse force microscopy [12,13] has allowed domain nucleation and growth dynamics to be studied with a spatial resolution approaching 10 nm, but switching without nucleation has yet to be observed. Thus the question remains whether, in sufficiently thin ferroelectric films, nucleation can be suppressed and switching can occur through a continuous mechanism. Discovery of conditions for switching without domain formation in ferroelectrics will allow study of the ultimate limit of stability for switchable polar states.

Here we report results of a new approach to observe and control switching in ultrathin films of a prototypical perovskite-structure ferroelectric,  $\text{PbTiO}_3$ . We determine

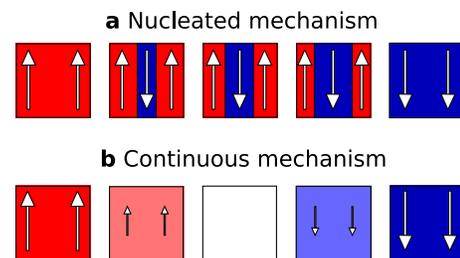


FIG. 1 (color online). Schematic of polarization evolution during switching in a uniaxial ferroelectric. (a) Discontinuous nucleation and growth of inverted domains. (b) Continuous, uniform decrease of the polarization magnitude through zero without domain formation. Arrows indicate the orientation and magnitude of polarization. The domain structures that appear during nucleated switching can be detected by x-ray scattering.

the presence or absence of domains during switching using *in situ* synchrotron measurements of diffuse x-ray scattering intensity. We also obtain the polarization magnitude and internal electric field of the ferroelectric film during switching by comparing the film lattice parameter to theory. To produce a well-defined strain state and minimize defects [26], we study epitaxial PbTiO<sub>3</sub> heterostructures with SrRuO<sub>3</sub> bottom electrodes coherently strained to SrTiO<sub>3</sub> (001) single crystal substrates. The compressive epitaxial strain forces the PbTiO<sub>3</sub> polarization to remain normal to the surface even during switching [27]. Film growth and x-ray measurements and analysis were carried out by methods similar to those described previously [27,28]. By changing the oxygen chemical potential in equilibrium with the film surface, switching is driven by controlling the ionic surface charge density rather than the applied voltage [28].

Bragg and diffuse x-ray scattering are directly sensitive to the presence or absence of domains. When domains are formed during switching, destructive interference between scattering from domains of opposite polarity will strongly reduce the Bragg intensity and produce diffuse scattering at in-plane wave vectors corresponding to the domain size range [28]. In contrast, when no domains are formed, no increase in diffuse scattering will be seen, while a weaker effect on the Bragg scattering will remain from the polarization dependence of the unit cell structure factor. This direct structural determination avoids the uncertainties discussed above when attempting to distinguish transition mechanisms by comparing external voltage measurements to calculated values of  $E_{IC}$ .

Measurement of the film lattice parameter during switching provides a second way to distinguish the mechanism and allows the true internal coercive field to be determined. Landau-Ginzburg-Devonshire (LGD) theory can be used to predict the relationships between the local polarization  $P$ , internal field  $E$ , and out-of-plane lattice parameter  $c$ , and the values expected for nucleated and continuous mechanisms [27,29]. The change in  $c$  is proportional to  $|P|^2$ , and  $c$  will go through a minimum when the polarization is switched. In the nucleated case, switching should occur at a value of  $c$  between the zero-field value  $c_0$  and the value  $c_{IC}$  at the intrinsic coercive field. In the continuous case, the minimum  $c$  should approach a lower value corresponding to  $P = 0$  at the midpoint of the switching process.

Figure 2 shows measurements of  $c$ , Bragg intensity, and diffuse scattering intensity versus external oxygen partial pressure ( $pO_2$ ) for a 4.9 nm thick PbTiO<sub>3</sub> film at 737 and 826 K. Both temperatures are below the measured Curie point [30] for this thickness,  $T_C = 885$  K. At high  $pO_2$ , the film is polarized positively (outward) with its surface compensated by an extra partial layer of oxygen ions; at low  $pO_2$ , the film is polarized negatively (inward) with compensation by fractional occupancy in the surface layer of oxygen ions [28]. When the  $pO_2$  is cycled, the film lattice parameter follows a “butterfly loop,” a standard signature

of polarization switching. The 737 K data show the characteristics of a nucleated mechanism. During switching, indicated by the minima in  $c$  [Fig. 2(a)], there is a decrease in Bragg intensity [Fig. 2(b)], accompanied by an increase in diffuse scattering around the Bragg peak [Fig. 2(c)]. The minimum value of  $c$  is near  $c_{IC}$  and stays well above  $c(P = 0)$ . In contrast, the 826 K data are consistent with a continuous mechanism. The minimum  $c$  during switching shown in Fig. 2(d) reaches the predicted value of  $c(P = 0)$ . Figure 2(e) shows relatively small changes in the Bragg intensity, consistent with the known polarization dependence of the structure factor [28], while Fig. 2(f) shows that there is negligible change in diffuse scattering during switching. Note that external  $pO_2$  is related more directly to the density of free charge on the surface than to internal electric field, while the response of  $c$  follows the polarization and internal field. Thus the coercive field at which switching occurs is indicated by the measured  $c$  lattice parameter, not the measured  $pO_2$ .

Figure 3 shows the change in diffuse scattering intensity at the decreasing  $pO_2$  switching point relative to the monodomain state at high  $pO_2$ , around a PbTiO<sub>3</sub> 304 peak, for the two cases shown in Fig. 2. At  $T = 826$  K, the diffuse scattering intensity is negligible, indicating that switching

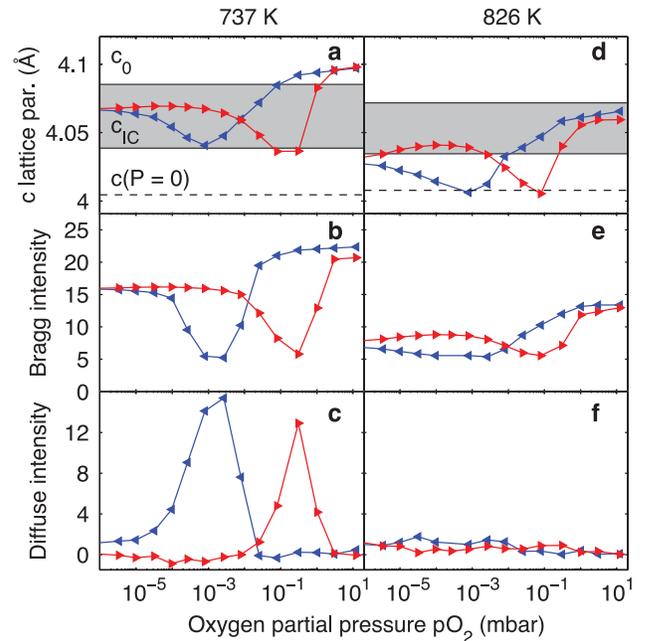


FIG. 2 (color). Measured behavior of a 304-type x-ray reflection at two temperatures from the same 4.9 nm thick PbTiO<sub>3</sub> film during cycling of  $pO_2$ . High or low  $pO_2$  induces positive or negative polarization, and the blue or red curves are for decreasing or increasing  $pO_2$ , respectively. (a) The  $c$  lattice parameter, (b) the Bragg intensity, and (c) the diffuse scattering intensity at 737 K, indicating domain formation during switching. (d)–(f) The same quantities at 826 K, indicating switching without domain formation. The predicted minimum  $c$  values for nucleated and continuous mechanisms are shown by the gray shaded region and the dashed line, respectively, in (a) and (d). Intensities are in arbitrary units.

occurs without domain formation. At  $T = 737$  K, scattering from domains is clearly present. The distribution of the diffuse scattering indicates an average in-plane domain size of  $\sim 6$  nm at the midpoint of switching. This is similar to the 4 nm size observed for equilibrium  $180^\circ$  stripe domains for 5 nm thick films grown directly on  $\text{SrTiO}_3$  [31].

Figure 4 summarizes the temperatures and  $\text{PbTiO}_3$  film thicknesses for which we have determined the mechanism of switching from the behaviors of the diffuse scattering and/or the  $c$  lattice parameter. We find that switching is continuous in sufficiently thin films, and that the boundary between nucleated and continuous occurs at a film thickness of  $6.4 \pm 0.5$  nm at 826 K and  $2.9 \pm 0.6$  nm at 645 K. As detailed in the supplementary material [27], at this boundary we observe a disappearance of the diffuse scattering during switching. Near this boundary the minimum  $c$  lattice parameter abruptly changes between values that agree with LGD theory for  $c_{\text{IC}}$  and  $c(P = 0)$ , indicating that the intrinsic coercive field is reached.

These results indicate that in sufficiently thin films, not only does switching occur by a continuous mechanism without domain formation at the intrinsic coercive field  $E_{\text{IC}}$ , but that inverted domains do not nucleate even on the long time scales of the measurements (hundreds of seconds at each  $p\text{O}_2$  step) when the initial monodomain polar state is subjected to reverse fields just below  $E_{\text{IC}}$ . Theory [14,15] and experiment [13,16] have found that switching typically

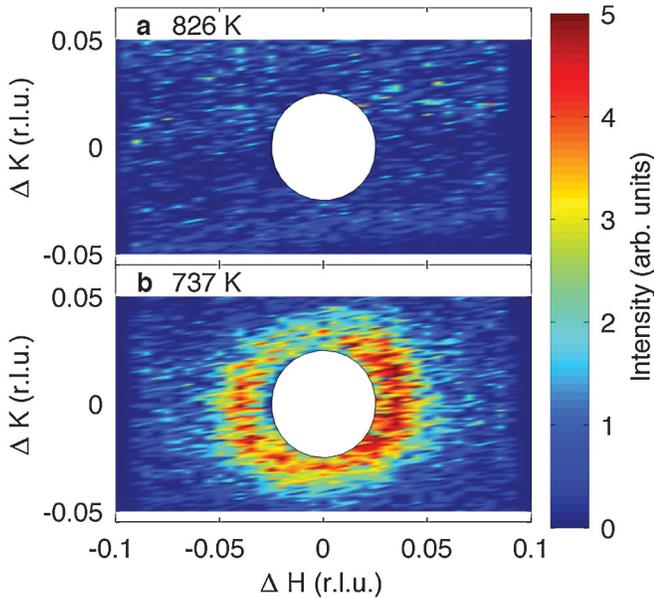


FIG. 3 (color). The change in diffuse intensity at the decreasing  $p\text{O}_2$  switching point relative to the monodomain state at high  $p\text{O}_2$ , plotted versus in-plane wave vector  $\Delta H$  and  $\Delta K$  around a  $\text{PbTiO}_3$  304 peak, integrated from  $L = 3.78$ – $3.94$  reciprocal lattice units (r.l.u.), for a 4.9 nm thick  $\text{PbTiO}_3$  film at two temperatures. The Bragg scattering at  $\Delta H = \Delta K = 0$  has been masked to reveal any diffuse scattering from domains. Data at 826 (a) and 737 K (b) show switching without and with domain formation, respectively.

occurs on nanosecond time scales under large applied fields approaching  $E_{\text{IC}}$ . The remarkable suppression of nucleation observed here can be explained by either equilibrium or kinetic considerations, taking into account the ionic compensation at the surface.

*Equilibrium model.*—Chemical equilibria with the vapor should be different for charged surface species stabilizing positively and negatively polarized films [28], giving two different relationships between  $p\text{O}_2$  and surface charge density. If at the intermediate  $p\text{O}_2$  values where switching occurs the densities of both species on the surface are sufficiently low that monodomain polar phases of both signs are unstable, the equilibrium structure would be either a nonpolar phase or  $180^\circ$  stripe domains. The Curie point  $T_C^{\text{str}}(t)$  for  $180^\circ$  stripe domains in a  $\text{PbTiO}_3$  film of thickness  $t$  with one uncompensated interface is shown in Fig. 4, from LGD theory [27,29,32]. The observed boundary at which domain formation ceases lies below this equilibrium prediction, suggesting either that the assumption of a fully compensated bottom interface is not satisfied or that formation of inverted domains may be additionally suppressed because of kinetics.

*Kinetic model.*—Because the density of compensating ions can only change through relatively slow chemical equilibration with the environment, the ionic compensation at the top surface is unable to respond on the time scale of polarization fluctuations that comprise the subcritical domain nuclei within the ferroelectric. Thus formation of nuclei is most favorable at the bottom interface, where the electrons in the conducting electrode can respond rapidly. In addition, for a fluctuation to become a stable nucleus without changing the ionic surface compensation,

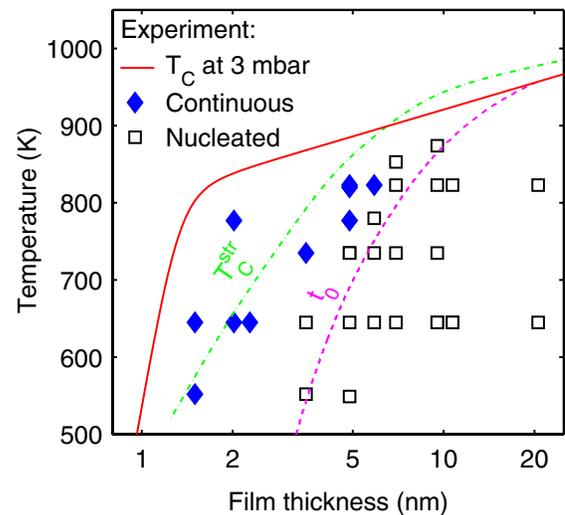


FIG. 4 (color online). Switching mechanism map. Symbols indicate whether a continuous or nucleated mechanism is observed for given  $\text{PbTiO}_3$  film thicknesses and temperatures. The solid curve shows the observed  $T_C$  at  $p\text{O}_2 = 3.0$  mbar [30]. The dash-dotted and dashed curves are equilibrium  $T_C^{\text{str}}(t)$  and kinetic  $t_0(T)$  predictions for the boundary between the continuous and nucleated regions.

the size of a stable nucleus must be smaller than the film thickness. Based on these hypotheses, we can develop a theoretical estimate for the film thickness below which nucleation is suppressed. The formation energy  $U$  of a half spheroid nucleus growing into the parent domain from the bottom electrode, with in- and out-of-plane radii  $r$  and  $l$ , has been given by Landauer [9] as

$$U = -2EP_0 \frac{2\pi r^2 l}{3} + \gamma \frac{\pi^2 r l}{2} + \frac{4\pi P_0^2 r^2 l}{3\epsilon_0 \epsilon_3} (\eta^2 - 1) \left[ \frac{\eta}{2} \ln \left( \frac{\eta + 1}{\eta - 1} \right) - 1 \right],$$

where  $E$  is the applied field,  $P_0$  is the remanent polarization magnitude,  $\gamma$  is the domain wall energy,  $\eta \equiv (\epsilon_1/\epsilon_3)^{1/2} l / [(\epsilon_1/\epsilon_3) l^2 - r^2]^{1/2}$ , and  $\epsilon_1$  and  $\epsilon_3$  are the in- and out-of-plane dielectric constants. The three terms in the energy are from the volume, surface, and depolarizing field, respectively. The volume term is negative, favoring nucleus formation, while the surface and depolarizing field terms are positive, tending to suppress nucleus formation. As  $E$  approaches  $E_{IC}$  the domain wall energy  $\gamma$  approaches zero [8], so the nucleus energy is dominated by the first and third terms. The minimum  $U$  at  $E = E_{IC}$  occurs at maximum  $l$  and minimum  $r$ . In our case, the maximum  $l$  is limited to about half of the film thickness  $t$ , since we assume that the ionic compensation of the top interface remains fixed and repels the nucleus tip, while the minimum  $r$  is given by the domain wall width. For a fluctuation to become a stable nucleus, the minimum  $U$  must be negative. The minimum nucleus energy becomes positive and nucleation is suppressed when  $t$  is smaller than the thickness  $t_0$  at which  $U$  is zero. The values of  $t_0(T)$  calculated from LGD theory are shown in Fig. 4. Considering the simplicity of this kinetic model and its lack of adjusted parameters, the prediction is in remarkably good agreement with the observed boundary between nucleated and continuous mechanisms.

These studies support the notion that interfacial chemistry is a key determinant of the behavior of ultrathin ferroelectric films [28], and of interfaces with polar discontinuities in general. Further measurements of the equilibrium domain structure phase diagram as a function of  $pO_2$  and temperature will help correlate the metastability and instability limits with the observed boundary between nucleated and continuous mechanisms. The current observations of coercive fields reaching the intrinsic limit and of a continuous mechanism when the switching of ultrathin films is driven chemically cross a new threshold in our understanding of interfacial effects on polarization dynamics and suggest that the differences in the *dynamics* of ionic and electronic compensation may be exploited to control ferroelectric function.

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