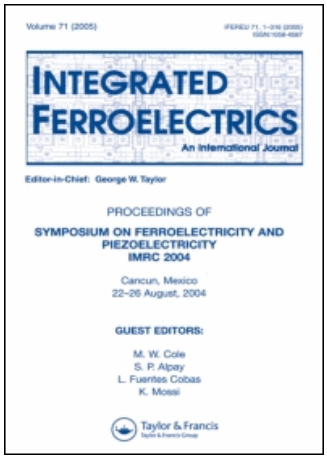

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Nanosecond Structural Visualization of the Reproducibility of Polarization Switching in Ferroelectrics

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ABSTRACT

As the polarization of a ferroelectric thin film reverses in response to an applied electric field, concomitant structural changes can be visualized using time-resolved x-ray microdiffraction. We report the details of this visualization approach and discuss the structural signature of polarization switching measured by time-resolved x-ray diffraction.

Keywords: Ferroelectrics; x-ray microdiffraction; polarization domain dynamics; time resolved scattering

The dynamics associated with polarization switching in ferroelectric devices have received continuous theoretical and experimental attention since the discovery of the remnant polarization of ferroelectric oxides [1, 2]. Even though the basic phenomena of domain nucleation and domain wall motion are reasonably well parameterized by conventional models, several important questions remain. For example, the relative importance of domain wall motion and nucleation, the scaling of domain wall velocities with the applied electric field, and ultimately the speed at which devices can be switched are not well known. The degree of repeatability of the domain wall dynamics from cycle to cycle of the electric field depends on these phenomena, and can be used to understand which processes are relevant in switching. Here we address the homogeneity and reproducibility of polarization switching in thin ferroelectric $Pb(Zr,Ti)O_3$ (PZT) films using time-resolved x-ray microdiffraction.

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Polarization switching is usually understood in terms of a three step model including the nucleation of polarization domains with the reversed polarization, the growth of domains along the electric field direction, and the finally lateral growth of domains involving motion of polarization domain walls. The usefulness of this model for thin ferroelectric films has been established in several experiments during last two decades [4–6]. Visualizing this process presents an experimental challenge since it is predicted that under some conditions it can take on the order of one nanosecond for a domain wall to propagate a lateral distance of 1 μm [1, 3]. We can address each of these steps independently using time resolved diffraction. Recently, for example, time resolved techniques have been used to probe the dynamics of polarization switching at scales of nanoseconds and hundreds of nanometers [7, 8].

The ferroelectric capacitors used in this study consisted of $Pb(Zr_{0.45}Ti_{0.55})O_3$ films of 300 and 400-nm thickness. The PZT film was grown on the top of conducting oxide electrode $SrRuO_3$ (SRO) on an (001)-oriented $SrTiO_3$ substrate. The top SRO electrode of 200 μm diameter was deposited on the top of PZT film using a shadow-mask process. The [001] crystallographic direction of the PZT film was oriented along the surface normal, so that the electric field applied between electrodes would have components only along the polarization direction. The preparation and characterization of this and similar complex oxide thin film heterostructures are described in detail in ref. [9].

X-ray scattering techniques have a combination of capabilities relevant to probing polarization switching in PZT thin films [7, 8, 10–12]. X-rays at hard x-ray photon energies penetrate micron lengths in solids, which makes x-ray characterization techniques particularly relevant in probing phenomena taking place in films confined between electrodes. At the Advanced Photon Source (APS), x-rays are generated in pulses with durations of tens of picoseconds and with small beam divergences. These x-ray beams can be focused using Fresnel zone plate optics to a spot of 100 nm or less. In our experiments we focused synchrotron x-rays with a photon energy of 10 keV from the APS to a 110-nm spot and synchronized the leading edge of an electrical pulse with probing x-ray pulses [7, 8]. Using this tool we probed the structural changes within time and spatial resolutions sufficient to image the growth of polarization switching domains in the PZT film.

The time resolved x-ray studies of polarization switching were pump-probe measurements in which the intensities of scattered x-ray beams were acquired over a number of switching cycles. Because the avalanche photodiode detectors used in these experiments were configured to count either one or zero photons per bunch the intensity measurements at each point in reciprocal space were integrated over 1000 cycles of the applied electric field to ensure adequate counting statistics. The results of an experiment measuring the c-axis lattice spacing of the PZT film using time resolved diffraction during electric field pulses with durations of several hundred ns are shown in Fig. 1. In order to

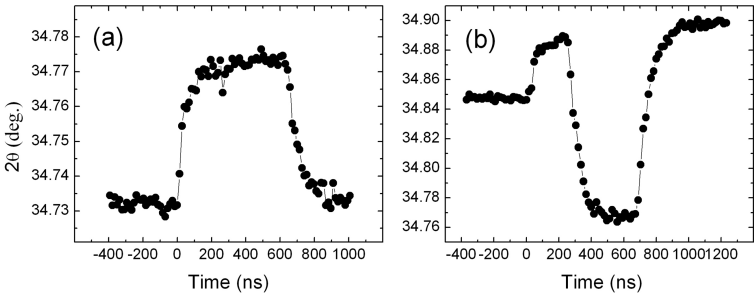

Figure 1. PZT (002) 2θ angle as a function of time during applied electric field pulses of (a) 200 kV/cm and (b) 500 kV/cm, measured with a photon energy of 10 keV.

measure the (002) PZT Bragg angle as a function of time, we applied 1000 $\times$ 101 $\times$ 21 = 2,121,000 cycles of the electric field. In Fig. 1a the electric field pulses had a single polarity and the only effect evident is the piezoelectric distortion of the lattice. For Fig. 1b the pulses alternated polarities and exceeded the coercive field, and the samples switched polarization in each cycle of the electric field. The initial distortion towards higher 2θ angles in this case is a result of the c-axis lattice constant initially decreasing in the applied field. The polarization switches at a time of 300 ns in Fig. 1b, resulting in a rapid decrease of the 2θ angle corresponding to an expansion of the lattice. The shift by 0.1° of the zero field 2θ angle between Figs. 1(a) and 1(b) is due to the injection of charge into the PZT film.

The leading and trailing edge transients (at 0 ns and 800 ns) of the time-resolved piezoelectric response shown in Figs. 1a and 1b reproduce the shape of leading and trailing edges of applied electrical pulses. From measurements of the piezoelectric effect with fast electrical pulses, we have obtained leading edge durations of 600 ps [13], which is an upper bound on the time resolution of this technique.

The structural signature of switching in Fig. 1b represents an average over a large number of cycles of the electric field and allows bounds to be placed on the degree of reproducibility of polarization switching. The transition caused by polarization switching signature occurs between approximately 250 and 400 ns in Fig. 1b.

Studies of the time at which polarization switching occurs as function of position are only meaningful if the switching time can be measured using time scans at a single diffraction angle close to the (002) PZT Bragg peak [7]. The time required for the complete measurement becomes impractically large if a large volume of reciprocal space must be probed. Measurements of the intensity as a function of time at fixed 2θ angles are shown in Fig. 2 for several spatial positions along a line on the sample. The switching time s is at the midpoint of the structural transient beginning at time a and ending at time b. The time

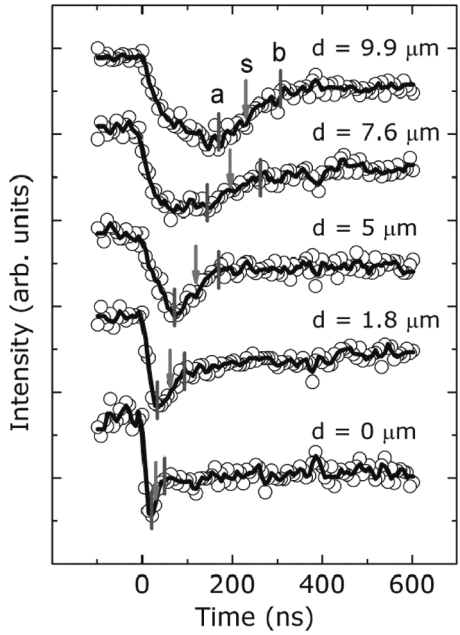

Figure 2. Time dependence of the x-ray intensities measured with $2\theta = 34.83^\circ$ at several positions on the PZT capacitor. Each curve is labeled with the distance from the position of the first measurement. The intensities at each position of the beam are offset vertically, after [7]. (See Color Plate IX)

at which a specific region of the sample switches polarization can be found by finding the time s as a function of position.

The piezoelectric effect alone, however, even without polarization switching can also lead to large changes in the intensity scattered to a fixed angle. In order to be sure that the transition between a and b in Fig. 2 is related to a reversal of the polarization, one can examine the intensities of the diffracted x-ray beams before and after the electric field pulse. The intensities of the (002) PZT Bragg peak before and after the switching pulse are compared in Figs. 3a and 3b for the $20\times 20\ \mu\text{m}^2$ area analyzed in [7]. The contrast ratio between the two polarizations (Fig. 3c) is uniform with most of the area producing a 30% change in the intensity of the (002) Bragg reflection. This change is consistent with the expected asymmetries in the intensities of beams from the (002) and $(00\bar{2})$ Bragg reflections of PZT. The asymmetry is a result of non-resonant anomalous scattering and agrees with the contrast observed in a quasi-steady-state experiment [12]. A closer examination of the maps of the contrast reveals that there are damaged areas in which the ferroelectric polarization is not switched by the applied electric field. In addition a few areas exhibit up to nearly 60% intensity

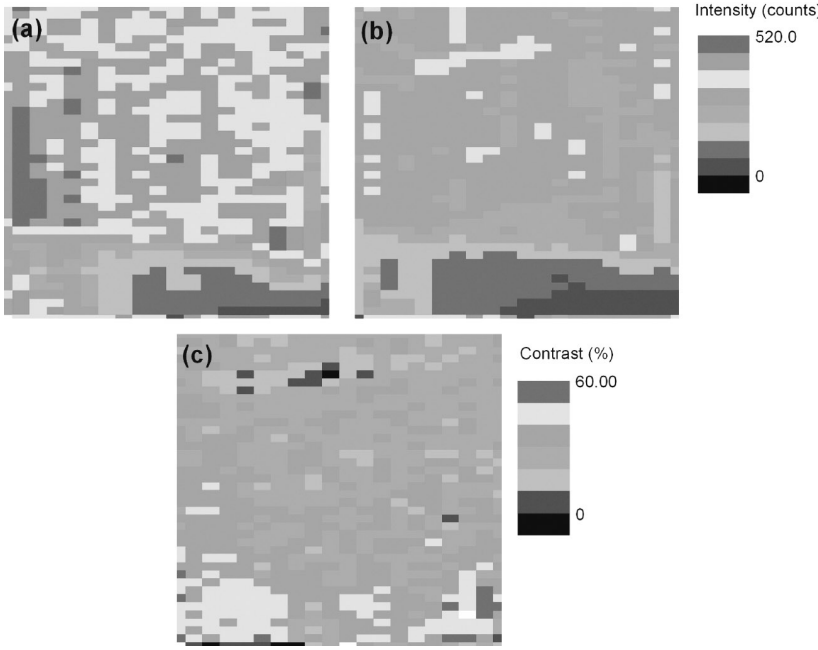

Figure 3. Intensity of the (002) Bragg reflection in a 20 × 20 μm^2 area (a) before and (b) after the switching electric field pulse of 230 kV/cm. The intensity contrast between (a) and (b) is shown in (c). (See Color Plate X)

change, which is likely due to a shift in the Bragg angle caused by charging of the PZT thin film.

The interval between times *a* and *b* in Fig. 2 can be used to understand the degree of reproducibility of the switching process. For example, in the extreme case where the nucleation of reversed domains and domain wall velocities and direction vary considerably from one switching cycle to another, the structural signature of polarization switching would be smeared across the entire time range of these measurements. However, since a transition is clearly observed in our experiments, the switching process must be reproducible within at least some bounds.

In the opposite extreme hypothetical limit the polarization switching would be completely reproducible, as if, for example, domains are nucleated heterogeneously and the domain wall velocities are exactly reproduced in each cycle of the electric field. The duration of the transition between times *a* and *b* in Fig. 2 in this case of extreme reproducibility is the time required for a polarization domain wall to propagate through the focused x-ray beam. A histogram of the transition durations for the area presented in Fig. 3 is shown in Fig. 4. The transition duration has a broad range of values centered at approximately 60 ns,

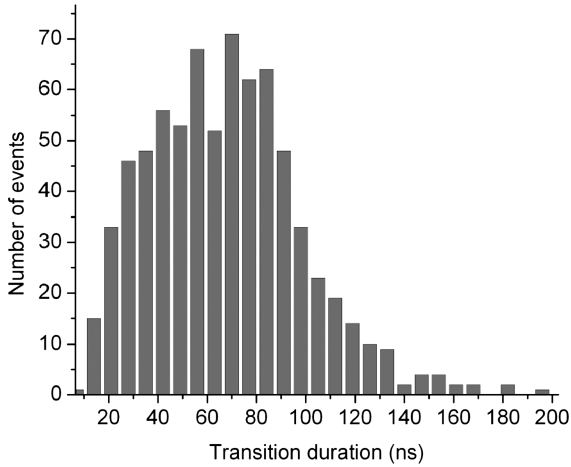

Figure 4. Histogram of the transition durations of the polarization signature switching within the PZT area shown in Fig. 3.

but extending from a few tens of ns to more than 100 ns. These durations are far greater than both the time resolution of the time resolved microdiffraction technique and the timing jitter of the measurement.

With an additional assumption that only one domain wall propagates through the x-ray spot, the value of the mean domain wall velocity required to produce the experimentally observed durations can be calculated. A combination of the aspect ratio of x-ray beams produced by synchrotron light sources and the asymmetric footprint of the focus beam on the sample surface combine to create an elliptical x-ray spot 110 nm by roughly 300 nm in total size. The mean domain wall velocity required to produce the durations shown in Fig. 4 would thus the range from 110 nm/60 ns = 1.83 m/s to approximately 6 m/s. This range of velocities predicted by this relation falls far below the value of 40 m/s, obtained using the time interval required for the domain to propagate over micron distances as shown in Fig. 5a. [7] The reproducibility of the polarization switching process thus lies somewhere in between the two extreme cases of completely reproducible and fully random switching.

The range of transition durations thus clearly indicates that the switching process involves a limited degree of randomness. Several potentially stochastic phenomena are thought to be active in polarization switching. For example, the nucleation of reversed domains and the propagation of domain walls during the polarization switching process can involve mechanisms that are thought to require thermal activation and are fundamentally random within some limits. These include some homogeneous contribution to nucleation and randomness in the discrete processes of domain wall pinning and creep. [5]

The lateral size of capacitor samples and the configuration of electrodes are extremely important in high speed measurements. In smaller capacitors the switching speed is reportedly faster, [14] in part because of reduced charging

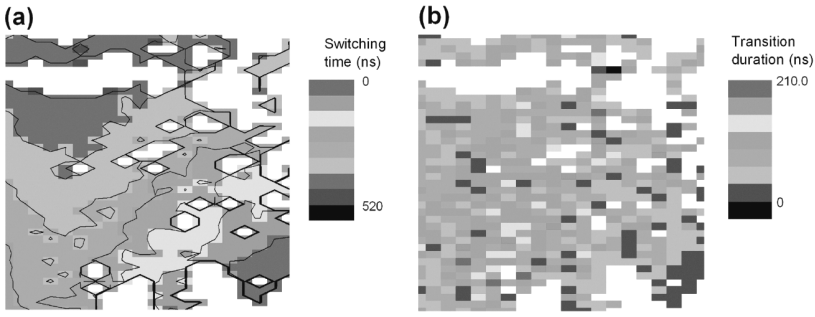

Figure 5. (a) Polarization switching times in a 20 × 20 μm^2 area of the thin film capacitor. The earliest and latest switching times are red and blue, respectively. It was not possible to unambiguously assign switching times to the white areas, after. [7] (b) Durations of the polarization switching transition in the same area as in Fig. 5a. (See Color Plate XI)

time constants and lower switching currents. We have developed strategies for isolating capacitors from initially uniform SRO/PZT/SRO heterostructures. A small ferroelectric capacitor for studies of polarization switching dynamics using time-resolved x-ray microdiffraction is shown in Fig. 6. This capacitor was isolated from the remainder of the SRO/PZT/SRO heterostructure using focused ion beam milling and can be contacted using two-probe high-frequency electrical connectors. The bridge structure to the top electrode limits the area in which polarization switching occurs and allows the device to be fabricated using only the three layers of the original heterostructure. These ferroelectric capacitor structures will aid in exploring the dynamics of polarization switching at higher speeds, and with lower uncertainties. In addition, because high-speed probes with large area contacts are used to make electrical connections to areas adjacent to the switching ferroelectric, these structures reduce the stress applied to the switching area by electrical contacts.

Based on our results the polarization switching in thin PZT film is controlled by heterogeneous nucleation of domains, which is highly reproducible in time and space. The duration time of the local polarization switching transition is longer than it would be in case of the absolutely reproducible switching process, indicative of a slight variation of the domain nucleation and propagation parameters.

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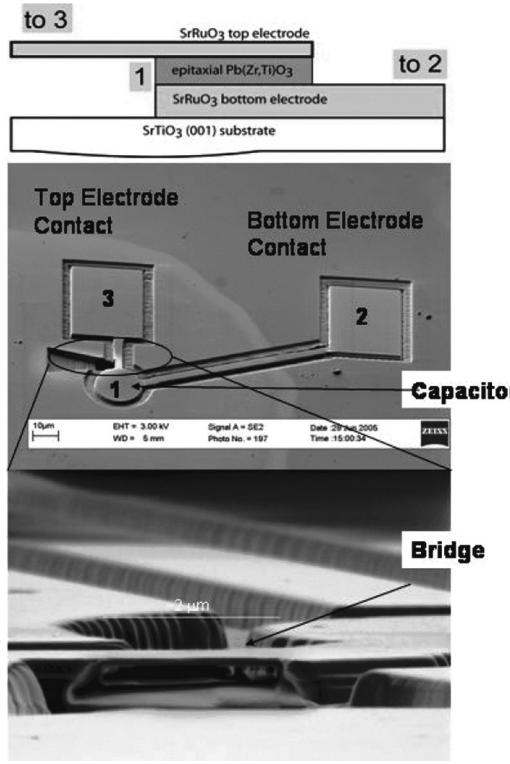

Figure 6. Ferroelectric capacitor structure for use with a two-contact high frequency electrical probe. The probe contacts connections to the bottom and top electrodes of the capacitor (1) in areas (2) and (3), respectively. The capacitor area 1 is isolated from the contacts using the bridge structure. (See Color Plate XII)

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