Synchrotron X-ray Microdiffraction Images of Polarization Switching in Epitaxial PZT Capacitors with Pt and $SrRuO_3$ Top Electrodes

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ABSTRACT

The evolution of stored ferroelectric polarization in PZT thin film capacitors was imaged using synchrotron x-ray microdiffraction with a submicron-diameter focused incident x-ray beam. To form the capacitors, an epitaxial $Pb(Zr,Ti)O_3$ (PZT) thin film was deposited on an epitaxially-grown conductive $SrRuO_3$ (SRO) bottom electrode on a $SrTiO_3$ (STO) (001) substrate. Polycrystalline SRO or Pt top electrodes were prepared by sputter deposition through a shadow mask and subsequent annealing. The intensity of x-ray reflections from the PZT film depended on the local ferroelectric polarization. With 10 keV x-rays, regions of opposite polarization differed in intensity by 26% in our PZT capacitor with an SRO top electrode. Devices with SRO electrodes showed just a 25% decrease in the remnant polarization after 10^7 switching cycles. In devices with Pt top electrodes, however, the switchable polarization decreased a by 70% after only 5×10^4 cycles.

INTRODUCTION

Ferroelectric oxides, including PZT, have excellent potential for electronic, photonic, and mechanical devices. One of the limitations of the use of PZT in memory devices is polarization fatigue, the reduction in the switchable polarization after repeated switching cycles. The development of polarization fatigue in operating devices can be influenced by the selection of electrode materials. PZT films with metallic oxide electrodes such as SRO, for instance, have shown little or no fatigue with 10^{10} or more switching cycles [1-3]. On the other hand, the use of elemental metal electrodes with PZT thin films leads to polarization fatigue within a relatively small number of cycles. Fatigue in capacitors with metal electrodes can be linked to interface defects caused by the migration of oxygen vacancies to the electrodes [3,4].

Since polarization fatigue is directly related to domain motion and is commonly thought to be caused by domain wall pinning or by the suppression of domain nucleation, it is useful to observe the behavior of ferroelectric domains. Techniques such as optical second harmonic microscopy [5], transmission electron microscopy (TEM) [6], and piezoresponse force microscopy (PFM) [7-9] have been used to investigate domain structure and motion. Among them, PFM, with 5-15 nm resolution, is the most common method for investigations of domain evolution. Since the scanned probe tip is often used as a top electrode, this approach can result in an inhomogeneous electric field and a potential drop between the tip and the sample surface due to a tip oxide [9]. Since the tip-sample interaction is an important factor, PFM can also be

sensitive to surface contamination. Synchrotron x-ray microdiffraction is a structural probe with sub-micron spatial resolution that provides a new way to observe the real space evolution of polarization domains and the development of fatigue in ferroelectric devices [10]. Since the absorption length of hard x-rays in common electrode materials is at least several microns, domains can be imaged through elemental metal or oxide electrodes. This allows measurements with realistic electrode compositions and under homogeneous electric field conditions. In this paper, we present synchrotron x-ray microdiffraction studies of the evolution of the ferroelectric polarization and the appearance of fatigue in PZT capacitors with SRO and Pt top electrodes.

EXPERIMENTAL DETAILS

Epitaxial $Pb(Zr_{0.45}Ti_{0.55})O_3$ films with thicknesses of 80 and 160 nm were grown by sputtering on SRO bottom electrodes on STO (001) substrates. Area-integrated laboratory x-ray diffraction measurements showed that the film was in a tetragonal structural phase and oriented almost completely with the c-axis normal to the surface. Two different top electrodes, SRO and Pt, were prepared for PZT capacitor devices. The SRO and Pt electrodes were sputter deposited on the PZT/SRO film using a 200 μm-diameter shadow mask, and then annealed under an oxygen atmosphere for 30 min. at 500 °C and 300 °C, respectively.

Synchrotron x-ray microdiffraction experiments were performed at beamline 7ID of the Advanced Photon Source of Argonne National Laboratory. A monochromatic beam of 10 keV x-rays was focused to an 800 nm diameter full width at half maximum spot using Fresnel zone plate optics [11]. A similar microdiffraction apparatus has been described by Cai *et al*. [12]. Images of the ferroelectric capacitor were formed by scanning the sample in real space while recording the intensity of the surface-normal PZT {002} reflection. Switching the polarization of the device also switches the indices of the surface-normal {002} reflection between (002) and $(00\bar{2})$. Oppositely polarized regions of the film were distinguishable based on the intensity of these reflections. Friedel's law, which normally requires that x-ray reflections with indices related by inversion have equal intensities [13], does not apply in this case because the atomic scattering factors are not purely real. This effect causes the (002) and $(00\bar{2})$ x-ray reflections of PZT to occur at the same Bragg angle but to have differing intensities. An identical mechanism has been used in x-ray topography experiments with lithium niobate since the early 1970's [14]. Electrical contact to the top electrode was maintained during the diffraction experiments using a 25 μm-diameter Pt wire spring which allowed diffraction experiments to be made on the majority of the area of the capacitor device. The x-ray experiments were performed without removing the sample from the diffractometer to apply external electric fields, which allowed measurements at identical reflection angles and sample position for each electrical polarization. Electrical measurements were performed using triangular voltage pulses applied to bottom electrode. The current from the device was recorded to produce hysteresis loops from which we obtained the switched polarization and coercive electric field.

RESULTS AND DISCUSSION

Relating x-ray microdiffraction and electrical measurements

Figure 1 shows the relationship between x-ray microdiffraction observations and electrical measurements of polarization switching in an 80 nm-thick PZT capacitor with a Pt top electrode.

Triangle wave voltage pulses of 500 μs total duration were applied to the bottom electrode with positive amplitudes 0.8, 1.2, 1.6, 2.0, and 2.8 V. Each positive pulse followed a -10 V pulse that reset the device to an initial polarization state. These positive pulse amplitudes were chosen to be near the coercive electric field measured using hysteresis loops, which corresponded to a voltage of 2.8 V. The pulses near this coercive voltage were thus expected to result in a partial reversal of the polarization of the capacitor. Following each pulse, images of the intensity of the surface-normal PZT {002} reflection were recorded (Figure 1(A)). The capacitor switched completely to the opposite polarization with a +10 V pulse. At intermediate voltages, however, the area of the region in which the intensity changed was proportional to the remnant polarization measured electrically (Figure 1(B)). We have thus empirically confirmed that the contrast observed in microdiffraction measurements following the voltage pulses is related to the *local* ferroelectric polarization.

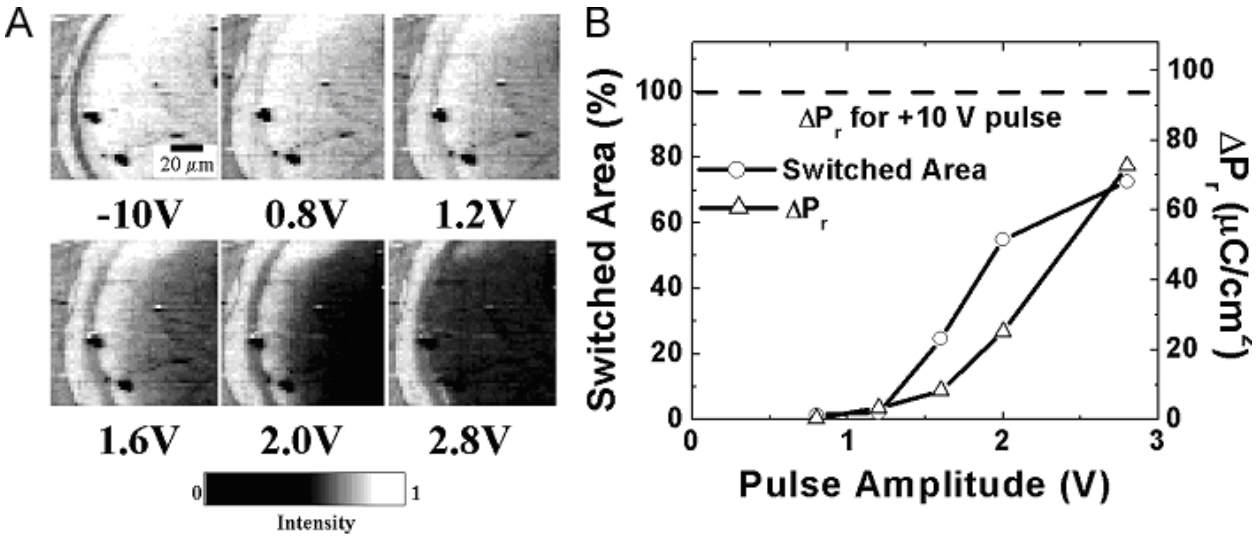

Figure 1. (A) Microdiffraction images of polarization reversal in a PZT sample with Pt electrodes. (B) The relationship between the switchable polarization measured electrically and the switched area fraction obtained from the x-ray microdiffraction images.

Fatigue in Capacitors with Pt and SRO Top Electrodes

A decrease in the remnant polarization of the PZT devices with Pt top electrodes occurred between 10^2 and 10^4 cycles in electrical measurements with 20 V peak-to-peak, 1 kHz triangle wave pulses (Figure 2). The switchable remnant polarization dropped to 30% of its initial value of $2P_r$=91 μC cm^{-2} after 5×10^4 cycles. The mechanisms of polarization fatigue in ferroelectric capacitors can depend on the composition of the top and bottom electrodes and it is commonly found that conducting oxide electrodes can lessen the effects of fatigue [15]. In addition, Stolichnov *et al*. have shown that fatigue-free behavior up to 10^{10} cycles can be obtained on conductive oxide electrode/PZT/Pt electrode or conductive oxide electrode/PLZT/Pt electrode using high electric fields [16]. However, significant degradation of switchable polarization is related to the PZT-Pt interface.

Unlike the Pt/PZT/SRO capacitors, the remnant polarization of symmetrical SRO/PZT/SRO devices switched by 10 V peak-to-peak 100 Hz triangle wave pulses decreased from its initial value of 107 μC cm^{-2} by only 25% after 10^7 cycles. Figure 3 shows pairs of images of a PZT

devices with an SRO top electrode following positive and negative voltage pulses at a series of steps in the total number of applied voltage cycles. Each image was taken at the remnant polarization state reached after applying negative and positive 5 V pulses, respectively. After 10 cycles, the positive and negative remnant states differed in intensity by 26%. The difference in mean intensities of the device images in the subsequent measurements are normalized to this difference. Figure 2 shows that the difference in the mean intensity of the device area in each pair of images is nearly always proportional to the switchable polarization. The approximately 10% variation of the intensity difference with the total number of cycles may indicate that even at a small number of cycles there are areas of the capacitor smaller than the x-ray spot size that are not completely switched by the voltage pulses. In the final pair of images, at 10^5 cycles, the intensity difference between the images is somewhat less than would be expected given the switchable polarization.

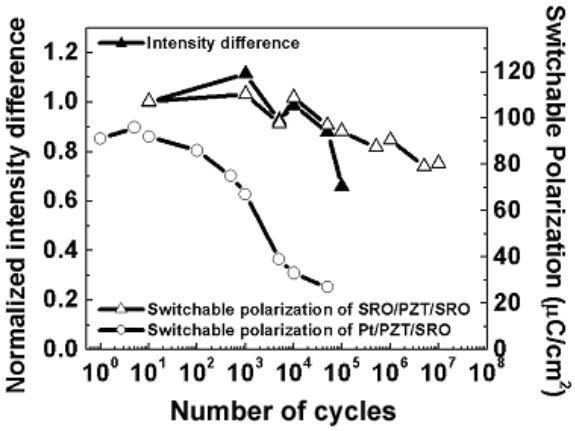

Figure 2. Intensity difference between oppositely polled states of SRO/PZT/SRO device (closed triangles) and remnant polarization of Pt/PZT/SRO (open circles) and SRO/PZT/SRO (open triangles) as a function of the number of cycles of the applied electric field.

A slight degradation of the switchable polarization in devices with SRO electrodes began at approximately 10^4 cycles of the applied field. We hypothesize that the eventual reduction in switchable polarization in this device is due to the degradation of the SRO top electrode. Scanning electron microscopy images show that the initially uniform contrast across the SRO top electrode evolved after 10^7 cycles to expose areas in which underlying PZT thin film was visible. Thus, after many voltage cycles, we surmise that the weak connections within electrode are partially broken – leading to an decrease in the effective active area of the SRO electrode and an decrease in the total area-averaged switchable polarization. Examining the pairs of images formed after 5×10^4 and 10^5 cycles shows that the intensity difference in the region marked with an arrow in Figure 3 was somewhat less than the average intensity difference. The coincidental appearance of the area of reduced switching within the area of these images may be the source of the discrepancy between the electrical and structural measurements of switching at 10^5 cycles.

CONCLUSIONS

We have investigated polarization switching and the development of fatigue in epitaxial PZT thin film capacitors with Pt and SRO top electrodes using synchrotron x-ray microdiffraction. Both x-ray and electrical observations showed that there was minimal

degradation in the switching in devices with SRO top electrodes, while capacitors with Pt electrodes showed rapid degradation after comparatively few cycles. X-ray microdiffraction measurements of the degree of switching and the total switched polarization agreed well with electrical measurements and hold promise as way to study ferroelectric devices at small length scales with quantitative structural specificity.

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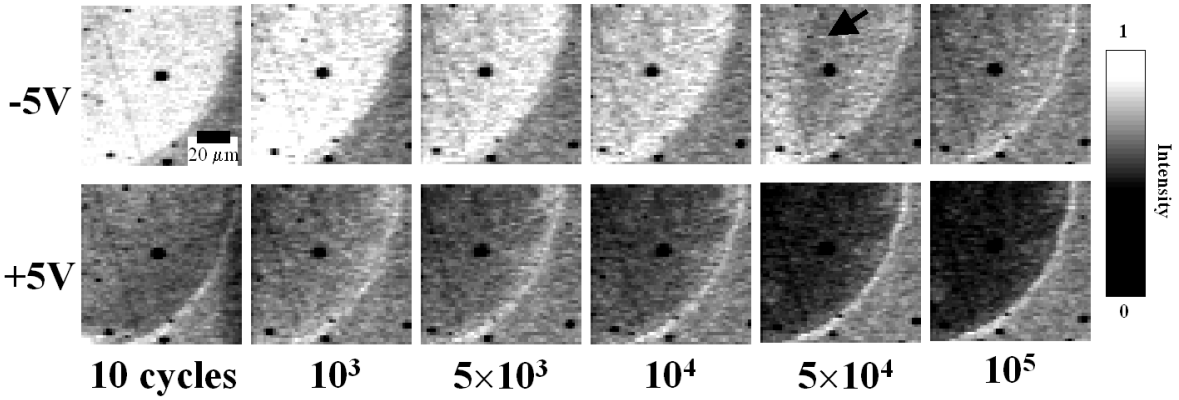

Figure 3. Images of the evolution of polarization in PZT capacitors with SRO top electrodes at up to 10^5 total cycles of the applied electric field. The 200 μm diameter SRO top electrode covers the area within the arc extending from lower left to upper right.

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