Acta Materialia 112 (2016) 285–294

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Phase field simulation of charged interface formation during ferroelectric switching

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ARTICLE INFO

Article history:
Received 10 January 2016
Received in revised form
31 March 2016
Accepted 8 April 2016

Keywords:
Ferroelectric
Domain boundaries
Phase field modeling
Thin films
Domain switching

ABSTRACT

Ferroelectric switching in thin films is a local process strongly influenced by the presence and spatial distribution of defects such as dislocations, grain boundaries and preexisting domains. Preexisting ferroelastic domains have been shown to inhibit 180° switching in (001)-oriented epitaxial $Pb(Zr_{0.2},Ti_{0.8})O_3$ (PZT) films, but ferroelectric switching pathways around these domains remain unclear. Here, phase field modeling with supporting high resolution transmission electron microscopy is used to investigate ferroelectric switching in PZT thin films around such a ferroelastic domain. We show 180° domain wall motion is arrested at moderate applied biases by the ferroelastic domain through formation of charged 90° domain walls during switching. This leads to an increased applied bias required for complete switching through the thin film. Charged 90° ferroelastic domain walls are found to be partially stabilized by local rotation of the polarization direction and significant broadening of the head-to-head wall to distribute the bound charge, leading to domain walls 5–6 nm in thickness compared to 0.5–2 nm for typical 90° domain walls. Ferroelectric switching continues only at higher applied electric fields. This study provides a more complete picture of the ferroelectric switching pathway around ferroelastic domains than has been previously available and may explain the experimentally observed lower stability of written domain structures around preexisting ferroelastic domain structures in epitaxial ferroelectric thin films.

1. Introduction

Complete switching of a polarization state is critical to a number of applications for ferroelectric thin films. Typical epitaxial thin films contain myriad domains each with an individual polarization state that are separated by domain walls with intermediate polarization. Reorienting the polarization in a ferroelectric crystal generally requires significant motion of these domain wall and a reduced switchable component of the polarization has been observed in systems with only limited domain wall mobility [1]. In perovskite ferroelectric thin films 180° domain wall motion has been widely reported to be inhibited by the existence of various defects in a film such as dislocations [2–4], free charge carriers [5–7], grain boundaries [8], or preexisting ferroelastic domains [9], which are able to locally pin domain walls through elastic and electrostatic interactions or screening of applied electric fields. With recent advancements in the quality of epitaxial thin films, however, concentrations of many of these defects can be reduced or eliminated in epitaxial $Pb(Zr_{0.2},Ti_{0.8})O_3$ (PZT) thin films. Above a critical thickness of about 100 nm, however, ferroelastic domains with a polarization rotated by 90° form dense domain structures to reduce elastic coherency strain in the film [10,11]. Due to the strong elastic driving force for formation of ferroelastic domains, this type of defect is difficult to avoid during film fabrication. As a result, understanding the ferroelectric switching behavior of ferroelastic domains in thin films is essential to the development of ferroelectrics for microelectronic applications.

Several studies have shown ferroelastic domains play critical roles in polarization switching in epitaxial PZT thin films [1,10,12–17]. Preexisting ferroelastic domains are often immobile in constrained thin films [3,9,18] and inhibit complete ferroelectric

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http://dx.doi.org/10.1016/j.actamat.2016.04.026
1359-6454/

switching when a film is poled [10,12,13]. Therefore, substantial increases in the remnant polarization and dielectric response can be achieved by increasing the mobility of these domains [1,15,16] or removing them entirely [19]. Internal ferroelastic domains have also been reported to degrade performance of ferroelectric devices by decreasing the stability of switched domains and rapid back-switching of written domains to the original domain configuration has been observed to begin near ferroelastic domain walls in PZT thin films [17].

The mechanism by which preexisting ferroelastic domains inhibit 180° switching and reduce the stability of written domain structures in PZT thin films remains unclear, however. Several studies have suggested that trapping of point defect dipoles around ferroelastic domains creates a built-in electric field that reduces the coercive field to back switching [7,19,20]. Quenching a random dipole structure in $BiFeO_3$ thin films, for instance, has been shown to reduce back switching of ferroelectric domain structures [7,16]. Defect-induced dipoles, however, may not exist in high densities in annealed thin films with low concentrations of oxygen vacancies. Other studies have indicated that back switching around 90° domain structures in tetragonal PZT is the result of depolarization fields created by incomplete switching of preexisting ferroelastic domains [17,21]. These depolarization fields were thought to be created by the formation of charged 90° domain walls between switched domains and preexisting ferroelastic domain walls. No charged domain walls, however, were directly observed in these studies since only surface sensitive techniques were used.

To overcome this limitation Gao et al. [12] used high resolution transmission electron microscopy to observe *in situ* ferroelectric switching around an embedded ferroelastic domain. In contrast to previous results, charged 90° domain walls formed during the switching process were found to remain stable once the applied electric field was removed. Tan and Shang [22] showed similar charged 90° domain walls between ferroelastic domains were created by the intersection of ferroelastic domain during switching of PMN-PT bulk crystals. These systems, however, appeared to be influenced by local dislocations noted in both studies. Tan and Shang, in particular, directly observed the creation of partial dislocations at the charged interface. Once stabilized by dislocations, the charged interfaces did not immediately revert to the original domain structure in the thin film. Ferroelectric switching behaviors in these films are clearly dependent on creation of charged 90° interfaces, but switching near ferroelastic domains in thin films free of dislocations remains poorly understood.

In this manuscript we report on phase field modeling and high resolution transmission electron microscopy of switching around an embedded ferroelastic domain in a $Pb(Zr_{0.2},Ti_{0.8})O_3$ epitaxial thin film using an inhomogeneous electric field generated by a local probe. Formation of transient charged domain walls at preexisting ferroelastic domains is observed during ferroelectric switching around an immobile ferroelastic domain. These charged domain walls are found to persist over a range of applied biases even without local dislocations, inhibiting complete switching through the thickness of the film at small applied electrical biases. The relative stability of charged 90° domain walls during switching is demonstrated to be the result of a reduction in local depolarization electric field at the domain wall associated with broadening of the charge distribution at the interface, which reduces the electrostatic energy and results in a partially stabilized domain wall. These results help explain back switching caused by incompletely switched 90° domains [17] and have implications for the role high-energy, charged domain interfaces have in the switching dynamics of ferroelectric thin films.

2. Simulation method

Evolution of the ferroelectric domain structures during switching was modeled in an epitaxial, (001)-oriented $Pb(Zr_{0.2},Ti_{0.8})O_3$ thin film using the phase field approach [23–25]. Polar domains in the system were described using a continuous vector field representing the three principal components of polarization in the system. Evolution of this vector field with time, t, during ferroelectric switching was modeled by solving the time dependent Ginzburg-Landau equations [24,26,27].

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

which evolve the components of the polarization, P_i, toward the minimum in the free energy of the thin film, F, with respect to the distribution of polarization in the film. In Eq. (1) L is a kinetic coefficient related to the domain wall mobility of the system. Ferroelectric domain structures were modeled in a coherent thin film on a thick substrate that was allowed to relax for a short distance beneath the thin film [27]. Allowing the substrate to partially relax is necessary to accommodate the domain structure in the thin film. A short distance from the film interface, the substrate was assumed to reach a bulk, unperturbed state. The system was also assumed to be much larger in lateral extent than in thickness and as a result periodic boundary conditions were used in the two in-plane directions while specific boundary conditions were used in the out-of-plane direction.

Total free energy in Eq. (1) consists of four contributions, the bulk free energy, f_{bulk}; the gradient energy, $f_{gradient}$; the electrostatic interaction energy, $f_{electric}$; and the elastic interaction energy, $f_{elastic}$, integrated over the volume of the film, V:

$$F = \int \left[f_{bulk} + f_{gradient} + f_{electric} + f_{elastic}\right] dV \tag{2}$$

The bulk free energy density was used to describe the local energy of the stress free crystal using the sixth order Landau polynomial

$$f_{bulk} = \alpha_i P_i^2 + \beta_{ij} P_i^2 P_j^2 + \gamma_{ijk} P_i^2 P_j^2 P_k^2 \tag{3}$$

with the phenomenological coefficients α_i, β_{ij}, and γ_{ijk} measured by Haun et al. [28] Repeated indices in Eq. (3) indicate summation over the repeated indices. For simplicity the gradient energy was assumed to be isotropic [29,30], leading to the expression for gradient energy of

$$f_{gradient} = G_{ij}\left(\partial_j P_i\right)^2 \tag{4}$$

Interactions between bound charges in the system lead to the electrostatic energy density in the system [31,32].

$$f_{electric} = -E_i P_i - \frac{1}{2}\varepsilon_0 \kappa_{ij} E_i E_j \tag{5}$$

where E_i is the ith component of the total electric field from the applied electric field and the depolarizing electric field, E_i^b, created by bound charges around the polarization distribution. In Eq. (5) ε_0 is the permittivity of free space and κ_{ij} is the background dielectric constant of PZT [33], which is assumed here to be isotropic and have a value of 100. Values of the dielectric constant between 10 and 200 were also tested and found to yield qualitatively similar results, but a thorough discussion of the effects of the dielectric constant on the phase field simulation is beyond the scope of this article. Electric fields around bound charges are