Nanosecond Domain Wall Dynamics in Ferroelectric Pb(Zr, Ti)O_3 Thin Films

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Domain wall motion during polarization switching in ferroelectric thin films is fundamentally important and poses challenges for both experiments and modeling. We have visualized the switching of a Pb(Zr, Ti)O_3 capacitor using time-resolved x-ray microdiffraction. The structural signatures of switching include a reversal in the sign of the piezoelectric coefficient and a change in the intensity of x-ray reflections. The propagation of polarization domain walls is highly reproducible from cycle to cycle of the electric field. Domain wall velocities of 40 $\mathrm{m\,s^{-1}}$ are consistent with the results of other methods, but are far less than saturation values expected at high electric fields.

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Improving the present understanding of the structural dynamics of solids at the nanoscale is an important challenge in the development of emerging nanotechnologies based on acoustics, phase transitions, and the coupling of applied fields to structures. As the relevant length scales shrink to the nanometer range, the time interval over which structural transformations occur also decreases and can be on the order of picoseconds. The relationship between the space and time scales of structural phenomena in solids is fundamentally determined by the speed at which elastic deformations of the crystalline lattice can propagate, roughly the speed of sound. Reversible effects that can be found, for instance, in ferroelectric and multiferroic materials are among the most practically and fundamentally important structural transformations [1,2].

The present understanding of steady-state and quasi-steady-state ferroelectric phenomena including polarization hysteresis is already satisfactory as a result of extensive experimental and theoretical studies [1,3,4]. The dynamics of polarization switching, however, are largely unexamined at small lengths and short times. The motion of polarization domain walls presents a challenge for theory and modeling because of the span of length and time scales involved, which can range from domain wall widths of 1 nm or less to devices sizes in length, and from picoseconds to microseconds in time. The switching process in a ferroelectric thin film occurs in three steps: the nucleation of a reversed polarization domain, domain propagation in the direction of the electric field, and lateral domain growth in the direction perpendicular to the electric field [5]. At progressively higher electric fields, the speed of polarization switching scales with the magnitude of the electric field but apparently is limited by the propagation velocity of elastic deformations in crystals, which is several $\mathrm{km\,s^{-1}}$ in single crystals of perovskite-type ferroelectrics [6]. Experimental studies with present techniques, primarily piezoelectric force microscopy (PFM) and electrical measurements of the displacement current, have established the utility of this three-step model [7–10]. Although these studies have considerably broadened what is known about switching phenomena in ferroelectrics, they have not visualized the process dynamically at scales appropriate for describing domain wall motion in large electric fields.

A unique combination of spatial and time resolution is experimentally available using synchrotron x-ray scattering, which presently achieves resolutions of less than 60 nm in space and less than 1 ps in time in separate experiments [11,12]. We have applied a combination of time-resolved scattering and x-ray microdiffraction to study the structural dynamics of polarization switching in ferroelectrics. We investigated polarization switching in a ferroelectric capacitor consisting of a 400-nm-thick tetragonal $\mathrm{Pb(Zr_{0.45}Ti_{0.55})O_3}$ (PZT) film between a uniform grounded $SrRuO_3$ (SRO) bottom electrode and a 200 μm-diameter polycrystalline SRO top electrode. The epitaxial PZT and bottom $SrRuO_3$ electrode layers were deposited by off-axis sputtering [13]. The SRO electrodes allowed the PZT capacitor to operate for more than 10^{10} switching cycles without polarization fatigue [14]. The remnant polarization measured with 1 kHz triangular electric field pulses was $2P_r = 104\ \mu\mathrm{C/cm^2}$. The electric field in the PZT film was applied in the surface-normal [001] direction, which is the direction of the remnant polarization.

The ferroelastic distortion of ferroelectrics allows structural techniques to probe the remnant polarization quantitatively. In PZT crystals, the (002) and $(00\bar{2})$ x-ray Bragg reflections of the tetragonal phase correspond to opposite polarization states and can differ in intensity by 30% or more [15,16], which is a result of the noncentrosymmetric unit cell of ferroelectrics. X rays of 10 keV photon energy from an undulator insertion device at sector 7 of the Advanced Photon Source were focused to a 115 nm spot by Fresnel zone plate optics. The fundamental time resolution for experiments using synchrotron radiation was set by the duration of individual x-ray pulses arising from the passage of single bunches of electrons through magnetic insertion devices [17]. At the Advanced Photon Source, successive 100 ps x-ray bunches are separated in time by 153 ns. A limit of 1.15 $\mathrm{km\,s^{-1}}$ on the highest velocities measurable using time-resolved microdiffraction can be obtained by considering time dependent scattering measurements at two locations separated by the spatial resolution. With larger distances, significantly higher speeds, up to those exceeding the speed of sound ($\sim$4 $\mathrm{km\,s^{-1}}$ for PZT) could be measured.

To perform a time-resolved study of polarization switching, an electrical pulse applied to the ferroelectric capacitor was synchronized with x-ray pulses arising from a single circulating electron bunch. The diffracted x rays were collected with an avalanche photodiode detector with sufficient time resolution to resolve individual x-ray pulses [18]. At each point in scans of delay time between the electric field pulse and the x-ray probe, 1000 electric field cycles were applied to the sample with an overall repetition rate of 10 kHz. The acquisition electronics were gated so that only photons scattered during these pulses contributed to the measured intensity.

Although, in principle, the time resolution is set by the duration of a single x-ray bunch, the actual sensitivity of time-resolved x-ray microdiffraction to transient structural changes in PZT is a function of several experimental details. Piezoelectricity is the fastest of the structural responses of ferroelectrics to applied electric fields, and can be used to measure an upper limit on the effective time resolution of the experiment. To probe the piezoelectric distortion, the lattice spacing of PZT in the [001] direction was measured as a function of the delay between the probing x-ray bunch and in 8 V electrical pulses. Each data point had an uncertainty in intensity due to counting statistics of less than 10%. At the onset of the electric field, the Bragg reflection shifted to a lower 2θ angle, commensurate with the expansion of the PZT lattice expected when the polarization and electric field are parallel (Fig. 1). In addition to the transient structural change during the pulse there was a long term shift in 2θ after a large number of unipolar voltage pulses corresponding to a strain of $\sim$0.05%, which we attribute to charging of the PZT thin film. The maximum transient strain, 0.18%, is in itself interesting for potential applications utilizing lattice distortions to modify electronic or magnetic structures [19,20]. From strain measurements, we conclude that the electric field applied to the ferroelectric capacitor was lower than what would be expected given the pulse voltage and film thickness. For 18 V pulses the electric field estimated using the strain was 230 $\mathrm{kV\,cm^{-1}}$, based on a piezoelectric coefficient of 53 $\mathrm{pm\,V^{-1}}$ obtained in low-frequency measurements.

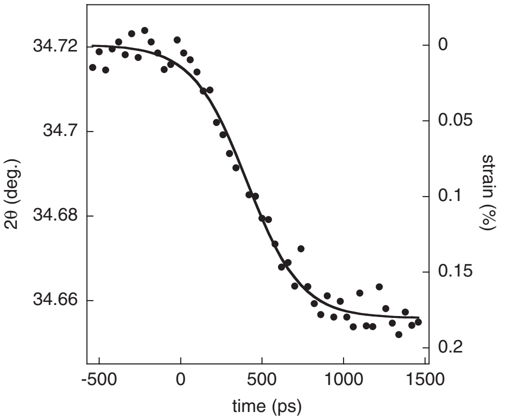

FIG. 1. Time-resolved x-ray microdiffraction measurement of the 2θ angle of the PZT (002) Bragg reflection as a function of the delay time after the onset of an 8 V electrical pulse. The effective time resolution of the measurement, corresponding to the 90% to 10% transition time, is 620 ps.

Bipolar electrical pulses switch the direction of the remnant polarization when the field exceeds the coercive electric field. With 18 V pulses, the intensity contrast between the two remnant states was 30% indicating that the polarization reversed during the pulse. The time dependence of the PZT (002) Bragg reflection is shown in detail in Fig. 2(a) during polarization switching in response to a -18 V voltage pulse. The polarization direction is reset prior to this pulse using a positive voltage pulse of the same magnitude. Turning on the negative voltage first shrinks the PZT lattice along the c axis, shifting the Bragg reflection to a higher 2θ angle. Hundreds of nano-

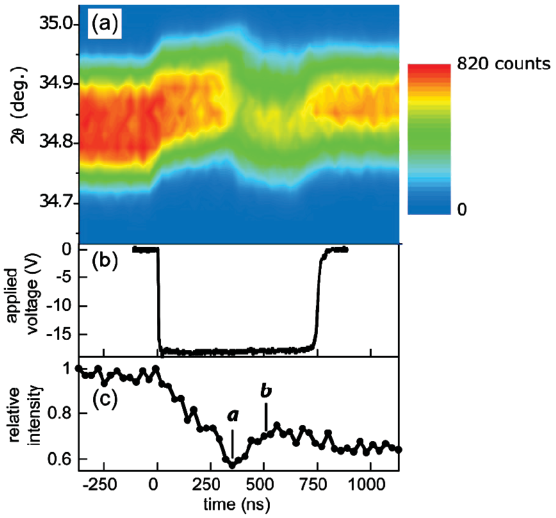

FIG. 2 (color). (a) The intensity of the PZT (002) Bragg reflection as a function of θ–2θ and time during the switching of the remnant polarization by a -18 V pulse to the capacitor. (b) Applied voltage as a function of time during polarization switching. (c) X-ray intensity as a function of time plotted from the data of part (a) along the line with $2\theta = 34.83°$. Points ***a*** and ***b*** denote the times of the beginning and end, respectively, of the structural signal associated with polarization reversal. The shift in absolute values of 2θ between Figs. 1 and 2 is the difference in the alignment of the x-ray diffractometer.

seconds later, the (002) reflection moves to a lower 2θ angle. The points ***a*** and ***b*** in Fig. 2(b) mark beginning and end of the scattering signature of the reversal of the piezoelectric response. With bipolar voltage pulses of smaller magnitude, the remnant polarization was not switched and the intensity of the Bragg reflection was unchanged before and after the electrical pulses. The difference in the Bragg angles of the reflections before and after the switching pulse is consistent with charging at the ferroelectric/electrode interfaces [21].

The time at which the remnant polarization switched varied with the position of the beam on the thin film capacitor due to the finite speed of the growth of polarization domains. We have defined the switching time for each position to be the period of time between the onset of the electric field pulse and the midpoint of the polarization switching structural transient ***a-b***. Assuming that the growth of domains in which the polarization has switched begins at the onset of the electric field, the switching time defined in this way corresponds to the time needed for a polarization domain wall to travel from the nucleation site to the measurement position. The structural transient associated with polarization switching can be observed using the time dependence of the intensity of x rays scattered to a fixed point in reciprocal space near the (002) Bragg reflection [Fig. 2(c)]. Measurements of the diffracted intensity as a function of time at different positions of the x-ray probe show that the switching time depends on the position (Fig. 3). The data presented in Figs. 2 and 3 support the assumption that the spatial distribution of nucleation sites, directions of domain growth, and domain wall velocities do not change significantly from one switching cycle to another. If the opposite were true, the structural signature associated with switching would be smeared over the entire measurement.

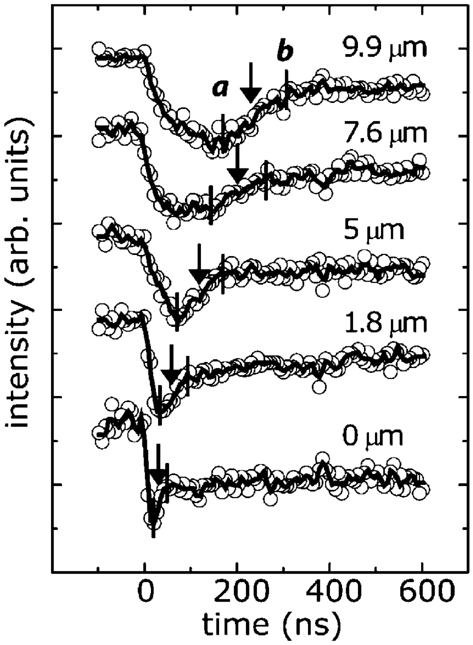

FIG. 3. Time dependence of the x-ray intensities measured with $2\theta = 34.83°$ at several positions on the capacitor. Each curve is labeled with the distance from the position of the first measurement. The intensities at each position of the beam are offset vertically.

The locations of polarization domain nucleation sites, domain growth directions, and domain wall velocities can be summarized on a map of the polarization switching time as a function of position [Fig. 4(a)]. The color scale in Fig. 4(a) corresponds to the time at which the midpoint of the ***a-b*** switching transient occurred at each point. The distribution of nucleation sites is not random, as would be expected based on homogenous nucleation [7,22,23], but rather is limited to a few widely separated locations. In Fig. 4(a) the polarization domain grows essentially from a single nucleus. Previous studies of polarization kinetics indirectly suggest a far higher nucleation rate than we have observed [4,7,9]. The area of the region shown in Fig. 4(a) is 400 $\mu\mathrm{m}^2$, much larger than the 1 $\mu\mathrm{m}^2$ area that is typically thought to contain a single nucleation site for polarization reversal [23]. The low nucleation rate, corresponding to only several hundred nuclei in the entire

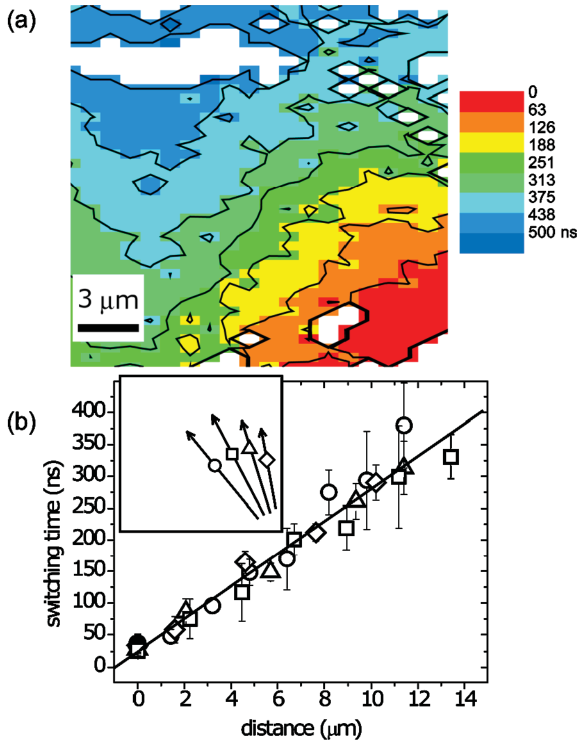

FIG. 4 (color). (a) Polarization switching times in a 20 × 20 $\mu\mathrm{m}^2$ area of the thin film capacitor. The earliest and latest switching times are red and blue, respectively. It was not possible to unambiguously assign switching times to the white areas. (b) Polarization switching time as a function of a distance along the arrows shown in the inset. The solid line is a linear fit giving a 40 $\mathrm{m\,s^{-1}}$ domain wall velocity. The error bars correspond to the uncertainty associated with assigning the switching time.

device, can be explained by a strong heterogeneity of the nucleation of reversed domains, perhaps at structural defects or even at the probe tip contacting the device [23]. The reproducibility of the domain wall motion between cycles of the electric field also suggests that the nucleation of reversed domains is not homogenous across the device.

The challenge of predicting domain dynamics is in part a result of the inability of theoretical descriptions, including Kolmogorov-Avrami models, to separate the relative importance of nucleation and domain wall motion in switching kinetics. Based on the parameters of these models, the switching process kinetics is commonly described as being determined either by the rate of nucleation or by the speed of domain walls [4,22]. The problems in distinguishing between these phenomena leads to difficulty in forming the connection between atomic scale simulations, including molecular dynamics studies of domain wall motion [24], and the larger-scale models needed for entire devices. The parameters of the three-step model of switching kinetics can be probed quantitatively and independently using the polarization switching map in Fig. 4(a). The domain wall velocity can be estimated using the portion of Fig. 4(a) in which domains propagate without interference from nearby nucleation centers. Crystallographic anisotropy does not appear to influence the polarization domain growth under these conditions.

A linear fit to a plot of the polarization switching time as a function of position gives an average domain wall velocity of $40\ \mathrm{m\,s^{-1}}$ for -18 V electric pulses [Fig. 4(b)]. Although $40\ \mathrm{m\,s^{-1}}$ is far below the limit set by elastic deformation, it is in reasonable agreement with recent experiments using PFM [7,25]. A domain wall velocity of $\sim 1\ \mathrm{m\,s^{-1}}$ in electric fields of $78\ \mathrm{kV\,cm^{-1}}$ was deduced from the evolution of domains following a series of electric field pulses [7]. Higher electric fields and smaller capacitor sizes are expected to yield considerably higher speeds for domain walls and could potentially shift the relative importance of nucleation and domain wall motion. Velocities near the speed of sound may not be reachable within the range of electric fields available below the breakdown field, 1.0 to $1.6\ \mathrm{MV\,cm^{-1}}$ for these films.

These time-resolved synchrotron x-ray microdiffraction experiments establish the reproducibility of the polarization switching process and the heterogeneity of polarization reversal in these ferroelectric thin films in the nanosecond time regime. Furthermore, synchrotron x-ray microdiffraction with the time resolution demonstrated in this letter is capable of quantifying transient structural processes at speeds up to those associated with the propagation of elastic deformations in crystals. The potential applications of this approach to ultrafast dynamics are not limited only to ferroelectric polarization switching, but include also a wide range phenomena, such as ferromagnetic and antiferromagnetic domain wall motion, the propagation of thermal waves in nanostructured materials, and the relationship between magnetism and polarization in multiferroics.

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