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First-order morphological transition of ferroelastic domains in ferroelectric thin films

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Abstract

Ferroelastic domains are common defects in epitaxial ferroelectric thin films, being typically observed around interfacial dislocations due to attractive elastic interactions. Because of their large stress fields, domain size and shape can influence local ferroelectric switching behavior. Here the morphology of ferroelastic domains in $Pb(Zr_{0.2}, Ti_{0.8})O_3$ thin films is investigated as a function of film thickness and substrate strain using phase field modeling in combination with transmission electron microscopy. Increasing film thickness or strain is found to induce switching from typical ferroelastic domains extending to the free surface of the film to nanosized domains localized near the substrate interface. An analysis of thermodynamic properties reveals hysteretic and discontinuous changes in the first derivatives of the free energy resulting from competing electrostatic and elastic energies. Such first-order morphological transitions are expected to be very common in epitaxial thin films during switching under an external electric or stress field.

Keywords: Ferroelectric; Phase morphology; Ferroelastic; Domain structures; Phase field modeling

1. Introduction

Materials in practical applications are generally structurally inhomogeneous and contain mesoscale morphological structures such as domains, grains or secondary phases that dictate properties critical to optimizing performance. At small length scales and near free surfaces, mesoscale structures are known to undergo several types of morphological transition [1–7]. For example, in magnetic fields abrupt transitions between vortex domains and single domains occur with decreasing particle size [1,2], and in thin films under elastic stresses twin boundaries form above a critical thickness [3,4]. Similar transitions in ferroelectric materials such as $Pb(Zr_x,Ti_{1-x})O_3$ are particularly interesting because of the possibility of using these materials in miniaturized electronic devices such as non-volatile high density random access memory [8–10]. Wang et al. used a modeling approach to show that nanosized ferroelectric particle domain structures depend on the system size and transition from a single domain to a more complex ferroelastic domain structure with decreasing aspect ratio [7].

Ferroelastic domain structures in tetragonal $Pb(Zr_{0.2}, Ti_{0.8})O_3$ PZT thin films are similarly affected by geometric constraints. The fraction of these domains, for instance, has been reported to decrease with film thickness [11,12] and coherency strain [13–16]. Commonly, ferroelastic domains in tetragonal PZT thin films on $SrTiO_3$ (STO) substrates become pinned by attractive elastic interactions with interfacial dislocations [17–19] that form during film growth to reduce the coherency strain [20,21]. Recently, high-resolution transmission electron microscopy (HRTEM)

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observations have shown that the domain morphology around these interfacial dislocations may change based on the local elastic conditions in the film. Ferroelastic domains in very thin compressively strained films and in films with little compressive coherency strain are observed to extend completely through the thin films [12]. This allows the 90° domain walls to lie on {1 0 1} planes that are both elastically coherent [22] and charge neutral. Small, tapered ferroelastic nanodomains, however, have been observed in thicker films around interfacial dislocations [12,23]. In contrast to typical ferroelastic domains in thin films, these nanodomains remain localized to within a few tens of nanometers of the substrate.

Ferroelastic domain configuration may have a disproportionately large impact on the thin film switching behavior because of strong electromechanical coupling in ferroelectric thin films [24,25]. In their investigation of the structure of static needle ferroelastic domains in bulk $PbTiO_3$ Novak et al. showed the needle domains to be associated with extended stress field distributions [26], which would make the domain particularly active during switching [27]. This study, however, did not account for the effect of the electric field around the needle domain. In fact, motion of domain walls in response to an applied electric field is thought to contribute up to 50% of the total response of a thin film [28–30] so that understanding their electrostatic and stress fields along with the ferroelastic domain geometry is critical to building reliable ferroelectric devices.

While both full ferroelastic domains extending completely to the thin film surface and partial ferroelastic domain terminating in the thickness of the film have been observed in epitaxial PZT thin films, the transition between the two with system geometry has not been previously investigated. Here we use phase-field simulations and HRTEM observations to investigate the morphology of ferroelastic domains associated with interfacial dislocations. We find that the domain geometry depends on the dimensions and elastic state of the thin film. Isolated ferroelastic domains are found to abruptly transition between typical full ferroelastic domains and nanosized partial domains with increasing film thicknesses or local coherency strain. These two domain configurations have very different local electrostatic and elastic states. Partial domains in particular are found to be associated with large built-in fields generated due to the inability of the partial ferroelastic domains to form low energy boundaries with the surrounding domain. These fields are largely absent around full domains. We also investigate the changes in the total free energy of the system throughout the transition and show that the first derivative of the free energy is discontinuous, demonstrating a first-order morphological transition in the system. Changes in the energy of the system between the domain configurations lead to hysteresis in the transition thickness or strain state. Our results provide new insights into the interactions governing domain morphologies in thin films. Large changes in the local state of the film along with the newly observed hysteresis in the domain structure have the potential to strongly impact local switching dynamics. Furthermore, this new understanding may illuminate the causes of other similar ferroelastic domain structure transitions.

2. Methods

2.1. HRTEM

We prepared a thin film PZT sample to observe the structure of the ferroelastic domains by growing a 50 nm thick epitaxial (0 0 1)-oriented PZT thin film on an STO substrate using pulsed laser deposition at 600 °C. Samples were prepared for microscopy by cross-sectioning the thin film and thinning the cross-sections with mechanical polishing and argon ion milling to electron transparency. Lattice images around ferroelastic domains in the sample were captured using a spherical aberration (C_s) corrected FEI Titan (TEAM 0.5) microscope operating at 300 kV. From these images specific atom positions were determined by fitting two-dimensional (2-D) Gaussian peaks to an a priori perovskite unit cell for PZT. Polarization was calculated by measuring the displacement of the Pb cations relative to the center of the surrounding Ti/Zr cation lattice. The geometric phase analysis technique used here was performed using the free FRWRtools plug-in for digital micrograph by Koch [31] based on the original work by Hÿtch et al. [32] and Hÿtch and Plamann [33]. More details about image processing and determining polarization distributions can be found in Ref. [34] and references therein.

2.2. Phase field modeling

Phase field modeling [13,35,36] was used to characterize the morphological transition between domain states. Equilibrium domain structures were determined by evolving the polarization, $\boldsymbol{P}$, through the time-dependent Ginzburg–Landau equation [37]:

$$\frac{\partial P_i}{\partial t} = -L\frac{\partial F}{\partial P_i} \tag{1}$$

with kinetic coefficient, L, to minimize the total free energy of the ferroelectric system, F, which consists of contributions from the bulk free energy density, f_{bulk}; the electric dipole interaction energy density, f_{electric}; the elastic strain energy density, f_{elastic}; and the polarization gradient energy density, f_{gradient}. Integrating over the film volume gives the total free energy as

$$F = \int_V \left[f_{\text{bulk}}(P_i, T) + f_{\text{electric}}(P_i, E_i) + f_{\text{elastic}}(P_i, \varepsilon_{ij}) + f_{\text{gradient}}(P_{i,j})\right] \mathrm{dV} \tag{2}$$

Bulk free energy density of the system was modeled with the sixth-order Landau polynomial developed by Haun et al. [38] for stress free $Pb(Zr_{0.2}, Ti_{0.8})O_3$,