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POLARIZATION SWITCHING IN (111) ORIENTED PZT THIN FILMS

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ABSTRACT

Local domain structures in $Pb(Zr,Ti)O_3$ (PZT) ferroelectric thin films have been investigated using linear finite element analysis to qualitatively assess the effect of crystal structure, domain wall orientation and mechanical constraints from electrodes on local polarization switching behavior. The finite element model was used to illustrate that the evolution of residual stress during polarization reorientation may play an important role in the backswitching behavior which has been observed experimentally in (111)-orientated PZT films. The domain size and orientation used in the finite element model utilizes domain sizes determined from piezoresponse force microscopy (PFM) measurements given in the literature together with domain wall orientation from strain and charge compatibility in the (111) orientation. During polarization switching, domains with polarization components aligned anti-parallel to the applied field are expected to switch 90° to partially align with the applied field. 180° switching is not expected to occur in the (111) oriented film. The 90° switching induces residual stress that is computed using the finite element model. It is illustrated that thicker top electrodes increase the residual stress in the ferroelectric layer which may play an important role in polarization retention behavior in ferroelectric capacitors.

1. INTRODUCTION

Ferroelectric materials have been considered in various active microelectromechanical systems (MEMS) due to their multifunctional capabilities in electric-field induced deformation. The solid state actuation and sensing capabilities provide key advantages in developing compact sensing and actuation systems, however as the size of these devices approach the micro- and nanoscale range, a careful assessment of crystal structure, domain size and evolution of polarization switching under electromechanical loading becomes paramount. A detailed review of ferroelectric material behavior in thin films is discussed by Damjanovic (1998) and Shaw et al. (2000).

Ferroelectric materials such as lead-zirconate-titanate possess electric dipoles that reorient under an applied electric field or stress (Lines and Glass, 1977). As the material cools below the Curie temperature, regions of uniform polarization, or domains, form to reduce the depolarization energy. Upon application of an electric field above the coercive field, domains will partially align with the external field creating piezoelectricity at the macroscopic length scale. In addition, the ability to switch polarization has provided advantages in a number of applications which utilize ferroelectric thin films, such as non-volatile memory devices.

Recent efforts have focused on increasing the storage capacity of ferroelectric thin films by reducing the size of the capacitors within the chip. As the size of the capacitors begin to approach the length scale of a domain (< 1µm), issues associated with local deformation of domain structures, crystal growth orientation and constraints from the substrate and electrodes must be addressed. Li et al. (2002) applied a Ginzburg-Landau model to investigate the effect of bottom substrate constraints on lead titanate ($PbTiO_3$) ferroelectric thin films grown in the (001) orientation. The bottom substrate constraint was predicted to have an effect on the domain wall orientation and sequential nucleation and growth of domains during the phase transformation from cubic to tetragonal. Brennecka et al. (2004) investigated the role of different substrate materials on the linear material properties of $Pb(Zr_{0.4}Ti_{0.6})O_3$ ferroelectric thin films. The different substrate materials resulted in a tetragonal phase ferroelectric layer with varying degrees of (001) and (111) crystal orientation. Piezoelectric properties and remanent polarization was found to be larger in the (001) orientation. Rodriguez et al. (2005) utilized 3-dimensional PFM to construct three dimensional polarization in (111)-oriented PZT thin film capacitors. The switching process was found to be dominated by 90°

switching. Differences in switching behavior between the center region and edges of the capacitor island have been investigated by Gruverman, et al. (2003). The effect of mechanical boundary conditions on the phase of epitaxial ferroelectric thin films was investigated by Pertsev, et al. (1998) who suggested a change in polarization order due to clamping from the electrodes. Strained and defect free ferroelectric thin films were analyzed using mean-field thermodynamic calculations to illustrate a dielectric anomaly should occur depending on the sign of the misfit strain at the substrate interface, Tagentsev, et al. (2001). Stolichnov et al. (2002) has observed reverse switching in PZT films grown in the (111) orientation. Upon applying a positive or negative field, domains would initially align with the applied field, however when the field was reduced to zero, a center region on the capacitor switched opposite to the poling direction. Backswitching occurred irrespective of the poling direction. It was proposed that a stress-induced isomorphic phase transformation was responsible for the backswitching behavior.

In the present analysis, the effect of the top electrode on polarization retention is investigated in tetragonal PZT ferroelectric thin films grown in the (111) orientation. The crystal structure and domain wall orientation for this growth direction are used to construct a finite element model with an assumed domain structure in the as-grown state. Changes in remanent strain during polarization reorientation and associated residual stress are estimated by assuming domains switch to partially align with the applied field. Differences in residual stress are computed when the top electrode thickness is either 50 nm or 250 nm.

2. (111) PZT CRYSTAL STRUCTURE AND DOMAIN WALL ORIENTATION

Following the analysis given by Romanov et al. (1999), the domain patterns that develop in (111)-oriented tetragonal PZT thin films is summarized to motivate implementation of the finite element model.

Three possible unit cell orientations and a total of six polarization orientations allowed in a ferroelectric sample with tetragonal perovkite structure are illustrated in Figure 1. In the (111)-oriented crystal, the reference frame can be rotated so that the unit normals are in the directions $[\bar{1}10]$, $[\bar{1}\bar{1}2]$, and [111] with the [111] direction orthogonal to the film substrate. In this orientation, three unit cells have positive polarization components in the [111] orientation and the remaining three unit cells have negative polarization components in the [111] direction.

During the phase transformation from cubic to tetragonal, the perovskite unit cells align to form certain domain structures to reduce the free energy. The domain patterns must satisfy both charge and strain compatibility. Charge and strain compatibility requires the normal component of electric displacement to be continuous across a domain boundary and the spontaneous deformation must have the same sense and magnitude at the domain boundary, respectively. In the (111) orientation, two sets of multiple domain patterns can be found to satisfy compatibility conditions. Romanov et al. (1999) has shown that twin planes can be normal to the film/substrate or at an angle of ~35°. These two sets of domain patterns give rise to different polarization behavior. When the twinned domain wall is normal to the film/substrate, the polarization component normal to the film alternates in sign between adjacent domains resulting in a macroscopically unpoled film. When the domain wall is at an angle of ~35°, the polarization component normal to the film is the same in adjacent domains resulting in a poled film, see Figure 2.

Based on previous PFM measurements of (111)-oriented tetragonal PZT thin film capacitors (Gruverman et al. 2003), the ferroelectric layer is typically unpoled in the as-grown state. Therefore, in the finite element analysis, domain patterns that contain domain walls perpendicular to the film/substrate are considered to evaluate residual stress during ferroelectric switching.

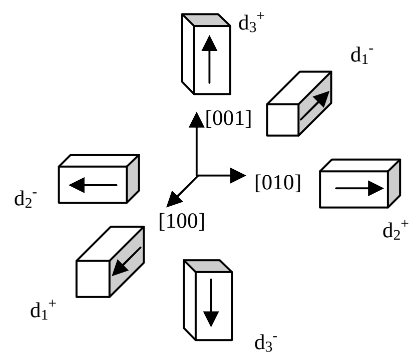

Figure 1: UNIT CELL ORIENTATIONS FOR THE PEROVSKITE TETRAGONAL FERROELECTRIC . THE SIX UNIT CELLS WITH DIFFERENT POLARIZATION ORIENTATIONS ARE LABELED AS $d_i^{+/-}$ FOR i=1 TO 3 WHERE THE SUPERSCRIPT IS FOR POSITIVE (+) OR NEGATIVE (-) ORIENTATION.

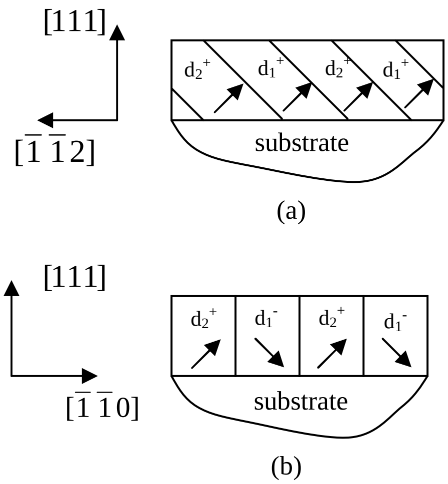

FIGURE 2: EXAMPLES OF POSSIBLE DOMAIN PATTERNS IN (111) ORIENTED THIN FILMS. THE UNPOLED CASE (B) WAS USED IN THE FINITE ELEMENT ANALYSIS.

3. FINITE ELEMENT ANALYSIS

A set of domain structures are implemented in a two-dimensional, plane strain linear finite element model using ANSYS to assess the role of residual stress during polarization reorientation in the ferroelectric thin film. The role of the top electrode is considered here to explain the previously reported results on spontaneous backswitching in PZT capacitors (Stolichnov et al. 2002) and qualitatively describe the driving force behind this effect.

The domain structures and the capacitor geometry used to model the thin film capacitor are given in Figure 2. The elastic material properties for the top iridium oxide (IrO_2) electrode, the bottom platinum (Pt) electrode and the PZT layer are given in Table 1. An electric potential is applied on the top of the ferroelectric capacitor and the bottom of the ferroelectric layer is grounded. Displacement is constrained in the [111] direction along the entire bottom platinum electrode and fixed in both directions at the bottom left corner to restrict rigid body translation. The dashed line represents the thinner top electrode (50 nm) of the two top electrode thicknesses modeled (the thicker top electrode is 250 nm). The capacitor is 1x1 μm^2 in lateral dimensions and the domain lateral size is assumed to be 200 nm based on previous PFM measurements (Gruverman et al. 2003). The PZT layer thickness underneath the top electrode is 200 nm while outside the top electrode it is a 100 nm thick. The bottom Pt electrode is 175 nm thick.

The initial polarization variants d_2^+ and d_1^- are used in the model shown in Figure 3. The domains with positive polarization components in the [111] direction (represented by the arrows) correspond to d_2^+ and similarly the variants with negative polarization components in the [111] orientation correspond to the d_1^- variants. The set of variants d_3^+ and d_2^- or d_1^+ and d_3^- could also be used, however the domain geometry and energy is equivalent in these configurations.

TABLE 1: ELASTIC MATERIAL PROPERTIES USED IN THE FINITE ELEMENT MODEL

	PZT	IrO_2	Pt
Modulus (GPa)	60	528	171
Poisson ratio	0.35	0.26	0.39

To estimate the amount of residual stress that may develop from the difference in the top electrode constraint, the initial domain structures are assumed to be a single-domain state poled in the negative [111] direction by an external electric field above the coercive field. Therefore, in the present case, the d_2^+ variants will switch into d_1^- variants. The change in strain is quantified using the difference in spontaneous strain between each variant. The spontaneous strain in the (001) orientation is defined by

$$\varepsilon_{ij}^{\alpha(s)} = \frac{\varepsilon_0}{2}\left(3\delta_{\alpha i}\delta_{\alpha j} - \delta_{ij}\right) \tag{1}$$

where ε_0 denotes the magnitude of spontaneous strain and the subscript α denotes the different unit cell orientations illustrated in Figure 1. A qualitative estimate on residual stress from changes in spontaneous strain is obtained based on lattice constants for lead titanate ($PbTiO_3$) (c=0.414 nm and a=0.389 nm, Jaffe et al., 1971) the spontaneous strain is $\varepsilon_0 = {(c-a)}/{a} = 0.064$.

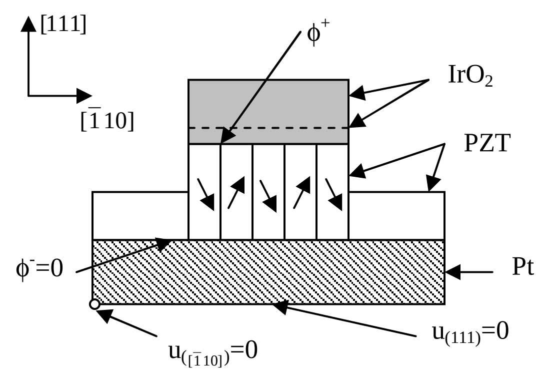

FIGURE 3: FINITE ELEMENT MODEL OF THE FERROELECTRIC THIN FILM CAPACITOR. TWO TOP ELECTRODE THICKNESSES WERE CONSIDERED (50 NM AND 250 NM). THE ARROWS IN THE PZT CAPACITOR ISLAND REPRESENT THE ORIENTATION OF POLARIZATION IN THE [111]-[$\bar{1}$10] PLANE.

The effect of changes in spontaneous strain on residual stress is implemented in the finite element model by computing the difference in strain when switching from the d_2^+

to d_1^- variants. The change in spontaneous strain in the (001) orientation is

$$\Delta\varepsilon_{ij}^{2\to1(s)} = \begin{bmatrix} \frac{3}{2}\varepsilon_0 & 0 & 0 \\ 0 & -\frac{3}{2}\varepsilon_0 & 0 \\ 0 & 0 & 0 \end{bmatrix}. \qquad (2)$$

For the (111) orientation, the spontaneous strain is rotated to the directions associated with unit normals in the $[\bar{1}10]$, $[\bar{1}\bar{1}2]$, and [111] directions according to

$$\Delta\bar{\varepsilon}_{ij}^{2\to1(s)} = a_i^m a_j^n \Delta\varepsilon_{mn}^{2\to1(s)} = \begin{bmatrix} 0 & 0.859\varepsilon_0 & -1.219\varepsilon_0 \\ 0.859\varepsilon_0 & 0 & 0 \\ -1.219\varepsilon_0 & 0 & 0 \end{bmatrix} \qquad (3)$$

where a_i^m and a_i^m are the unit normal components. For the two dimensional problem considered here, only the in-plane shear $0.859\varepsilon_0$ is considered.

Figures 4 and 5 illustrate the changes in stress based on the assumption that domains switch into a single d_1^- domain state. The deformation has been amplified in the plots to illustrate the larger constraint imposed by the thicker top electrode. The linear finite element analysis provides an estimate on the *initial* driving force for reverse switching. The results illustrate that the thicker top electrode may store additional elastic energy that can be transferred back to the ferroelectric layer upon reducing the electric field to zero after polarization switching. The residual stress is found to be significantly larger when the top electrode thickness increases to 250 nm which may explain backswitching behavior previously observed by Stolichnov et al. (2002). The large stress observed in the thicker top electrode extends through the entire ferroelectric layer in comparison to the thin electrode where large stress is only observed near to the bottom electrode.

4. SUMMARY

The effect of the top electrode constraint in ferroelectric thin films grown in the (111) orientation is considered. In the (111) orientation, domain structures are expected to rotate 90° from an applied field in the (111) direction which has been experimentally verified (Rodriguez et al., 2005). 90° switching induces residual stress between the PZT layer and the electrode/substrate constraint. By introducing a set of domain structures based on previous PFM measurements and charge and strain compatibility, a finite element analysis was performed to estimate changes in residual stress during ferroelectric switching. Larger residual stress was observed when the top electrode was 250 nm. This suggests more elastic energy is available to drive backswitching which may play a major role in polartization retention behavior.

It should also be noted that this analysis has been restricted to a predefined set of variants based on previous PFM measurements that quantify domain size as well as charge and strain compatibility relations governing the orientation of domain walls. During ferroelectric switching processes within a three dimensional structure, additional domain patterns may form and reorient in complex configurations to reduce the internal energy. This behavior is currently under investigation to quantify the backswitching mechanisms.

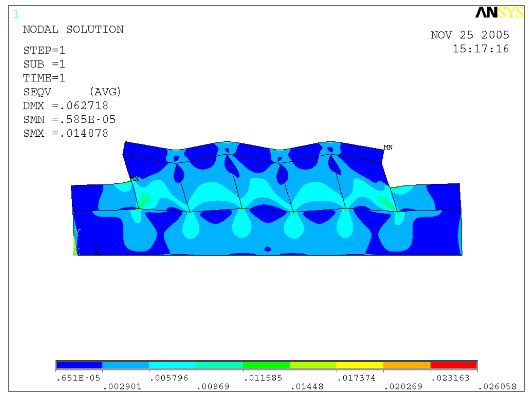

FIGURE 4: VON MISES STRESS FOR THE FERROELECTRIC THIN FILM AFTER POLARIZATION SWITCHING FOR THE 50 NM THICK TOP ELECTRODE. THE DEFORMATION HAS BEEN AMPLIFIED IN THE PLOT TO ILLUSTRATE COMPLIANCE IN THE TOP ELECTRODE.

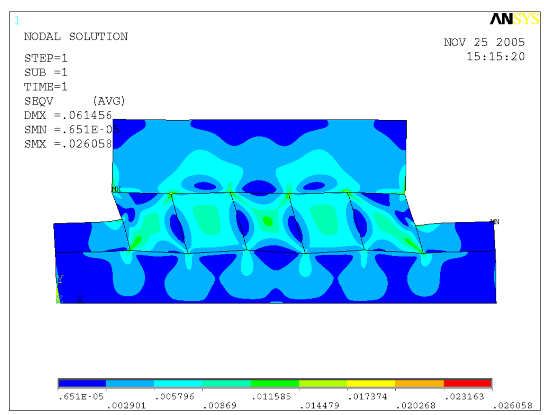

FIGURE 5: VON MISES STRESS FOR THE FERROELECTRIC THIN FILM AFTER POLARIZATION SWITCHING FOR THE 250 NM THICK TOP ELECTRODE. THE DEFORMATION IS AMPLIFIED HERE TO SHOW SIGNIFICANT CLAMPING EFFECTS IN THE TOP ELECTRODE.

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