Lateral size and thickness dependence in ferroelectric nanostructures formed by localized domain switching

Ng, Nathaniel; Ahluwalia, Rajeev; Su, Haibin; Boey, Freddy Yin Chiang

2008

Ng, N., Ahluwalia, R., Su, H., & Boey, F. (2009). Lateral size and thickness dependence in ferroelectric nanostructures formed by localized domain switching. *Acta Materialia*, 57(7), 2047-2054.

<https://hdl.handle.net/10356/92670>

<https://doi.org/10.1016/j.actamat.2008.10.022>

© 2008 Acta Materialia Inc. This is the author created version of a work that has been peer reviewed and accepted for publication by Acta Materialia, Elsevier, on behalf of Acta Materialia Inc. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at:
<http://dx.doi.org/10.1016/j.actamat.2008.10.022>.

Downloaded on 26 Apr 2023 20:55:39 SGT

Lateral size and thickness dependence in ferroelectric nanostructures formed by localized domain switching

Nathaniel Ng^{a,b,*}, Rajeev Ahluwalia^a, H.B. Su^b, F. Boey^b

^a Materials Theory and Simulation Laboratory, Institute of High Performance Computing, #16-16, Connexis, 1 Fusionopolis Way, Singapore 138632, Singapore

^b School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

* Corresponding author. Tel.: +65 98444476; fax: +65 64191290. E-mail addresses: nathaniel@pacific.net.sg, ngkc@ihpc.a-star.edu.sg (N. Ng).

Abstract

Ferroelectric nanostructures can be formed by local switching of domains using techniques such as piezo-force microscopy (PFM). Understanding the dependence of the switching behavior on the lateral size of the electrode is important to determine the minimum feature size for writing ferroelectric nanostructures. To understand these lateral size effects, we use the time-dependent Ginzburg–Landau equations in a two-dimensional square to rectangle ferroelectric transition to simulate localized switching of domains for PFM-type and parallel-plate capacitor configurations. Our investigations indicate that fringing electric fields lead to switching via intermediate 90° domains even in the absence of substrate or clamping effects for films of sufficient thicknesses, and via 180° rotations at smaller thicknesses. The voltage required to switch the domain increases by decreasing the lateral size, and at very small lateral sizes the coercive voltage becomes so large that it becomes virtually impossible to switch the domain.

Keywords: Lateral size effects; Phase field simulation; Piezo-force microscopy; Ferroelectric switching; Nanostructures

1. Introduction

With the current advancement in nanotechnology and device miniaturization, there is much interest in studying size effects in ferroelectrics. The properties of nanoscale ferroelectric thin films differ substantially from the bulk [1], and it has been shown that strong depolarization effects can completely suppress ferroelectricity below a critical thickness. In fact, thickness dependence of ferroelectric behavior has been well studied both theoretically and experimentally [2,3], but not

much attention has been devoted to the role of lateral size. Scanning probe techniques such as piezo-force microscopy (PFM) allow the polarization to be switched locally and arrays of these locally switched domains are the building blocks of ferroelectric memory devices (e.g., ferroelectric capacitors and dynamic random access memory applications). In such devices, the main limitation on lateral width is due to fringing electric fields [4], and reduction of the lateral size is key to allowing very high-density memories to be achieved [5].

Apart from the technological interest, it is also important to understand the role of the complex long-range elastic as well as electrostatic interaction on selectively switched domains. Fringing of the electric field [4] due to edge effects as well as inhomogeneous elastic deformations will crucially influence the behavior of locally switched domains. These long-range interactions will influence the local polarizations in the neighborhood of the domains, thereby influencing the effective properties, such as the polarization vs. electric field response (P–E). For example, in a recent work, Chen et al. [6] studied the local 180° switching in epitaxial PZT by PFM. They found that the 90° domain formation relaxes the internal stresses associated with inhomogeneous electric fields. This underscores the importance of studying the effect of finite lateral width from a theoretical point of view to understand the underlying mechanisms that play a role in local switching of the domains. Such a study may provide a guideline for choosing the optimal thicknesses and widths of the selectively switched domains.

The effect of lateral size in ferroelectric films was studied experimentally by Lee et al. [7] and Chen et al. [6], as well as analytically by Wang et al. [8] and Roytburd et al. [9]. The latter two analyses, however, did not incorporate domains and domain wall motion. In fact, both models neglected electrostatic effects, and Wang et al.'s model also neglected elastic effects. A framework that takes into account elastic as well electrostatic long-range interactions is a useful technique to study the domain switching under inhomogeneous electric fields. In this paper, we investigate the two-dimensional (2D) domain evolution using an LGD (Landau–Ginzburg–Devonshire) approach with the TDGL (time-dependent Ginzburg–Landau) relaxational equations with both electrostatic and elastic effects, focusing on local switching mechanisms for a PFM-type configuration as well as for parallel-plate capacitor geometry. In fact, a TDGL model was used to investigate PFM measurements in BiFeO_3 [10]. However, a detailed study on size effects and the related nucleation mechanisms was not carried out. While previous TDGL models incorporated Fourier transform techniques for their numerical solvers, we solve these equations in real space for the displacement fields as well as for the electrostatic potentials for ease of introduction of the boundary conditions. We should point out that this real space method is especially convenient to simulate the physics of localized switching in a PFM setup and the parallel-plate capacitor geometry. Since our investigations focus on the role of the fringing electric fields, which arise due to the

finite lateral width of the electrode, we do not introduce the conventional sources of domain nucleation such as thermal noise (except in the initial conditions) and static defects due to dipoles or free charge. We also assume a stress-free film and do not incorporate clamping effects arising from a substrate.

The paper is organized as follows. In Section 2 we describe the TDGL model, which is used in Section 3 to understand localized domain switching in a configuration similar to a PFM setup along with a parallel-plate capacitor geometry. Section 4 ends the paper with a summary and discussion of the results.

2. Model

Landau theory is a mean-field framework to study phase transitions, based solely on symmetry considerations [11]. In 1954, Devonshire adapted Landau's model to ferroelectrics, whereby he described thermodynamic behavior in the BaTiO₃ system, which is now called the LGD approach to ferroelectrics. This was later used by Haun et al. [12] to develop a thermodynamic theory of the PZT system. This model has been applied to various materials and been shown to be able to explain properties such as the spontaneous polarization, the intrinsic coercive field and hysteresis loops [13], and temperature dependence.

In ferroelectrics, the total free energy of the system, F_T , is given by:

$$F_T = F_{\text{Landau}} + F_{\text{Gradient}} + F_{\text{electrostatic}} + F_{\text{elastic}} \quad (1)$$

where F_{Landau} , F_{Gradient} , $F_{\text{electrostatic}}$ and F_{elastic} represent the Landau, Gradient, electrostatic and elastic energies, respectively, and may be obtained as a function of the polarizations, P_i , which is described as follows:

The 2D Landau-type free energy expansion of the order parameter, P_i , is given by:

$$\begin{aligned} F_{\text{Landau}}(P_x, P_y) = & \frac{1}{2} \alpha_0 (T - T_c) (P_x^2 + P_y^2) + \frac{1}{4} \alpha_{11} (P_x^4 + P_y^4) \\ & + \frac{1}{2} \alpha_{12} P_x^2 P_y^2 + \frac{1}{6} \alpha_{111} (P_x^6 + P_y^6) \\ & + \frac{1}{2} \alpha_{112} (P_x^4 P_y^2 + P_y^4 P_x^2) \end{aligned} \quad (2)$$

Eq. (2) is a symmetry-allowed expansion in the polarizations, and the coefficients $\alpha_0, \alpha_{11}, \alpha_{12}, \alpha_{111}$ and

α_{111} are phenomenological coefficients that can in principle be obtained from experimental data or first-principles calculations [11]. Eq. (2) applies to homogeneous systems, and is used to describe the phase transitions as a function of temperature. For $T < T_c$, the polynomial in Eq. (2) has four minima, given by $(\pm P_s, 0)$ and $(0, \pm P_s)$, corresponding to the four tetragonal ferroelectric variants in 2D, and a local maxima at $(0, 0)$, corresponding to the cubic paraelectric phase. Here P_s corresponds to the spontaneous polarization at that temperature. Inhomogeneous systems may be investigated by introducing an energy cost associated with creating domains in the system, i.e., the domain wall energy:

$$F_{\text{Gradient}} = \frac{1}{2}K \left(|\vec{\nabla} P_x|^2 + |\vec{\nabla} P_y|^2 \right) \quad (3)$$

where K is a constant related to the domain wall energy.

Electrostatic effects, due to dipoles, free charge and the electrostatic potential, are considered by the introduction of the term:

$$F_{\text{electrostatic}} = -(\mathbf{E} \cdot \mathbf{P} + \frac{1}{2}\epsilon_0 \mathbf{E} \cdot \mathbf{E}) \quad (4)$$

where the electric field, $\mathbf{E}$, is obtained from the constraint given by Gauss's Law:

$$\nabla \cdot \mathbf{D} = \nabla \cdot (-\epsilon_0 \nabla \phi + \mathbf{P}) = \rho \quad (5)$$

and $\rho = 0$ in the absence of free charge.

Similarly, elastic effects are considered by adding the elastic energy given by:

$$F_{\text{elastic}} = \frac{1}{2}C_{11}(\tilde{\epsilon}_{xx}^2 + \tilde{\epsilon}_{yy}^2) + C_{12}\tilde{\epsilon}_{xx}\tilde{\epsilon}_{yy} + \frac{1}{2}C_{44}\tilde{\epsilon}_{xy}^2 \quad (6)$$

where

$$\begin{aligned} \tilde{\epsilon}_{xx} &= \epsilon_{xx} - (Q_{11}P_x^2 + Q_{12}P_y^2) \\ \tilde{\epsilon}_{yy} &= \epsilon_{yy} - (Q_{11}P_y^2 + Q_{12}P_x^2), \\ \tilde{\epsilon}_{xy} &= \epsilon_{xy} - Q_{44}P_xP_y \end{aligned} \quad (7)$$

and

$$\epsilon_{ij} = \frac{1}{2}(\partial u_i / \partial x_j + \partial u_j / \partial x_i) \quad (8)$$

Here, C_{11} , C_{12} and C_{44} are the elastic constants, Q_{11} , Q_{12} and Q_{44} are the electrostrictive coefficients, ϵ_{ij} is the strain and u_i is the displacement subject to the constraint of mechanical equilibrium given by

$$\nabla \cdot \sigma = \sigma_{ij,j} = 0 \quad (9)$$

where the stress, σ_{ij} , is given by $\sigma_{ij} = \delta F_{elastic} / \delta \epsilon_{ij}$,

The kinetics of the LGD approach are investigated with the TDGL relaxational equation (also called the Allen–Cahn relaxational equation) [14], which is

$$\frac{\partial P_i}{\partial t} = -\Gamma \frac{\delta F_T}{\delta P_i} \quad (10)$$

where t is time and Γ is a constant related to the domain wall mobility.

These equations have been successfully used to simulate domain formation and switching in ferroelectrics [14].

These TDGL equations are rescaled for numerical convenience. In rescaled units, we put $P'_x = P_x/P_0$, $P'_y = P_y/P_0$, for the polarizations, where P_0 is set to the spontaneous polarization of the material. The length scale is rescaled as $x' = x/\delta$, $y' = y/\delta$, where δ is chosen such that the simulation widths agree with the experimentally observed domain wall widths. We set $\Phi' = \Phi/\Phi_0$, where $\Phi_0 = \theta[P_0\delta/\epsilon_0]$, for the electrostatic potential, where θ is a dimensionless parameter, arbitrarily chosen as 1.0. The elastic constants are rescaled as $C'_{ij} = C_{ij}/C_{11}$, while the electrostrictive constants are rescaled as $Q'_{ij} = Q_{ij}/Q_{11}$. For the strains, we use the rescaling, $\epsilon'_{ij} = \epsilon_{ij}/\epsilon^0$ and $\tilde{\epsilon}'_{ij} = \tilde{\epsilon}_{ij}/\epsilon^0$ where $\epsilon^0 = Q_{11}P_0^2$, and for the stresses, the rescaling is $\sigma'_{ij} = \sigma_{ij}/\sigma_0$, where $\sigma_0 = C_{11}\epsilon^0 = C_{11}Q_{11}P_0^2$. Hence the TDGL equations may be written in rescaled form as follows:

$$\frac{\partial P'_x}{\partial t} = \Gamma |\alpha_1| \left[\begin{aligned} & -\frac{\alpha_1}{|\alpha_1|} P'_x - \frac{\alpha_{11} P_0^2}{|\alpha_1|} P'^3_x - \frac{\alpha_{12} P_0^2}{|\alpha_1|} P'_x P'^2_y - \frac{\alpha_{111} P_0^4}{|\alpha_1|} P'^5_x \\ & - \frac{\alpha_{112} P_0^4}{|\alpha_1|} (P'_x P'^4_y + 2 P'^3_x P'^2_y) + \frac{K}{|\alpha_1| \delta^2} \nabla'^2 P'_x \\ & - \frac{\theta}{\varepsilon_0 |\alpha_1|} \phi'_{,x'} - \frac{C_{11} Q_{11}^2 P_0^2}{|\alpha_1|} [2(\sigma'_{xx} + Q'_{12} \sigma'_{yy}) P'_x + Q'_{44} \sigma'_{xy} P'_y] \end{aligned} \right] \quad (11)$$

$$\frac{\partial P'_y}{\partial t} = \Gamma |\alpha_1| \left[\begin{aligned} & -\frac{\alpha_1}{|\alpha_1|} P'_y - \frac{\alpha_{11} P_0^2}{|\alpha_1|} P'^3_y - \frac{\alpha_{12} P_0^2}{|\alpha_1|} P'^2_x P'_y - \frac{\alpha_{111} P_0^4}{|\alpha_1|} P'^5_y \\ & + \frac{\alpha_{112} P_0^4}{|\alpha_1|} (P'_y P'^4_x + 2 P'^3_y P'^2_x) + \frac{K}{|\alpha_1| \delta^2} \nabla'^2 P'_y \\ & - \frac{\theta}{\varepsilon_0 |\alpha_1|} \phi'_{,y'} - \frac{C_{11} Q_{11}^2 P_0^2}{|\alpha_1|} [2(\sigma'_{yy} + Q'_{12} \sigma'_{xx}) P'_y + Q'_{44} \sigma'_{xy} P'_x] \end{aligned} \right] \quad (12)$$

where the constant $\Gamma |\alpha_1|$ may be absorbed into the time scale [15].

In a similar manner, Gauss's law is rescaled as:

$$(P'_{x,x'} + P'_{y,y'}) - \theta(\phi'_{,x'x'} + \phi'_{,y'y'}) - \rho' = 0 \quad (13)$$

and the equilibrium equation is rescaled as:

$$\begin{cases} \sigma'_{xx,x'} + \sigma'_{xy,y'} = 0 \\ \sigma'_{xy,x'} + \sigma'_{yy,y'} = 0 \end{cases} \quad (14)$$

The rescaled TDGL equations, Eqs. (11) and (12), and the constraints in Eqs. (13) and (14) are discretized onto uniform spatial grids (400 x 64, 256 x 64 and 256 x 16) using second-order symmetric finite differences and solved in real space using an iterative method with explicit time stepping. In the present paper, we use the material parameters for tetragonal $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ [12]. At $T = 298$ K, the parameters are $\alpha_1 = -2.494 \times 10^8$ m/F, $\alpha_{11} = 2.5832 \times 10^7$ m⁵/C²F, $\alpha_{12} = 1.0218 \times 10^9$ m⁵/C²F, $\alpha_{111} = 1.4088 \times 10^9$ m⁹/C⁴F, $\alpha_{112} = 2.05 \times 10^9$ m⁹/C⁴F, $Q_{11} = 7.887 \times 10^{-2}$ m⁴/C², $Q_{12} = -2.480 \times 10^{-2}$ m⁴/C², $Q_{44} = 6.356 \times 10^{-2}$ m⁴/C², $C_{11} = 1.746 \times 10^{11}$ N/m², $C_{12} = 7.937 \times 10^{10}$ N/m², $C_{44} = 1.111 \times 10^{11}$ N/m². This corresponds to a stable tetragonal ferroelectric phase given by the spontaneous polarization, $P_0 = 0.647$ C/m². We also set $K' = K/[|\alpha_1| \delta^2] = 1$ and $\delta = 1$ nm, which sets the gradient coefficient, K , as $|\alpha_1| \delta^2 = 1.247 \times 10^8$ Jm³C⁻². From our simulations, we have confirmed that with these choices, our domain wall thicknesses are of the same order as the experimental domain wall thicknesses of 1.3 nm [17] in PZT.

In order to test the validity of our elasticity solver, we performed test simulations for homogeneous

stress-free systems. The stress-free strains obtained by us were found to be consistent with the analytical formulae in Eq. (7), i.e., $\varepsilon_{xx} = Q_{11}P_x^2 + Q_{12}P_y^2$, $\varepsilon_{yy} = Q_{11}P_y^2 + Q_{12}P_x^2$ and $\varepsilon_{xy} = Q_{12}P_xP_y$. Similarly to test the solver for Maxwell equations, we applied external electric fields to homogeneous stress-free states and found that the obtained values of the electrical polarization were consistent with the analytically obtained polarization vs. electric field curve for homogeneous systems. The intrinsic coercive field, E_c (i.e., the electric field required to homogeneously reverse all the dipoles which may be obtained from the condition, $\partial F_T / \partial P_x = 0$ for homogeneous stress-free systems), was also obtained from the simulations and was found to be consistent with the analytical solution.

Since the aim of the present paper is to study localized switching of domains, the potentials are applied in selective regions of space. The two configurations studied in this paper are a parallel-plate capacitor geometry (electrode/ferroelectric-electrode, Fig. 1a), which is the building block of many devices [16], as well as a geometry somewhat approximate to that in a PFM setup (Fig. 1b). The boundaries are assumed to be traction-free, with zero gradients in the polarization ($P_{i,j} = 0$). The vanishing polarization gradients also imply that the bound charge is assumed to be perfectly compensated and hence there are no internal depolarization fields. For the electrostatic potential, we assume that $\vec{\nabla}\Phi \cdot \vec{n} = 0$, where $\vec{n}$ is the unit normal to the surface, except at the electrodes where the potential is specified. The use of traction-free boundary conditions and neglecting the depolarization fields allow us to isolate phenomena that are occurring purely due to the fringing of the electric field caused by the discontinuity in the applied potential.

3. Simulation

Initially, a single domain state with polarization direction normal to the film surface is created for both configurations. This is achieved by setting the polarization at every point inside the grid to the spontaneous polarization, P_0 , with a small initial random thermal noise (Gaussian distribution with mean $P_y/P_0 = 1.0$, standard deviation = 0.001) to ensure that any form of nucleation in the microstructure does not occur due to numerical artifacts. The system is allowed to equilibrate for 20,000 time steps to ensure a stable remnant state with $P_y > 0$. Thereafter, the film is switched by changing the boundary condition for the electrostatic potential at the electrodes as shown in Fig. 1, with $V_0 = \theta[P_0\delta/\varepsilon_0]\Phi'_0$, for different values of the film thickness t_{film} and the electrode width w . The frequency ω is chosen such that a full hysteresis loop occurs over 800,000 time steps. The average electric field in the region below the top electrode is calculated as $E_y = -\Delta V/t_{film}$, where ΔV is the potential

difference between the two electrodes.

To understand the switching mechanism, it is important to analyze the electric field distributions obtained due to the applied potentials for both the configurations. Fig. 2 shows the electric field distributions for both the capacitor and PFM-like geometry for the 64 nm film. The snapshots in Fig. 2a and b correspond to a situation where the polarization below the electrode has still not switched. It is clear that significant fringing of the electric field is observed for both cases. The fringing electric fields form due to the discontinuity in the boundary conditions, where $\Phi_{,y} = 0$ at the top and bottom boundaries except at the electrodes, where the boundary condition is of the form $\Phi' = \Phi'_0 \sin(\omega t)$. Notice that, due to the fringing effects, the influence of the applied potential extends to a region far beyond the region over which the potential is applied. Figs. 3 and 4 show that fringing effects strongly influence the switching process. In particular, components of the electric field along the film surface (i.e., the $\pm x$ directions) have the tendency to drive the local polarizations to the free energy minima at $(\pm P_s, 0)$. This leads to switching via two 90° rotations of the polarization vector for both geometries. We should point out that, while 90° domains are often associated with substrate constraints [18,19], in the present model these are formed purely due to the fringing electric fields that can be clearly seen in Figs. 2 and 5. This is also evidenced by a lack of 90° domains at the bottom electrodes for the PFM case (Fig. 3), where the potential does not encounter a discontinuity. We note that in a real system, although there may be other nucleation sources, such as static defects and substrate effects, the discontinuity in the boundary conditions at the electrodes will still contribute towards a lateral component in the electric field and may therefore influence the switching process.

For the PFM geometry, the domain evolution for the case $t_{\text{film}} = 64$ nm, $w = 32$ nm is as shown in Fig. 3. The corresponding polarization–electric field (P–E) hysteresis loops, as well as the strain–electric field butterfly loops are also shown. Here, $\langle P_y/P_0 \rangle$ is calculated by averaging the polarization in the region below the top electrode. The domain patterns in Fig. 3 are plotted using a color scheme in which the polarizations point downwards in the blue regions, upwards in the green regions, left in the white regions and right in the red regions, while regions of zero polarization appear as black. Hence, interfaces between a red/white region and a blue/green region indicate the presence a 90° domain wall (polarization vectors oriented at 90° to each other), while interfaces between a green and blue region or red and white region indicates a 180° domain wall (polarization vectors oriented at 180° to each other). The red and black electrodes in Fig. 1 are plotted as horizontal lines at the top & bottom of the domain structures (A) to (P) in the leftmost

and rightmost columns of Fig. 3. The simulation starts with a single domain state with polarization vector pointing upwards. This corresponds to point (A) of Fig. 3. As the switching progresses, fringing of the electric fields leads to 90° domain wedge nucleation at point (B). These domain wedges grow in length and width at (C), and allow a second 90° rotation of the polarization vector, resulting in the appearance of blue regions (with polarization vector pointing downwards) in (D). These regions grow at the expense of other regions until the domain is completely switched (H). Note that the lateral size of the switched domain extends well beyond the top electrode. This can be understood by examining Fig. 2b, where the influence of the electric field is observed beyond the top electrode due to fringing. In the reverse switching process, nucleation of inclined domain wedges occurs (J), and these wedges grow until they merge with the 180° domain walls (K), leading to the collapse of these walls (L and M), and further increase of the electric field leads to disappearance of the remaining domain structures (N and O), until the reverse switching is complete (P). The inclined 90° ferroelastic domains near points (F–G) and (N–O) of Fig. 3, and later near points (O–P) of Fig. 4, are somewhat similar to those observed by Chen et al. [6] in their PFM setup.

In the case of the ferroelectric capacitor geometry, the domain evolution is shown in Fig. 4. The polarization–electric field curve as well as the strain–electric field curve are obtained in the same manner as before in Fig. 3. As in the case of the PFM-like geometry, nucleation of inclined 90° domain wedges occurs at point (B). However, unlike the PFM geometry case, wedges appear from the top as well as bottom electrodes. As the switching proceeds, these wedges merge (C) and grow (D). The blue reverse-switched regions start to appear at point (D) and grow at the expense of the other regions until the domain is completely reversed (I). Even for this case, due to the fringing effects observed in Fig. 2a, the switched domain extends beyond the electrodes. Reversal of the electric field again leads to nucleation of inclined 90° domain wedges at the point of discontinuity between the electrode edges. The growth of these wedges (K) leads to the collapse of 180° domain walls (L, M and N). Green regions appear at (M) and grow at the expense of other regions until point (P).

Next, we focus our attention on films with smaller thickness to investigate whether the switching mechanism discussed above persists at very small thicknesses. To address this question, switching simulations similar to those in Figs. 3 and 4 were performed for several thicknesses, ranging from 64 to 12 nm for both configurations for several values of the electrode width w . Since we have shown that fringing of the electric field strongly influences the switching process, it is important to examine the nature of fringing at smaller thicknesses. Fig. 5a and b depicts the distribution

of the electric fields due to the applied potentials for both the PFM and the capacitor set up for a film with thickness $t_{\text{film}} = 16$ nm. As in Fig. 2a and b, this situation corresponds to the situation where the domain below the electrode is still not switched. Notice that the fringing is much less pronounced compared to Fig. 2a and b. The reduced extent of fringing has important consequences for the domain switching at smaller thicknesses. For the case of electrode width, $w = 32$ nm, we find that switching occurs below a thickness of about 14 nm for the PFM and about 24 nm for the capacitor, by a pure 180° switch and no intermediate formation of 90° domains is observed. The direct 180° switching for a film with thickness $t_{\text{film}} = 12$ nm is depicted in Fig. 6 for the PFM set up. It can be seen that a direct switch initiates from the middle of the film and the reversed domain then grows by sideways motion. Here also we observe that the lateral size of the switched domain extends beyond the top electrode. The fact that the reversed domain initiates from the middle of the film points to the fact that the component of the electric field along the switching direction is largest in the middle.

From the above results we conclude that competition between the fringing-induced electric field component parallel to the film surface and the component normal to the film (along the switching direction) governs the polarization switching behavior. At greater thicknesses, the component parallel to the film nucleates 90° domains whereas at smaller thicknesses, this component is weaker and the switching occurs by direct 180° switching. In fact, for some simulations at intermediate thicknesses, we found both processes occurring together.

To study lateral size effects, the width of the top electrode (Fig. 1), w , is set as $w = 10, 32, 48, 64$ and 128 grid steps, which correspond to approximately 10, 32, 48, 64 and 128 nm, based on a grid size of $\delta = 1$ nm. We performed simulations for several values of the width w , whereby we observed fringing behavior similar to the case $t_{\text{film}} = 64$ nm, $w = 32$ nm with the capacitor (Fig. 4) as well as the PFM-like geometry (Fig. 3). However, it is instructive to compare the switching loops as a function of w as well as the film thickness t_{film} for both the PFM case as well as the parallel-plate capacitor. The hysteresis loops are computed using the same method as in Fig. 3. The results for the two different thicknesses, $t_{\text{film}} = 16$ nm and $t_{\text{film}} = 64$ nm, are shown in Figs. 7 and 8 for the PFM and the parallel-plate capacitor, respectively. It is clear from these figures that the coercive field increases for decreasing values of the lateral size, w . This can also be seen by replotting the coercive field data from Figs. 7 and 8 as shown in Fig. 9.

In all cases, at very small lateral sizes (i.e., $w = 10$ nm), where the electric field becomes highly inhomogeneous, the coercive field becomes much larger than the intrinsic coercive field, E_c , implying that there is a minimum lateral size whereby the film becomes very difficult or virtually impossible to switch. At very small lateral sizes, the fringing fields from the two edges overlap and this results in a reduced net component the electric field normal to the film (i.e., along the switching direction). This reduction in the electric field is responsible for the increase in the coercive field at small lateral widths of the electrode. Our lateral sizes of about 10 nm are close to the results of Wang et al. [8], who proposed a minimum critical width of 7.4 nm for PbTiO_3 and 9.1 nm for BaTiO_3 . At the other extreme, when the lateral size becomes much larger, the coercive field appears to approach that of the intrinsic coercive field (Fig. 9).

In the previous sections, the electric field was calculated using $E_y = -\Delta V/t_{\text{film}}$. However, it is also instructive to examine the thickness and lateral size dependence of the switching behavior in terms of the average electric field in the entire film, $E_y^{\text{average}} = \langle -\frac{\partial \Phi}{\partial y} \rangle$. This is because due to fringing, the internal electric field extends beyond the electrode. Remarkably, in Fig. 10 we observe the opposite trend to that of Fig. 9, where the coercive field increased with decreasing lateral size. The average electric field is related to total stored electrostatic energy in the entire film, and we would expect that lower electrostatic energy is required to switch domains with smaller lateral sizes. This is the case in Fig. 10 for all the configurations, although in the 64 nm PFM case we note a slight deviation, possibly due to the effects of fringing.

Due to the fringing electric fields (Figs. 2 and 5), the width of the switched area becomes larger than that of the electrode (Fig. 11) in all cases. For both geometries, we observe a lack of intermediate 90° domains at smaller thicknesses. This is in agreement with experimental observations showing the disappearance of such domains for small sizes [5,7]. We also note that the coercive field is always larger than that of the intrinsic (Fig. 9) and that, even for the 64 nm thick film, the presence of 90° domain wedges does not reduce the coercive field below that of the intrinsic.

4. Conclusions

We have investigated the localized switching of nano-scale ferroelectric domains in ferroelectric thin films using real space TDGL simulations in two dimensions that take into account the long-range elastic and electrostatic fields. Using the boundary conditions on the electrostatic potential we simulated two configurations, one that mimicked a PFM setup and another that is relevant to a

parallel-plate capacitor. Although our simulations are in two dimensions, most of the conclusions of this paper are general and are valid for 3D systems as well. However, the appropriate microstructure in three dimensions will be more complex due to larger number of the variants which may change the results quantitatively.

We studied the effects of fringing of the electric field on the switching process. Fringing introduces an electric field component parallel to the film surface which at sufficiently large thicknesses becomes large enough to nucleate intermediate 90° domains. However, these intermediate domains do not occur in films with smaller thicknesses where the fringing effects are reduced. At smaller thicknesses, the film instead undergoes direct switching via 180° reversals of the polarization vector. An important finding, regardless of geometry and thickness of the film, is that the coercive field increases with decreasing the lateral size of the electrode and approaches the intrinsic coercive field for the large lateral sizes. In fact, for very small lateral size, it becomes very difficult or impossible to switch the domain. Another important consequence of the fringing electric fields is that the switched region in ferroelectric thin film can extend beyond the width of the electrode, which may have consequences in the packing density for nanoscale features in ferroelectric thin film.

Acknowledgements

The authors would like to acknowledge Chen Lang and David Srolovitz for useful discussions.

References

- [1] Tagantsev AK, Gerra G. J Appl Phys 2006;100:051607.
- [2] Streiffner SK, Eastman JA, Fong DD, Thompson C, Munkholm A, Ramana Murty MV, et al. Phys Rev Lett 2002;89(6):067601.
- [3] Junquera J, Ghosez P. Nature 2003;422:506–9.
- [4] Scott JF. Annu Rev Mater Sci 1998;28:79–100.
- [5] Buhlmann S, Dwir B, Baborowsky J, Muralt P. Appl Phys Lett 2002;80(17):3195–7.
- [6] Chen L, Ouyang J, Ganpule CS, Nagarajan V, Ramesh R, Roytburd AL. Appl Phys Lett 2004;84(2):254–6.
- [7] Lee K, Yi H, Park WH, Kim YK, Baik S. J Appl Phys 2006;100:051615.
- [8] Wang YG, Zhong WL, Zhang PL. Phys Rev B 1995;51(23):17235–8.
- [9] Roytburd AL, Alpay SP, Nagarajan V, Ganpule CS, Aggarwal S, Williams ED, et al. Phys Rev Lett 2000;85(1):190–3.
- [10] Kalinin SV, Rodriguez BJ, Jesse S, Chu YH, Zhao T, Ramesh R, et al. Proc Natl Acad Sci USA 2007;104(51):20204–9.
- [11] Chandra P, Littlewood PB. A Landau primer for ferroelectrics. In: Rabe KM, Ahn CH, Triscone JM, editors. Physics of ferroelectrics. Berlin, Heidelberg: Springer-Verlag; 2007. p. 69–115.
- [12] Haun MJ, Zhuang ZQ, Furman E, Jang SJ, Cross LE. Ferroelectrics 1989;99:45–54.
- [13] Ducharme S, Fridkin VM, Bune AV, Palto SP, Blinov LM, Petukhova NN, et al. Phys Rev Lett 2000;84(1):175–7.
- [14] Chen LQ. Annu Rev Mater Res 2002;32:113–40.
- [15] Bray AJ. Adv Phys 1994;43(3):357–459.
- [16] Xiao Y, Shenoy VB, Bhattacharya K. Phys Rev Lett 2005;95:247603.
- [17] Choudhury S, Li Y, Chen LQ. J Am Ceram Soc 2005;88(6):1669–72.
- [18] Kwak BS, Erbil A, Budai JD, Chisholm MF, Boatner LA, Wilkens BJ. Phys Rev B 1994;49(21):14865–79.
- [19] Roytburd AL, Alpay SP, Bendersky LA, Nagarajan V, Ramesh R. J Appl Phys 2001;89(1):553–6.

List of Figures

Fig. 1. (a) Parallel-plate capacitor geometry and (b) geometry approximate to a PFM setup.

Fig. 2. Electric field vectors as obtained from the solution to Eq. (13) for (a) the capacitor geometry (at $t = 37,500$, $\Phi' = \Phi'_0 \cos(\omega t) = 27.4$) and (b) the PFM-like geometry (at $t = 30,000$, $\Phi' = \Phi'_0 \cos(\omega t) = 31.4$). The electrode width $w = 32$ nm and the film thickness $t_{\text{film}} = 64$ nm for both configurations.

Fig. 3. Domain evolution for film thickness $t_{\text{film}} = 64$ nm and lateral size $w = 32$ nm. Domain structures (A) to (P) correspond to the points (A) to (P) marked on the hysteresis loop ($\langle P_y/P_0 \rangle$ vs. E_y/E_c) and butterfly loop ($\langle \epsilon_{yy} \rangle$ vs. E_y/E_c). Black arrows refer to the polarization directions.

Fig. 4. Domain evolution for capacitor geometry with film thickness $t_{\text{film}} = 64$ nm and lateral size $w = 32$ nm. Domain structures A to P correspond to the points A to P in the hysteresis and butterfly loops.

Fig. 5. Electric field for (a) the capacitor geometry and (b) the PFM-type geometry just before switching ($t = 80,000$). The electrode width $w = 32$ nm and the film thickness, $t_{\text{film}} = 16$ nm for both configurations.

Fig. 6. Domain evolution during switching near the coercive field for the PFM-type geometry with $t_{\text{film}} = 12$ nm, $w = 32$ nm at (a) $t = 20,500$ time steps, (b) $t = 75,000$ time steps, (c) $t = 75,500$ time steps and (d) $t = 80,000$ time steps. The color scheme is the same as in Fig. 3. A direct 180° switch that initiates from the center can be clearly seen.

Fig. 7. Average polarization vs. electric field in rescaled units for film thicknesses $t_{\text{film}} = 16$ and 64 nm and lateral sizes $w = 10, 32, 48, 64$ and 128 nm in the capacitor geometry.

Fig. 8. Average polarization vs. electric field in rescaled units for film thicknesses $t_{\text{film}} = 16$ and 64 nm and $w = 10, 32, 48, 64$ and 128 nm in the approximate PFM geometry.

Fig. 9. Rescaled electric field, E_y/E_c as a function of lateral size $w = 10, 32, 48, 64$ and 128 nm, at different thicknesses.

Fig. 10. Rescaled electric field, $E^{average}_y=E_c$ (electric field averaged over the whole film) as a function of lateral size $w = 10, 32, 48, 64$ and 128 nm, at different thicknesses.

Fig. 11. Size of the region switched by the electric field for (a) capacitor geometry and (b) PFM geometry as a function of the lateral size of the electrode, w .

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.