

Edge and finite size effects in polycrystalline ferroelectrics

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Abstract

This paper proposes a method to engineer the effects of mesa aspect ratio on polarization switching for single-crystal and polycrystalline PZT nanostructures. The out-of-plane polarization switching of single-crystal and polycrystalline structures as a function of crystallographic orientation, epitaxial strain and mesa aspect ratio are explored. The results are summarized in terms of the mesa geometrical parameters, crystallographic orientation and epitaxial strain. The results demonstrate a strong correlation of single-crystal properties to the polarization hysteresis behavior of a central representative grain in a polycrystalline film. The average remnant polarization and its reliability are controlled through the aspect ratio of the mesa. Calculations demonstrate that the stresses at the edges are relaxed for film height, h_f , to mesa width, w , ratios $h_f/w \leq 1 \times 10^{-4}$. For $h_f/w \geq 1 \times 10^{-2}$, the effective in-plane stress is relaxed throughout the deposited film. Moreover, the effective stresses at the center of the mesa are 15% of the stresses of an infinite film.

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1. Introduction

Thin-film ferroelectrics have generated a great deal of interest in the fabrication of non-volatile, low-voltage memory, sensors and actuators [1–3]. In thin-film ferroelectrics, the stress state of a thin film influences its response to an externally applied electric field. The stress state leads to electrostrictive, ferroelectric or piezoelectric behavior, and influences the coercive field necessary to switch the symmetry of the hysteresis loop and the remnant polarization value [4–10].

The thickness-to-width aspect ratio of ferroelectric films has been found to be of great importance in determining their underlying effective stress [11–16]. Thus, mesa structures with large aspect ratios have lower stress values at the edges, when compared with the biaxial stress in a continuous film. The stress state and switching behavior of a polycrystalline film also depends on the crystallographic orientation of the grains in the film. The distribution of ori-

entations (texture) determines the grain-to-grain interactions, and built-in stresses which result from cooling of the film from the Curie to the operating temperature [17–24]. Adjustment of properties through modification of the stress in a thin film has also been modeled and experimentally characterized as a function of composition, temperature and externally applied stress gradients [7,25–27]. Analytical and numerical results predict that mesas with an aspect ratio close to unity reduce clamping stresses, enhance piezoelectric response and affect the domain structure [28–31]. Experimental results on discrete epitaxial PZT mesas show that the piezoelectric response is clamped by the substrate, and suppressed to values much below the bulk values, unless the film is patterned into discrete mesas with lateral dimensions of less than 100 nm [32]. For such small devices, the clamping of the substrate is limited by the total size of the device, so the piezoelectric response approaches bulk values [33]. PZT capacitor mesas with an aspect ratio of unity exhibit hysteresis loops with no change in coercive field with respect to the reported bulk behavior [34]. Thin-film composites and mesas have also shown size-dependent behavior [1,12,13,35–42]. Suhir and

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coworkers proposed and experimentally verified that the epitaxial strain in finite-size thin-film structures is dramatically different from the same material in continuous film form. Recent work focuses on film thickness effects [43–48], and passivation layer effects [49].

Past modeling efforts used misfit or epitaxial strain to analyze the effects of built-in electric fields [50] and film thickness for PZT [51]. Other modeling efforts focus on PbTiO_3 and BaTiO_3 systems to predict the effect of compressive epitaxial strain on the polarization switching behavior [52]. Thin film polarization response has also been studied as a function of material symmetry, polarization displacement mechanisms [6,9,39,53,54] and grain size [55–57]. In this context, a previous publication predicted the out-of-plane hysteretic response of a single-crystal PZN-PT film as a function of misorientation angle, θ , and epitaxial strain, $\Delta\epsilon$ [22]. Fig. 1 reproduces such results. The calculated behavior is a consequence of the anisotropy of the properties of the deposited ferroelectric material and its crystallographic orientation (see Table 1). Results show that residual stresses are tensile for small misorientations and compressive for large angles. In addition, the epitaxial strain enhances or suppresses the remnant polarization and out-of-plane effective coercive field. The dashed curve outlines the boundaries for three types of out-of-plane polarization behavior: ferroelectric (α), piezoelectric (β) and electrostrictive (γ). The different ranges of behavior are a strong function of the specific PZT chemistry. Thus, for a commercial PZT (see Table 2), the different regimes of behavior shift as a result of stiffer elastic properties, weaker

Table 1

Physical properties used to describe simulated PZN-PT film [22].

Symbol	Value	Units	Symbol	Value	Units
C_{11}	111.0	GPa	Q_{11}	0.186	m^4/C^2
C_{33}	105.0	GPa	Q_{12}	−0.09	m^4/C^2
C_{44}	64.0	GPa	Q_{44}	0.013	m^4/C^2
C_{12}	102.0	GPa	a	−23,310,023	$\text{J m}/\text{C}^2$
C_{13}	101.0	GPa	b	372,960,372	$\text{J m}^3/\text{C}^4$
C_{66}	63.0	GPa	c	0	$\text{J m}^9/\text{C}^6$
ϵ_{11}^0	26.562×10^{-6}	F/m	ϵ_{33}^0	8.854×10^{-6}	F/m
d_{33}	200.0×10^{-11}	C/N	α_{11}	5×10^{-7}	1/K
d_{31}	$−97.0 \times 10^{-11}$	C/N	α_{33}	$−3 \times 10^{-6}$	1/K
d_{15}	14.0×10^{-11}	C/N	M_P	1×10^{-5}	S/m

electrostrictive constant and larger stress-free remnant polarization. Fig. 2 shows the corresponding butterfly loop response for the same two materials.

In general, it is not clear how edge effects and grain–grain interactions affect the out-of-plane response in polycrystalline thin-film ferroelectrics. The complexity of the problem demands simultaneous consideration of both the effect of anisotropy and grain misorientation in order to assess the importance of each feature on the resultant built-in electric fields and out-of-plane switching. The model presented herein extends previous work and incorporates the effects of the macroscopic edges of the sample. The crystallographic orientation of each grain and the finiteness of the mesa are considered to determine the resultant out-of-plane switching behavior. The results are summarized graphically in terms of crystallographic orientation, film width, height and epitaxial strain.

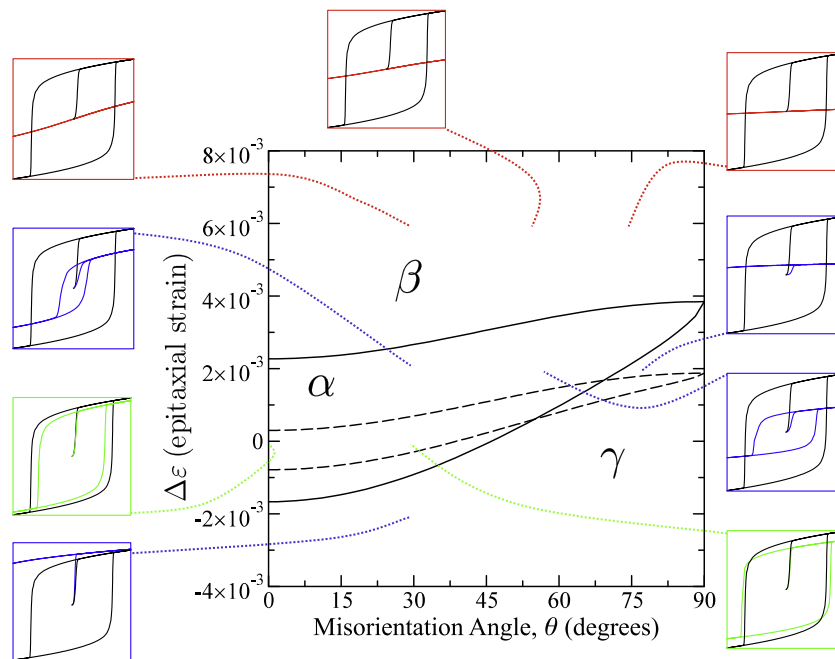


Fig. 1. Predicted single-crystal ferroelectric PZT behavior (solid line) and PZN-PT behavior (dashed line) [22]. The region marked as α indicates the range of $\Delta\epsilon$ and θ that results in ferroelectric behavior. In the region marked as β , the material exhibits electrostrictive behavior. In the region marked as γ , the material exhibits piezoelectric behavior. The material properties for PZT promote a wider range of $\Delta\epsilon$ values where ferroelectric response is favored in comparison to PZN-PT. Insets correspond to representative hysteretic response at selected epitaxial strain and crystallographic orientation values for PZT.

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