Mater. Res. Soc. Symp. Proc. Vol. 902E © 2006 Materials Research Society 0902-T06-09.1

Structural dynamics of PZT thin films at the nanoscale

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ABSTRACT

When an electric field is applied to a ferroelectric the crystal lattice spacing changes as a result of the converse piezoelectric effect. Although the piezoelectric effect and polarization switching have been investigated for decades there has been no direct nanosecond-scale visualization of these phenomena in solid crystalline ferroelectrics. Synchrotron x-rays allow the polarization switching and the crystal lattice distortion to be visualized in space and time on scales of hundreds of nanometers and hundreds of picoseconds using ultrafast x-ray microdiffraction. Here we report the polarization switching visualization and polarization domain wall velocities for $Pb(Zr_{0.45}Ti_{0.55})O_3$ thin film ferroelectric capacitors studied by time-resolved x-ray microdiffraction.

INTRODUCTION

An important problem in physics is the study of structural phase transitions in solid state systems. A displacive phase transition in ferroelectrics results in the reversal of the remnant polarization direction in response to a briefly applied electric field. This polarization switching in solid ferroelectrics, such as the perovskites $BaTiO_3$ or $Pb(Zr,Ti)O_3$ (PZT), is a complex process involving nucleation and growth of polarization domains. There are constraints on the transition speed, which is ultimately limited by the speed of sound to several km/s [1]. To resolve structural details of the polarization domain evolution it is essential to combine sub-micrometer spatial resolution and sub-nanosecond time resolution in one experiment.

The spatial resolution of traditional microscopies, scanning and transmission electron microscopies and scanning tunneling microscopy is sufficient in many cases to observe individual atoms. The time resolution of these methods is, however, fundamentally limited by probe-sample interactions and the response time of the probes that makes their application to structural dynamics problems seldom [2]. X-rays are better suited for studying dynamics. At present, the best time-resolution demonstrated in x-ray pump-probe experiment is less than 1 ps [3].

X-ray diffraction is not only sensitive to subtle changes of a lattice spacing of a crystalline solid but it is also able to distinguish between structurally similar polarization states using anomalous x-ray scattering [4]. The contrast between opposite polarizations is a result of the noncentrosymmetric unit cell of ferroelectrics. The (002) and (00-2) Bragg reflections of the tetragonal phase of PZT correspond to opposite polarization states and can differ in intensity by 30% or more [4]. The development of x-ray microscopy is closely coupled to advances in x-ray radiation sources [5]. The best spatial resolution of a synchrotron x-ray microscope in the hard x-ray energy range is now less than 60 nm [6]. Although the time-resolved x-ray scattering and

x-ray microscopy are well established techniques, the potential of their combination has not been exploited.

EXPERIMENTAL DETAILS

We investigated the piezoelectric structural response and polarization switching using ferroelectric capacitors consisting of thin $Pb(Zr_{0.45}Ti_{0.55})O_3$ (PZT) single crystalline film (tetragonal phase) between conducting $SrRuO_3$ (SRO) electrodes. The bottom SRO electrode was grounded and the signal line was connected to the top SRO electrode (figure 1). The diameter of the top electrode was 200 μm that defines the ferroelectric capacitor area.

Essential details of the time-resolved x-ray microdiffraction setup are shown in figure 1. Experiments were carried out at station 7-ID of the Advanced Photon Source (APS) at Argonne National Lab, IL, using 10 keV photon energy. The synchrotron x-ray beam was focused to a sub-micrometer size spot by Fresnel zone plate optics (Xradia, Concord, CA). The focusing spot size of 115 nm full width at half maximum (FWHM) was measured using a knife edge scan. The diffracted x-ray beam was detected using an avalanche photodiode (APD). X-rays are coming from synchrotron in short 100 ps FWHM pulses. This time defines the ultimate time resolution of our experiment. The actual time resolution of the experiment was defined by the 300 ps 10%-90% transient time of electrical pulses applied to the PZT capacitor by the pulse generator (Picosecond Pulse Labs, Inc., Boulder, CO). The electrical pulses were synchronized with incoming x-ray pulses. The electric field was applied to the PZT film in the surface-normal [001] crystallographic direction, which is the direction of the remnant polarization.

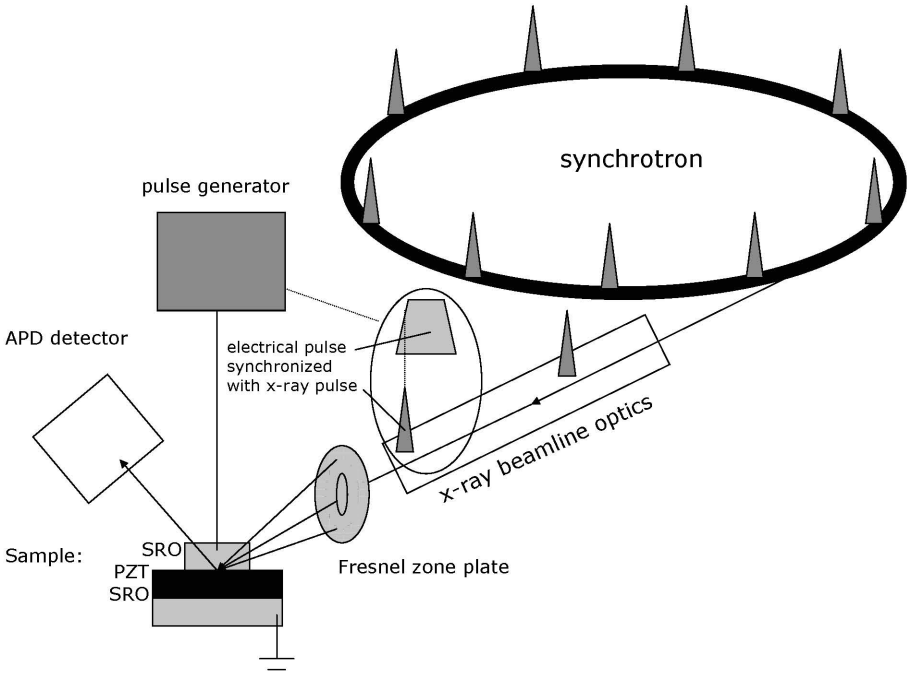

Figure 1. Time-resolved synchrotron x-ray microdiffraction experiment layout.

RESULTS AND DISCUSSION

An x-ray diffraction scan along the [001] crystallographic direction of the tetragonal PZT reveals several Bragg reflections corresponding to different components of our ferroelectric system (PZT, SRO and STO). Here our attention is entirely focused on the PZT (002) Bragg reflection. The peak position of the (002) reflection results from the periodicity of the lattice in the PZT [001] direction and can be considered as an indicator of lattice spacing changes caused by the piezoelectric effect.

Electrical pulses were applied to the sample with a time delay (positive or negative) relative to incoming x-ray pulses. The APD detector electronics was setup to count only x-ray pulses which have corresponding electrical pulses. By changing the time delay between an electrical pulse and an x-ray pulse, one can study the sample structure before, after, or during the applied electric filed. The lattice constant change of the PZT film reveals a sub-nanosecond response to the applied electric field 260 kV/cm (figure 2). The electrical pulses were of the same polarity so that the polarization direction was not switched.

When electrical pulses of alternating polarity are applied to the sample the polarization of the PZT film will be switched by each pulse, assuming that there is a sufficient magnitude of the applied electric field. It is important to establish an unambiguous procedure of measuring the polarization switching time. Although the intensity contrast of the (002) PZT Bragg reflection can be a solid indicator of the polarization switching, this contrast is difficult to measure when it is accompanied by dynamical changes of the electric field, lattice constants, and the width of the Bragg reflection. The piezoelectric response is a sufficient indicator of the polarization switching since the sign of the response depends directly on the polarization direction relative to the direction of the applied electric field. The **c** lattice constant is shown in figure 3 as a function of time. The electrical pulses used to measure the data in figure 3 were preceded by the pulses of the opposite polarity resetting the polarization direction. Since the data presented in figure 3 represent changes within only a 115 nm spot of the sample, the polarization does not switch until

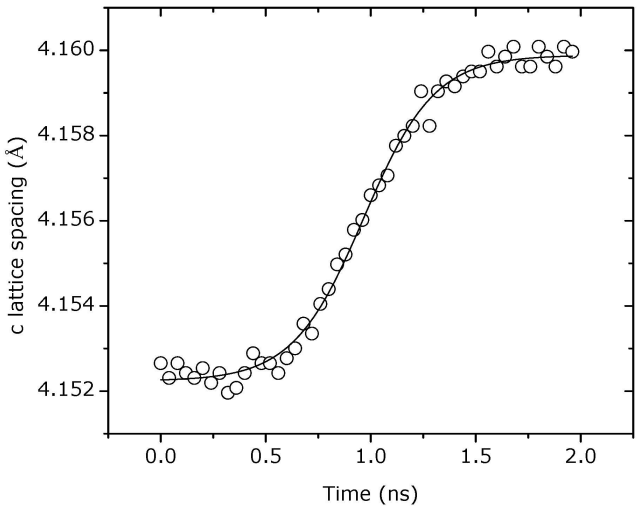

Figure 2. The **c** lattice constant of PZT as a function of time during the onset of electric field of 260 kV/cm. The 10%-90% transition time is 620 ps.

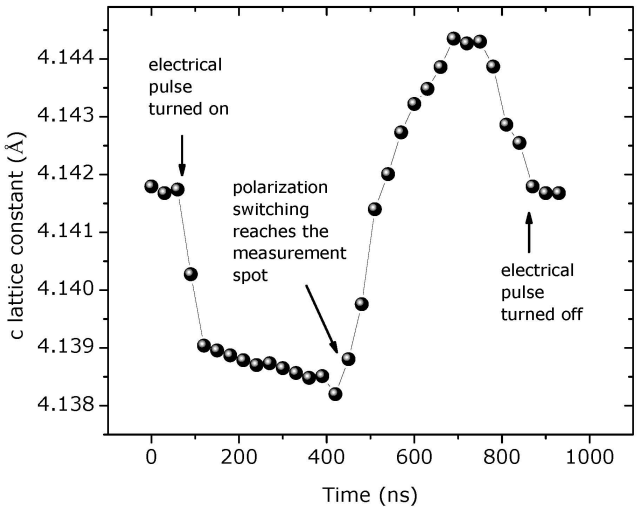

Figure 3. The **c** lattice constant as a function of time during 450 kV/cm electric field. The piezoelectric response direction changes at the time when the polarization domain wall reaches the measurement spot. The data are corrected for charging effects.

the switching domain reaches the observation spot. When an electric field is just turned on, the electric field and the polarization are anti parallel, resulting in a contraction of the c-axis lattice constant. Some time later the **c** lattice constant eventually increases at the time when the polarization domain reaches the spot of observation. If this switching time is measured systematically for different spots on the sample then the polarization switching domain evolution can be visualized in space and time.

The polarization domain structure is presented in several maps of a $19 \times 19\ \mu m^2$ region in figure 4. The maps are spaced in time during a 1 μs electrical pulse and show switching domain propagating through the PZT film. The mean value of the polarization domain wall velocity calculated using this visualization is 40 m/s. Although this speed is considerable slower than the speed of sound in PZT, it agrees well with recent measurements by indirect methods [7]. The electric field of larger magnitude necessary to reach significantly higher domain wall velocities will be more easily achieved in micron scale devices [8].

The high-field response of ferroelectrics can begin to be probed even in 100-μm-scale devices. The piezoelectric response of the PZT lattice depends on the ferroelectric capacitor thickness and the magnitude of the applied field. We have measured the magnitude of the piezoelectric response as a function of the electric field (figure 5). The saturation of $\Delta\mathbf{c}$ ($\Delta\mathbf{c}=\mathbf{c}(E)-\mathbf{c}(E=0)$) at high electric fields is likely due to a combination of non-linearity of the piezoelectric modulus d_{33} and a capacitive charging of the ferroelectric film [9].

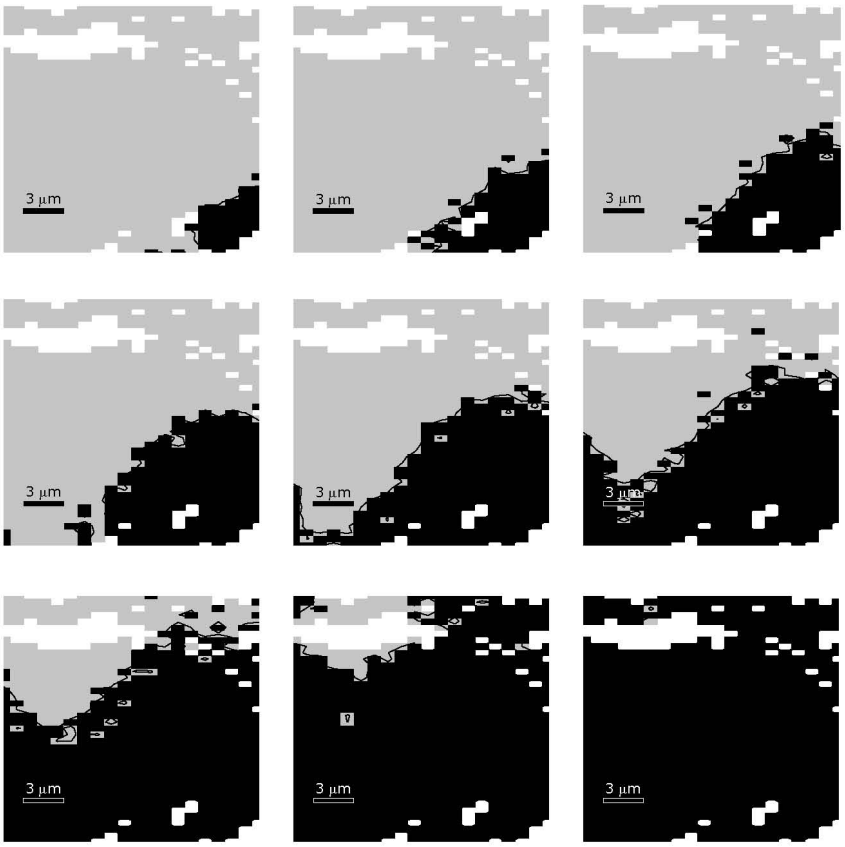

Figure 4. Polarization domain evolution in 19×19 μm^2 sample area during 450 kV/cm electric field applied to the PZT sample. The time step between maps is 50 ns. The scale bar is 3 μm. Gray and black areas correspond to opposite polarization directions.

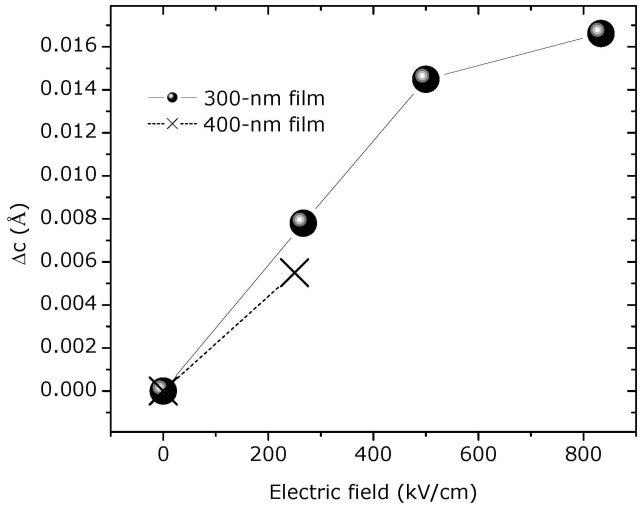

Figure 5. The change in the PZT **c** lattice constant as a function of the electric field.

CONCLUSIONS

The structural dynamics of ferroelectric thin film capacitors has been studied at sub-micrometer spatial and sub-nanosecond time scales by a combination of x-ray microdiffraction and ultrafast pump-probe techniques. Apart from structural dynamics in ferroelectrics the approach will be useful in resolving such important structural dynamics issues as the heat dissipation in nanostructures, magnetic domain evolution and shock wave propagation at the nanoscale.

ACKNOWLEDGEMENTS

This work was supported by the US Department of Energy, Office of Basic Energy Sciences. C.B.E. acknowledges support from NSF DMR-0313764 and ECS-0210449. Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

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