Domain Nucleation And Relaxation Kinetics In Ferroelectric Thin Films

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ABSTRACT

The time-dependent relaxation of the remanant polarization in epitaxial lead zirconate titanate ($PbZr_{0.2}Ti_{0.8}O_3$, PZT) ferroelectric thin films, containing a uniform 2-dimensional grid of 90° domains (*c*-axis in the plane of the film), is examined using piezoresponse microscopy. The 90° domain walls preferentially nucleate the 180° reverse domains during relaxation, with a significant directional anisotropy. Relaxation occurs through the nucleation and growth of reverse domains, which subsequently coalesce and consume the entire region as a function of time.

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Relaxation phenomena form a subject of continued scientific inquiry in view of their occurrence in diverse systems and processes. The time scales of such phenomena reflect a complex measure of the strengths of various participating interactions and the evolution of their mutually interdependent dynamics. Understanding of this kinetics is not only of interest from the fundamental standpoint, but is of critical significance to certain application areas, where the applicability of a material or a process is directly tied to the control of this kinetics. The phenomenon of ferroelectricity is one such case in point. Ferroelectric thin films have been attracting much attention recently for applications in non-volatile random access memories (NVRAMS), electromechanical sensors and actuators and as pyroelectric infrared detectors[1-3]. Specifically in the case of NVRAMS the ferroelectric thin film layer is switched into one of two remanant polarization states [+Pr or -Pr], corresponding to logic "1" and "0" states respectively. It is expected to remain in the written state until the subsequent read operation (retention).[4] The remanant polarization states are both thermodynamically metastable with respect to a multi-domain state. In high quality thin film capacitors, relaxation of the remanant polarization can be quite small over the time period of testing (typically a few days), and involves an interplay between fluctuations caused by local perturbations in the microstructure and/or depoling fields, leading to the nucleation and growth of reverse domains. Consequently, field or temperature accelerated testing is required to accentuate the relaxation process to enable experimental measurements and modeling of the relaxation behavior.[5] This can be achieved in different ways: a) by inducing depoling fields in the capacitor by changing the nature of the contact electrode(s) [6], and b) by eliminating the top electrode in the capacitor stack, as done in this research.

Piezoresponse microscopy, which we use in this work, has been employed to study the piezoelectric effect in ferroelectric lead zirconate titanate (PZT) films.[7-9] For our experiments, we used a commercial Digital Instruments Nanoscope IIIA Multimode atomic force microscope (AFM) equipped with standard silicon tips (radius 5 – 15 nm) coated with nickel silicide for electrical conduction. Further details are published elsewhere[10]. The ferroelectric films consisted of epitaxial 4000Å thick $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) films grown on a [001] single crystal $SrTiO_3$ substrate with a 500 Å thick La-Sr-Co-O (LSCO) layer as the bottom electrode. The details of the deposition process are given elsewhere.[11] The PZT film contained a uniform 2-dimensional grid of 90° domains (i.e., *c*-axis in the plane of the film). Such 90° domains have been shown to have a strong impact on the hysteretic polarization behavior of ferroelectric films.[12]

Piezoresponse image of the surface of the PZT film, Fig. 1(a), shows the presence of long, needle-like, orthogonal structures, which have been identified to be 90° twin domains[10] (denoted as T in the image) which form to relax the strains associated with lattice mismatch and phase transformation from the cubic (paraelectric) to the tetragonal (ferroelectric) phase.[13, 14] The image contrast in-between the needle-like regions is uniformly bright, suggesting that the entire region is pre-poled in a specific direction. This was confirmed by measurements of the piezo-hysteresis loop from a local region, Fig.1 (b), which showed a marked asymmetry indicating a built-in internal field. This as-grown state was then switched into the opposite state by scanning the surface of the film with the AFM tip biased at –10V (scan speed 1Hz.), leading to a strong change in image contrast from bright to dark, as observed in the inner part of Fig. 1(a). (We note that the "writing" did not rotate the polarization vector of the 90° domains from the in-plane to out-of-plane

configuration but we do expect it to rotate in-plane by 180º). However, we did observe that this switched state (in the *c*-axis regions of the film) began to relax back into the original state, the kinetics of which is the focus of this paper.

For the relaxation experiments, a 3μm x 3μm area of the sample was switched from its original state (bright contrast) to the reversed state (dark contrast) by scanning the film with the AFM tip biased at -10V. Piezoresponse images were recorded from the same region as a function of time, from a few minutes to several days. The polarization spontaneously reversed its direction, as illustrated in the sequence of piezoresponse images in Figs. 2(a-d). It is driven by an internal field present due to the asymmetry of the electrode structure. Nucleation of reverse domains was found to occur preferentially at the twin boundaries in the form of elliptical regions and was followed by the movement of the reversed regions through the crystal to cause polarization reversal. These observations were found to be very repeatable in several experiments conducted over various parts of the sample.

The observations presented in Fig. 2 suggested that we could use a square grid of orthogonal 90° domains to create a single "cell" with a lateral extent of about 200nm x 200nm, Fig.3 (a-d). Reversal in this case also nucleates primarily at the 90° domain boundaries and progresses inwards (identified as "P"). An important difference in this case was that for almost 1 hour, there was no measurable evidence of reversal in this cell, an aspect that is discussed further in Fig. 4. As the relaxation proceeded, we observed the formation of other secondary nuclei, identified as "S", which in this case appear circular in cross-section that ultimately coalesce with the secondary nuclei, as seen in (d).

Fig. 4 plots the fraction of the reversed region as a function of time for several different experiments including the data shown in Fig. 3. The data for the 200nm x 200nm single "cell" experiment is especially of interest since it reveals an early state during which there is no measurable reversal. This time period, t_0, is to be associated with the nucleation of a reverse domain in this cell. It is equally interesting that the large 3μm x 3μm cell data does not obviously show the existence of this nucleation time period. However, careful modeling of the data clearly reveals the existence of the "nucleation time" in the early stages of relaxation. The data presented in Fig. 4(a) was fitted with several functional forms, including the log-time, power law and a stretched exponential dependence of the polarization on relaxation time. We found that the stretched exponential model yielded the best fit, consistent with our earlier studies[8] and with the observations of Hong *et al.*[9] We discuss the fit for the 200nm x 200nm single "cell" relaxation first. In this case, if the data from the early stages of relaxation is included we obtain very poor fits with a conventional stretched exponential. Therefore, we performed the fits to the data with a constant t_0 added to the fit to yield $f = 1 - e^{-k(t-t_0)^n}$, where "f" is the area fraction of reversed polarization and k, n and t_0 are the key parameters defining the stretched exponential fit. This yields a constant, t_0, of the order of 2500 seconds, which we identify to be the time required to nucleate a reverse domain. The same functional form was used to fit the data for the 3μm x 3μm cell; as shown in Fig. 4(b), we obtain an excellent fit for the data with the key parameters (k, n and t_0) very close to those for the 200nm x 200nm single cell data. Subsequently, we have repeated both these experiments and have obtained essentially the same values of k, n and t_0.

We now summarize this paper with some discussion of the key observations. This paper clearly shows that polarization reversal occurs through the nucleation and subsequent growth of reverse domains. Nucleation appears to occur almost exclusively at heterogeneous sites; in this specific case these sites are the 90° domain wall surfaces. The key to understanding the relaxation kinetics is the physical meaning of the three parameters, namely t_0, k and n. t_0 is the time required to nucleate a reverse domain that is larger in size than a critical nucleus. Closer examination of the images obtained for the 200nm x 200nm cell experiment showed that indeed first nuclei appear at about 2000-2500 seconds after the relaxation process has begun with a size of the order of 20-30 nm in lateral dimensions. We note that this size also corresponds to the resolution limit of our experiment; therefore we would have to treat this value as an upper bound on the critical nuclei size; once this size is reached, growth is much more rapid. $(1/k)^n$ is a decay constant which provides a measure of the time required for the polarization to relax to e^{-1} of the starting. The term "n" is the stretching parameter, which coupled with "k" provides the full measure of the relaxation kinetics. Seeking a connection between n and k, and the intrinsic energy and frequency (time) scales corresponding to the basic interactions and elementary excitations in the system, remains a formidable challenge for the theory.

Stretched exponential relaxation phenomena are observed in many materials systems, including time decay of remanant magnetization in spin glasses and dispersive transport of hydrogen through amorphous silicon.[15-18] An important point to note is that in all these cases, one is describing the kinetics of point objects (i.e., magnetic spins in the spin-glass, transport of hydrogen atom, etc.). In our experiments, however, we are measuring the kinetics of motion of an interface (i.e., the interface separating regions

poled "UP" from those poled "DOWN"). It is tempting to correlate the stretched exponential relaxation behavior to the transport of point defects, such as oxygen vacancies to and away from domain surfaces as being responsible for the local reversal of polarization. Although this is one likely scenario, it is not apparent that it is the only possibility. Thermal and field activated relaxation measurements, which are currently in progress, will enable us to better elicit the fundamental origin of the observed kinetics.

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FIGURES:
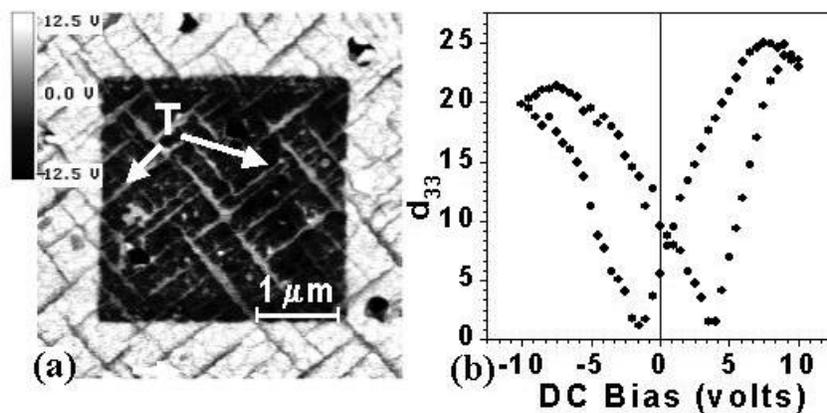
Figure 1: (a) 4μm x 4μm piezoresponse scan of the 4000Å thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film. *a*-domains are identified by the letter "T" in the image. A 3 μm x 3μm area in the center of the scan has been switched into the opposite polarization state by scanning the surface with the tip biased at –10 volts. (b) Piezoresponse hysteresis loop obtained from a region between two *a*-domains.
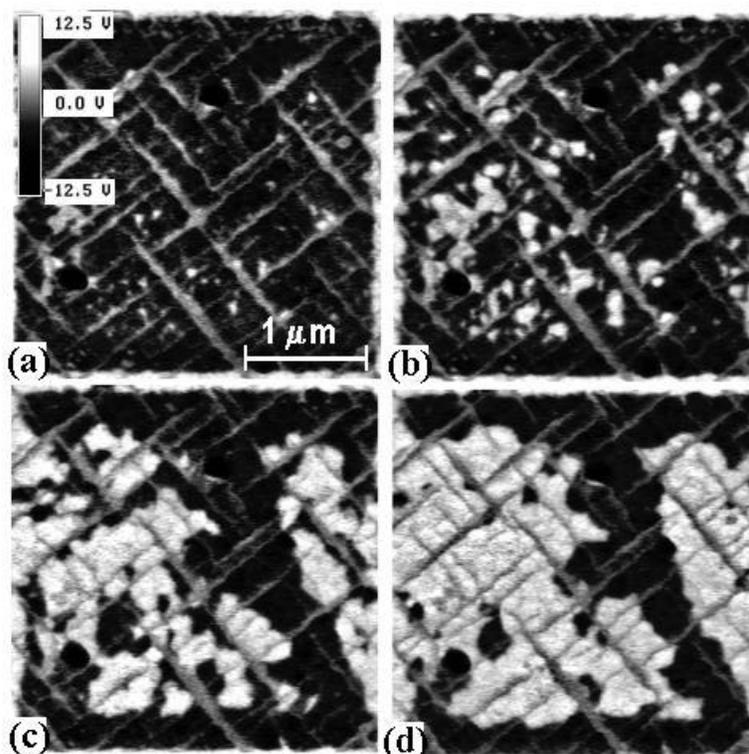
Figure 2: (a) through (d) Piezoresponse images of the 3μm x 3μm area from figure 1(c) which was switched into the opposite polarization state by scanning the surface with the tip biased at –10 volts. Images taken after wait times of (a) 3.1 x 10^3 s, (b) 9.9 x 10^3 s, (c) 7.5 x 10^4 s and (d) 2.6 x 10^5 s.
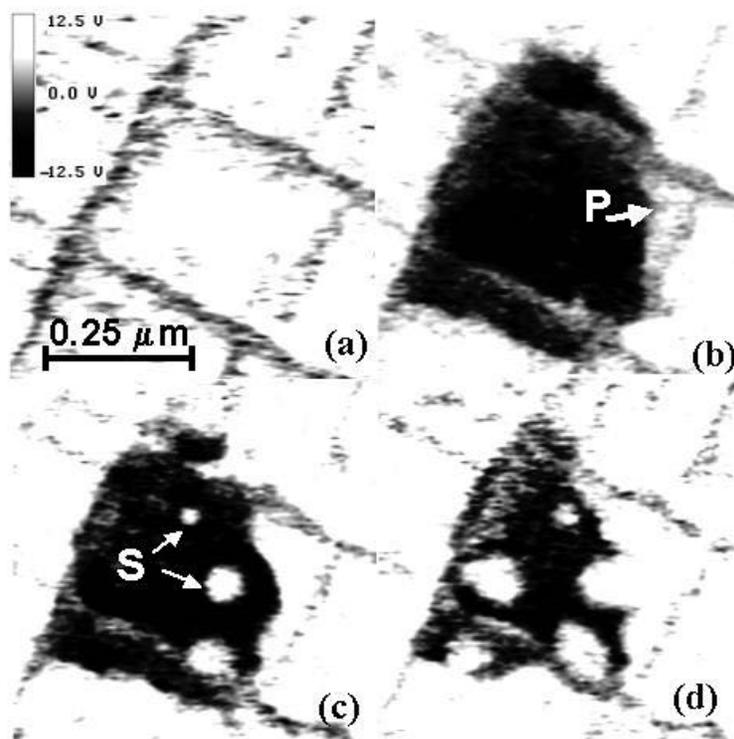
Figure 3: (a) Piezoresponse scan of a single "cell" in PbZr$_{0.2}$Ti$_{0.8}$O$_3$. Figures (b) through (f) illustrate the spontaneous reversal of polarization within this region after wait times of (b) 2.8 x 10^3 s, (c) 5.7 x 10^3 s and (d) 1.8 x 10^4 s.
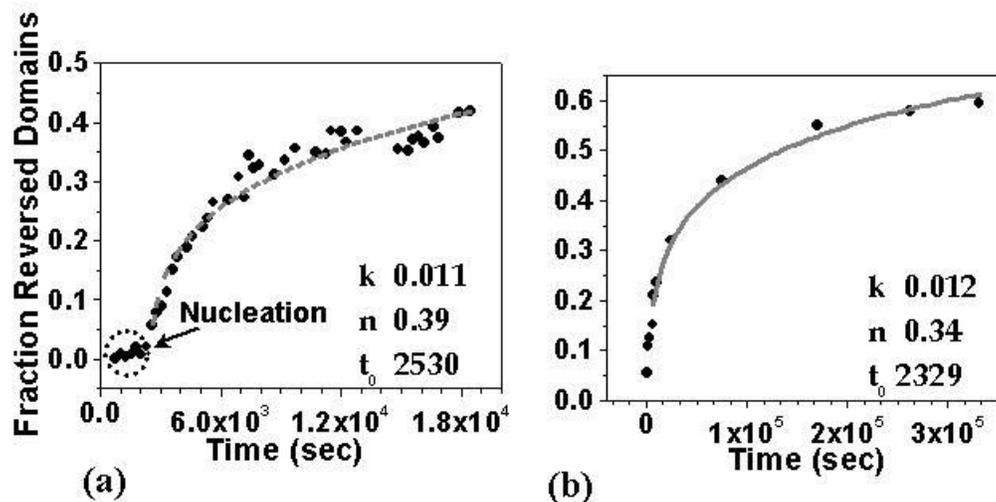
Figure 4: Fraction of reversed domains plotted as a function of time for (a) single "cell" area, approximately 250nm x 250nm (see figure 3 (a) through (d)) and (b) for a 3μm x 3μm area (see figure 2 (a) through (d)).