Peculiar Effect of Mechanical Stress on Polarization Stability in Micrometer-scale Ferroelectric Capacitors

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Piezoresponse force microscopy (PFM) has been used to study the polarization stability in micrometer size Pb(Zr,Ti)O 3 capacitors. It is shown that the top electrode thickness has a profound effect on the equilibrium polarization state of poled capacitors triggering spontaneous polarization backswitching in the absence of an applied electric field and leading to the formation of an abnormal domain pattern. PFM examination of poled capacitors with thick (250 nm) top electrodes reveals domain patterns with the central regions always oriented in the direction opposite to the applied field. It is suggested that the driving force behind the observed effect is a transient response to the residual shear stress created by the top electrode in the poled capacitors during field-induced polarization switching. The proposed mechanism is quantified using finite element ferroelectric phase field modeling. The observed effect provides valuable insight into the polarization retention behavior in micrometer size ferroelectric capacitors.
A unique combination of dielectric, piezoelectric and optical properties puts ferroelectrics among the most important groups of electronic materials which makes them attractive for a variety of microelectronic applications [1, 2]. Investigation of polarization reversal processes in ferroelectrics is of fundamental and practical importance for understanding their quasi-static and dynamic behavior. Reduction of the free energy via formation of ferroelectric domain structures gives rise to a profound mechanical stress effect on the physical properties of ferroelectrics. Accommodation of the misfit strain in epitaxial heterostructures can result in the appearance of new phases forbidden in bulk samples and significant size dependence on the dielectric and piezoelectric properties [3]. Numerous attempts have been made to develop a thermodynamic theory that would account for the effect of the mechanical boundary conditions on structural transformations in ferroelectric films [4, 5, 6, 7, 8]. However, up to now almost all of these studies took into account the mechanical boundary conditions only at the film/substrate interface. On the other hand, the effect of the top interface on the polarization state has largely been ignored. Furthermore, due to the pronounced size effect exhibited by ferroelectrics [9, 10, 11, 12, 13, 14], scaling of ferroelectric structures brings about an additional aspect to their static and dynamic behavior that needs to be thoroughly understood.

Generally, the polarization state in ferroelectric heterostructures, determined by the thermodynamic minimum of free energy, is a function of electrical and mechanical boundary conditions and depends upon the film defect structure, thickness, crystallographic orientation, lattice misfit strain, electrode material, poling conditions, etc. Application of advanced characterization techniques, primarily piezoresponse force microscopy (PFM) [15, 16, 17, 18], has provided new insight into the microscopic mechanisms of electrically-induced transformations in ferroelectric structures.

In this letter, we report on the first observation of the mechanical stress effect imposed by the top electrode on polarization stability in micrometer scale Pb(Zr,Ti)O$_3$ (PZT) capacitors. We
show that the top electrode drastically affects the polarization stability in these capacitors by triggering spontaneous polarization backswitching leading to formation of abnormal domain configurations. It is proposed that the driving force behind the observed instability is residual shear stress in the poled capacitor, which increases with an increase in the top electrode thickness. The electromechanics governing this behavior is described using nonlinear finite element phase field analysis.

The PFM studies have been performed in the (111)-oriented tetragonal PZT capacitors [18]. The top IrO$_2$ electrodes of several square microns have been produced on the PZT surface by reactive ion etching. PZT capacitors with both 50-nm thick top electrodes (TEL) and 250-nm thick TEL have been tested using PFM. Visualization of domain patterns in individual capacitors has been performed by applying an oscillating bias of 0.6 V (peak-to-peak) at 10 kHz to the top electrode with a conductive probing tip.

Figure 1 shows surface topography, PFM amplitude, and phase images of the poled 1×1.5 $\mu$m$^2$ capacitors with a 50-nm thick TEL. Capacitors in the upper row have been poled by -5 V, 1 s voltage pulses applied to the top electrodes, while the bottom row capacitors have been poled into opposite direction by the +5 V, 1 s voltage pulses. The PFM phase signal, which provides information on the direction of out-of-plane polarization component, differs by 180º in the oppositely poled capacitors. The PFM amplitude signal is related to the magnitude of the atomic force microscope cantilever tip oscillation (due to the piezoelectric response integrated over the capacitor thickness) and is the same for oppositely poled capacitors. Uniform amplitude and phase contrast indicate complete and uniform switching of the capacitors into a stable polarization state.

On the other hand, PFM imaging of the poled capacitors with the 250-nm thick TEL (Fig. 2(a)) reveals unusual domain patterns. The PFM phase image in Fig. 2(b) shows that after a poling voltage has been turned off, the central regions of the capacitors exhibit polarization opposite to the polarity of the applied voltage. The PFM amplitude signal (Fig. 2(c)) is the same across the domain boundaries in each capacitor suggesting that the inverse domains in the center extend from
the bottom to the top electrodes of the capacitors. The observed effect is symmetric with respect to the voltage polarity, i.e. the central part of the capacitors always exhibit polarization opposite to the polarity of the applied bias. It should be mentioned that imaging the same capacitors in the PFM mode with an additional dc bias superimposed on the ac imaging voltage resulted in complete switching of polarization in the whole capacitor indicated by a uniform PFM signal across the top electrode (not shown here). However, after the dc bias is turned off, the inverse domain in the center region appears again. This behavior is indicative of spontaneous backswitching occurring in the center of the capacitors after application of the poling voltage. This effect has been observed in 250-nm thick TEL capacitors with the TEL area in the range of several square microns and it gradually disappears in the larger capacitors.

Previously, a similar backswitching effect observed in PZT capacitors with the same crystallographic orientation, composition, and lateral dimensions but with the patterned top electrode thickness just slightly above 50 nm [19] has been explained by an isomorphic phase transition in the PZT layer due to a tensile stress induced by a Si substrate. However, our results indicate that the backswitching effect in the PZT capacitors is actually not affected by the substrate but is the result of the presence of a thick (250 nm) top electrode. This apparent contradiction could be explained by the fact that, to overcome a technical problem of contacting the micrometer scale capacitors, the authors of Ref [19] additionally deposited ~250-nm thick Pt dots of 0.6 mm in diameter over the electrode-patterned PZT film effectively emulating structures with thick top electrodes used in our studies. Therefore, as the observed effect is polarization-independent (and thus, a built-in field effect can be ruled out as a possible explanation) and is observed only in the capacitors with 250-nm thick electrodes, we conclude, that the anomalous backswitching effect in micrometer PZT capacitors shown in Fig. 2 is induced by the top electrodes. We suggest that this effect is a result of residual shear stress imposed by a thick top electrode.

Before considering the backswitching mechanism let us mention that, generally, the ferroelectric switching behavior is strongly dependent on the crystallographic orientation of the
PZT layers. In the (001) orientation, ferroelectric switching is predominantly 180° polarization reorientation which results in no change in strain. In contrast, field induced 90° polarization switching, which involves significant strain changes, is energetically favorable in the (111) oriented capacitors. Once the potential is removed, residual elastic energy remains in the film and can potentially provide a mechanical driving force for backswitching.

This effect is simulated using a fully-coupled ferroelectric finite element phase field (FEPP) model described as follows. The FEPP model includes mechanical equilibrium, Gauss’ law, and the time-dependent Ginzburg-Landau equation (see [20] for details). The three governing equations are obtained by taking the variation of the Gibbs electric energy density

\[
\frac{\partial g_2}{\partial P_{i,j}} - \frac{\partial g_2}{\partial P_i} = \beta_{ji} \frac{\partial P_i}{\partial t} \quad (1)
\]

\[
\sigma_{y,j} = 0 \quad (2)
\]

\[
D_{i,i} = 0 \quad (3)
\]

where \( g_2 = \psi - E_i D_i \) is the electric Gibbs energy density and \( \psi \) is the Helmholtz energy density. The polarization is denoted by \( P_i \), \( \sigma_{y,j} \) is the stress, \( D_i \) is the electric displacement, and \( \beta_{ji} \) is a positive definite inverse mobility tensor. Indicial notation has been used where summation applies on repeated indices.

The Helmholtz free energy used in the finite element model is based on parameters given by Pertsev et al [3] for lead titanate. An additional term defining exchange energy via polarization gradients is included in the model and given in [21]. The backswitching behavior is quantified for the two top electrode thicknesses using a two dimensional analysis on the (111)-(\(\bar{T}\)2) planes where the the (111) plane is perpendicular to the film and the out-of-plane polarization component normal to the (\(\bar{T}\)10) plane is ignored. The PFM measurements are modeled using the following sets of boundary conditions. Domains in the ferroelectric layer are first allowed to evolve under short-
circuit conditions from a quasi-cubic state with a small random polarization ($|\mathbf{P}| \sim 1 \times 10^6 \text{ C/m}^2$). This results in formation of an initial (as-grown) domain structure with alternating normal (out-of-plane) polarization components. This polarization state is consistent with PFM observations of the as-grown PZT capacitors.

From this as-grown state, the capacitors of both TEL thicknesses are poled to a state with uniform distribution of the (111) polarization component using the same electric potential. The FEPP simulations show that the presence of a thick top electrode causes a large number of twinned domains in the poled capacitor. This effect is illustrated by Fig. 3, which displays maps of the (111) polarization components in the poled capacitors. While the capacitor with 50-nm thick TEL exhibits almost a single domain state, the capacitor with thick top electrode shows significant variations of the (111) polarization component due to strong residual stress. It should be noted that these twinned domains would be difficult to quantify using PFM since the (111) component of polarization is uniform for both the thin and thick TEL capacitors.

After the external potential is turned off and the capacitors are allowed to relax to equilibrium, a significantly larger amount of polarization switches back in the 250-nm thick TEL capacitor (Fig. 4). Residual elastic energy is larger in the center away from the stress-free edges which explains why backswitching mainly occurs in the central parts of the capacitors; however, a single center domain is not predicted. This may be due to the PbTiO$_3$ thermodynamic potential used to approximate the Pb(Zr, Ti)O$_3$ composition or possibly a three dimensional effect. Nevertheless, it should also be noted that this same model correctly predicts the absence of the backswitching effect in the (001)-oriented PZT capacitors in agreement with the experimental results by Stolichnov et al [19].

This model does not account for flexoelectric effect [22]. However, strain gradients near the electrode interfaces may lead to higher order ferroelectric switching mechanisms. This may play a role in the capacitor size dependence of the abnormal switching: PFM measurements show
that reverse switching gradually disappears as the lateral dimensions of the capacitor increase. To illustrate the strain gradient effect, consider a boundary value problem consisting of a set of self-equilibrated residual stress loads applied along the surface of an infinitely thick elastic strip of finite width $W$. This boundary value problem approximates the stress at the PZT / top electrode interface. The solution to this problem can be represented by a stress vector potential using Stroh’s formalism, $\varphi = \Re \{ \mathbf{B} (e^{-\lambda z}) \mathbf{q} \}$ [23]. Using traction free edges along the lateral edges, the smallest eigenvalue ($\lambda$) that satisfies equilibrium gives the slowest stress decay $\sigma_{ij} \propto e^{-\Re(\lambda) y}$, where $y$ is the distance in the normal direction from the interface. For isotropic materials under anti-plane deformation, $\lambda = \pi/W$ [23]. Similar relations are found to exist for in-plane normal or shear loading of an elastic strip of finite thickness [24]. When the thickness and width are comparable in size, as is the case for a 1 $\mu$m$^2$ capacitor with a 250 nm TEL, the stress decay rate becomes sensitive to further reductions in the lateral dimension. The stress gradient converges to the exponential relation as the thickness to width ratio becomes very large. This size scaling relation suggests that flexoelectricity may play a role in the reverse switching behavior. Since the shear strain changes sign upon polarization reversal, the shear strain gradient also changes sign and therefore correlates with the bi-directional spontaneous reverse switching behavior.

In summary, we have shown that the top electrode thickness has a dramatic effect on equilibrium domain structures in micrometer thin film capacitors. Mechanical constraints are found to create residual shear stresses during ferroelectric switching in films grown in the $<111>$ orientation leading to complex, twinned domain structures. The residual elastic energy results in spontaneous polarization backswitching in the central regions of capacitors. The observed effect should be taken into account while considering the retention behavior of ferroelectric-based devices.

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**Figure Captions**

FIG. 1. (a) Topographic, (b) PFM phase, and (c) PFM amplitude of the poled PZT capacitors with 50-nm thick top electrodes. Upper row capacitors poled by negative voltage pulses (-5V, 1s), bottom row capacitors poled by positive pulses (+5V, 1 s). The scanning size is 6x6 µm².

FIG. 2. (a) Topographic, (b) PFM phase, and (c) PFM amplitude of the poled PZT capacitors with 250-nm thick top electrodes. Upper row capacitors poled by negative voltage pulses (-5V, 1s), bottom row capacitors poled by positive pulses (+5V, 1 s). The scanning size is 6x6 µm².

FIG. 3. Finite element phase field map of the *in-plane* (1 1 2) polarization component (P₁) in two poled ferroelectric capacitors with a lateral size of 1 µm immediately after they have been short-circuited: (a) 250-nm thick TEL; (b) 50-nm thick TEL. Highly refined finite element mesh densities are used in both models to resolve nanometer size domain wall structures. The polarization vectors are plotted on a coarser length scale for illustrative purposes.

FIG. 4. Finite element phase field map of the *out-of-plane* (1 1 1) polarization component (P₂) in two short-circuited ferroelectric capacitors with a lateral size of 1 µm under equilibrium conditions: (a) 250-nm thick TEL; (b) 50-nm thick TEL.
Fig. 1

Fig. 2
Fig. 3
References

The exchange energy is given by $\psi_G = \frac{1}{2} a_0 \left( P_{1,1}^2 + P_{2,2}^2 + P_{1,2}^2 + P_{2,1}^2 \right)$ where $a_0 = 8 \times 10^{-13} \text{Vm}^3 / C$. 
