Stability of a Ferroelectric Phase with Electrical Domains in Multilayers

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Multilayer $BaTiO_3$-$SrTiO_3$ and $PbTiO_3$-$SrTiO_3$ structures with different electrical domain states are studied using a Landau-Ginzburg-Devonshire free energy. Polarizations in the layers are computed for multi-domain and single-domain states where the paraelectric-to-ferroelectric volumetric layer ratio is varied. It is shown that the ferroelectric layers with electrical domains are thermodynamically more stable than the single-domain ferroelectric state. High domain wall energies result in the stabilization of the paraelectric state in the ferroelectric layers for large depolarizing fields. It is concluded that the stability of single-domain state ferroelectric layers correspond to a very small paraelectric-to-ferroelectric ratio after which multi-domain ferroelectric state is favored.

Ferroelectric (FE) thin heterostructures have been the focus of both the industry and the scientific community owing to their attractive electrical properties that could be tailored as functional components in new generation devices. Within the last two decades, possibility of growing FE structures together with another functional component either in a bilayer or a multilayer form on a misfitting substrate has been demonstrated. This has opened the gate to new possibilities where the properties of the entire multilayer system can be tuned towards a desired application through component fractions. Enhancement of the electric polarization [1-3], a giant dielectric response at critical component fractions and alteration of the Curie points (T_C) of the constituent layers were among the reported and predicted [4-13].

In a series of articles, Bratkovsky and Levanyuk theoretically demonstrated that a FE thin film with 180º electrical domains is more stable when in the form of a capacitor sandwiched between electrodes if there are depolarizing fields (DFs) due to either ferroelectrically dead layers near the FE-electrode interface or if there is imperfect electrode screening [14-16]. As the DFs scale with $1/\varepsilon_0$ where ε_0 is the permittivity of free space ($\varepsilon_0 = 8.85\times10^{-11}$ F/m, in SI units), a slight polarization variation ΔP (C/m^2) normal to a surface or an interface can create very strong electric fields, close to a form $\Delta P/\varepsilon_0$, that is sufficient to suppress ferroelectricity when there are no free charges. Keeping in sight the magnitude of the order of the polarization energy in FEs such as $BaTiO_3$ (BT), $PbTiO_3$ (PT) or solid solutions of Ba,Sr,TiO_3 (BST) and Pb,Zr,TiO_3 (PZT), even a 10^{-5} or 10^{-6} ΔP can introduce an additional energy to the system comparable to polarization energy sufficient to destabilize the ferroelectricity and the system will want to lower its energy by existing in the paraelectric (PE) state.

All what is explained until now can happen well below the T_C of the FE. The debate at this point has been whether the FE really switches to the paraelectric state to lower its energy due to the DF or it splits into electrical domains that lead to a globally zero DF, stabilizing a FE state within each domain. Thermodynamically, it is now well-established that the latter option should be the path to minimize the DF energy but at the expense of the domain wall (DW) energy. If the film is too thin to sustain the DW energy arising from a short period alternating up-down polarization configuration of the 180º domains, the PE state will be preferred and thus become stable. It must also be kept in mind that the electrical domain periodicity, hence the DW energy density, is one of the consequences of the competition between DWs and the system's tendency to compensate for DF as the film thickness is reduced (higher surface area-to-volume ratio). This has very important implications when designing integrated systems employing FEs as functional components in the form of films as well as multilayers.

In this letter, the stability of ferroelectric layers in FE-PE multilayers are analyzed using a Landau-Ginzburg-Devonshire free energy where the strain effects, electrostatic coupling, freedom of electrical domain formation are taken into account in the continuum limit at room temperature (RT). Supposing a perfect interface between the FE and the PE and that the FE can either exist in a single-domain (SD) state or a multi-domain (MD) state, the free energy is written in a modified form of the energy expression used in Refs. 8 and 10 that were for SD states. The energy expression in this work also allows the system to exist in MD state by assigning the FE layer two degenerate polarization states, similar to the approach in Ref. 9. The approach is applied to the BT-$SrTiO_3$ (BT-ST) and the PT-ST both with (100)//(100) epitaxy assuming the FE layers to be fully strained *c*-

phase structures on thick single crystal (100) ST substrates [17] with short-circuit boundary conditions (Figure 1). Neglecting spatial fluctuations other than short range variations of polarization at DWs, the free energy of a FE-PE multi component system can be written as:

$$F = F_1 + F_2 + F_{EL} + F_{ELASTIC} + F_{DW} \tag{1}$$

$$F_1 = (1-\alpha)\{(1-\beta)[aP_1^{\ 2} + bP_1^{\ 4} + cP_1^{\ 6} - EP_1] + \beta[aP_2^{\ 2} + bP_2^{\ 4} + cP_2^{\ 6} + EP_2]\} \tag{2}$$

$$F_2 = \alpha[dP_3^{\ 2} + eP_3^{\ 4} + fP_3^{\ 6} - EP_3] \tag{3}$$

and $$F_{EL} = \frac{1}{2}\alpha(1-\alpha)[(1-\beta)P_1 + \beta P_2 + P_3]^2 \tag{4}$$

where α is the volumetric layer fraction of the PE component ($\alpha = (L - L_1)/L$, see Figure 1), β is the fraction of ferroelectric domains that have negative vector sign (taken as 0.5 in this study assuming degeneracy). $P_{1,2}$ are the degenerate polarization states in the 180º domains of the FE, P_3 is the polarization of the PE, *E* is the externally applied field (zero in this work). *a*, *b*, *c* are the misfit strain-modified free energy coefficients of the FE layer, *d*, *e*, *f* are the free energy coefficients of the PE layer that were published elsewhere [18], F_{EL} is the electrostatic coupling energy responsible for the depolarization effect in the FE component, $F_{ELASTIC}$ is the elastic energy of the layers in the form $u_M^2/(S_{11}+S_{12})$ where u_M is the pseudocubic misfit[17], S_{ij} are the elastic compliances of the layers in Voigt notation [18]. F_{DW} is the DW energy in the FE approximated as $A(P_1 - P_2)^2$ where *A* scales the volumetric DW energy density cost to the system [19]. Value of *A* normally depends on additional material parameters[19] but is varied here to demonstrate the competition of this term with F_1 when the FE is allowed to split into domains (i. e., when $\beta > 0$). Note that $\beta = 0$ imposes a SD state in the FE layer and no DW term exists.

The total free energy in (1) is minimized with respect to P_1, P_2 and P_3 for $\beta = 0$ and $\beta = 0.5$ and simultaneously solved using a Newton-Rhapson iterative scheme for the BT-ST and PT-ST system with α values ranging from 0 (pure FE) to 1 (pure PE). The polarization solutions as a function of α for the BT-ST and PT-ST systems are given in Figure 2 for different magnitudes of DW energy as well as SD states. As expected, for zero DW energy (A=0), the FE layer can exist in a MD state until very small fractions (large α) in the continuum limit. With increasing DW energy density (A>0), there exists a critical α beyond which the FE layer is forced to exist in the PE state dictated by the strength of DF. On the other hand, as seen in Figure 2a and 2b, when there is electrical domain stabilization in the FE, the ST remains macroscopically at zero polarization. Examining the polarization profile for $\beta = 0$ in Figure 2c and 2d, the PE layer has to exist at values well beyond its bulk (zero for ST at RT) to compensate for the DF due to the polarization jump at the interface (See Figure 2). In both SD BT-ST and the PT-ST, there is a critical α beyond which the system is either entirely PE or has very small values of remnant polarization. This point has sometimes been discussed to be the critical PE fraction beyond which electrical domains are stabilized in the FE. In order to verify this, one has to compare the free energies of the systems in SD and MD states. Figure 3 gives the free energies for BT-ST and PT-ST using the polarization solutions of MD and SD states given in Figure 2.

Figure 3a and 3b shows that the free energies of the MD states, despite the DW energy, are much lower than the SD states. Besides, the full SD state energy exhibits a broad hump with α in both Figure 3a and 3b (partly visible as red dots). This happens due to three reasons: First, the FE layer is not in the polarization state corresponding to the minima of the free energy. Second, the PE layer is forced to exist in a FE state which again is not the minimum free energy of itself and third, there is still a polarization jump at the interface resulting in a large, non-zero DF energy. Note that PE state has lower energy than a SD-FE state nearly in the entire α range. In addition, the PT-ST system prefers the PE state in a wide range of α for large DW energy density when $\beta = 0.5$. The very reason for this is the strain where ST substrate induces a slight tensile in-plane strain on *c*-axis oriented PT, reducing T_C with respect to its bulk counterpart, raising the F_1 value beyond that of the PE state. Also note that the formation of elastic domains to relax the self-strain of the PE-FE phase transformation in form of *a*1/*a*2 or *a*/*c* configurations, depending on the extent of misfit dislocation formation and thermal strains, is not considered in this work.

In order to determine the α until which a SD state could exist, one has to zoom into the small α region to compare the free energies of the multi- and single-domain states of BT-ST and PT-ST in Figure 3a and 3b. It can immediately be realized that the transition from the SD to the MD state occurs at very small α values and the corresponding PE layer thickness can hardly be resolved from Figure 3, at the order of 10^{-4}. This result is entirely consistent with the findings of theoretical studies of pure FE thin film capacitors and recent findings for superlattices [16, 20, 21]. Moreover, the PE state is stabilized for high DW energy densities for $\beta = 0.5$ as seen in the enlarged insets of Figure 3. Such a picture could of course change when there is an internal bias field resulting from asymmetric FE-electrode interfaces or other secondary effects such as fields due to defects and etc.. In the presence of strong DFs due to, for instance, thin layers (small α), the system cannot accommodate high DW energy density in FE state, stabilizing the PE phase. Theoretically, had there been no DW energy cost, MD state could remain stable for large PE/FE ratios as seen in Figure 2a and 2b. In reality, there is always a DW energy cost to the system both due to polarization variation and the related local elastic effects arising from the strong electrostrictive nature of FEs [16, 22].

Assuming a multilayer system that consist of FE components instead of a FE and PE, the SD state can be maintained for α larger than what is shown in this work. This critical α for MD formation in a FE-FE system, however, will still not be substantially greater than the α for a FE-PE multilayer as the DF energy will become dominant when the polarizations of the two layers differ by fraction of a few percent. For a FE-FE multilayer with each layer having different T_C, the layer that has the higher T_C will split into domains first upon cooling as also recently discussed by Roytburd *et al.* [9].

In summary, it is demonstrated that the MD state of FE layers in FE-PE multilayers or bilayers is thermodynamically favored over the SD states in BT-ST and PT-ST multilayers. When the DW energy is too costly for the system, PE state will be favored to avoid complications arising from the existence of a spontaneous polarization. The phase stabilities in this work were analyzed considering the competing DF and DW energies with renormalized free energy coefficients on (001) ST and not temperature. An externally applied field can stabilize a SD state and even remnancy can be observed in dynamic hysteresis measurements when the FE does not have sufficient time to relax into the MD state.

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13. See for example F.A. Urtiev, V.G. Kukhar and N. A. Pertsev, Appl. Phys. Lett., **90**, 252910 (2007), J.H. Lee, U.V. Waghmare and J.J. Yu, J. Appl. Phys., **103**, 124106 (2008).

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17. For fully coherent BT-ST on (001) ST, the pseudocubic misfit strain is used that has a value of -2.54% (compression) and for fully coherent PT-ST on (001) ST -1.18% (compression). The net strain changes with electrostrictive effects below T_C that is self-consistently taken into account in the calculations.

18. Free energy coefficients for BT, PT and ST and how strain modifies these can be found in N. A. Pertsev, A. G. Zembilgotov and A. K. Tagantsev, Phys. Rev. Lett., **80**, 1988 (1998), M. J. Haun, Z. Q. Zhuang, E. Furman, S. J. Jang and L. E. Cross, Ferroelectrics **99**, 45 (1989) and N. A. Pertsev, A. K. Tagantsev and N. Setter, Phys. Rev. B, **61**, R825 (2000). S_{ij} of components can also be found from the references cited herein. The elastic energy does not significantly alter the domain stabilities as there is nearly two orders of magnitude energy difference between the pure elastic energy and the polarization energy and exists in both MD and SD.

19. The original form of the DW energy is $a\delta^2(dP/dx)^2$ and acts as an energy penalty for spatial variations for a polarization wave propagating along x-axis ($\vec{P} \perp x$) with a being a function of the Curie point and δ is the correlation length, also expressed as $(a\delta^2/\Delta x^2)(P_i - P_{i-1})^2$ in a discretized form. Δx depends on the discretization and could be taken comparable to the unit cell

dimensions. $A(P_1 - P_2)^2$ term in this work is an approximate cost of DW energy density when DF energy is compensated by degenerate polarization states in a MD state and is intended for demonstrative purposes. The system is sensitive to the ratio of this term to the rest of the free energy terms, putting an imposition on the polarization solutions of a FE phase similar to the former original form of the DW energy.

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Figure Captions

Figure 1. (Color online) The schematic for the system considered in this study for the FE and PE layers.

Figure 2. (Color online) Polarization solutions in the FE layers as a function of α when electrical domains are allowed ($\beta = 0.5$) in (a) BT-ST, (b) PT-ST, P_1 and P_3 only when a SD state is imposed ($\beta = 0$) in (c) BT-ST and (d) PT-ST. Note the impact of volumetric DW energy density on stability of FE phase in (a) and (b). P_3 (polarization of ST layer) has always zero polarization for all A values when $\beta = 0.5$ in (a) and (b). In (c) and (d) for $\beta = 0$, the polarizations of each component (P_1 and P_3) are nearly the same, resulting in an overlap.

Figure 3. (Color online) Free energies of (a) the BT-ST system and (b) the PT-ST system for various magnitudes of DW energy ($\beta = 0.5$) and SD state ($\beta = 0$). Region inside the dashed line is enlarged for better visualization of the free energies of different states. The MD and PE states have always lower energy than the case for $\beta = 0$ with FE state in the layers. Note that the energies of the systems increase with larger A when $\beta = 0.5$. Only two values, A=0 and $A=10^8$ ($5\text{x}10^7$ for PT-ST) are denoted here for brevity and space limitations.

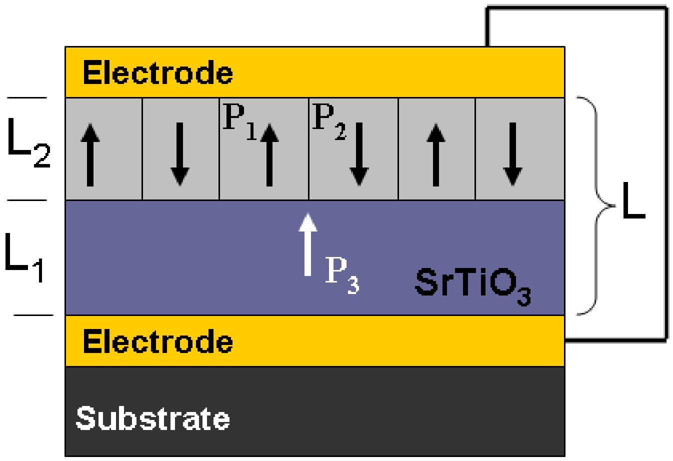

Figure 1. Misirlioglu, APL

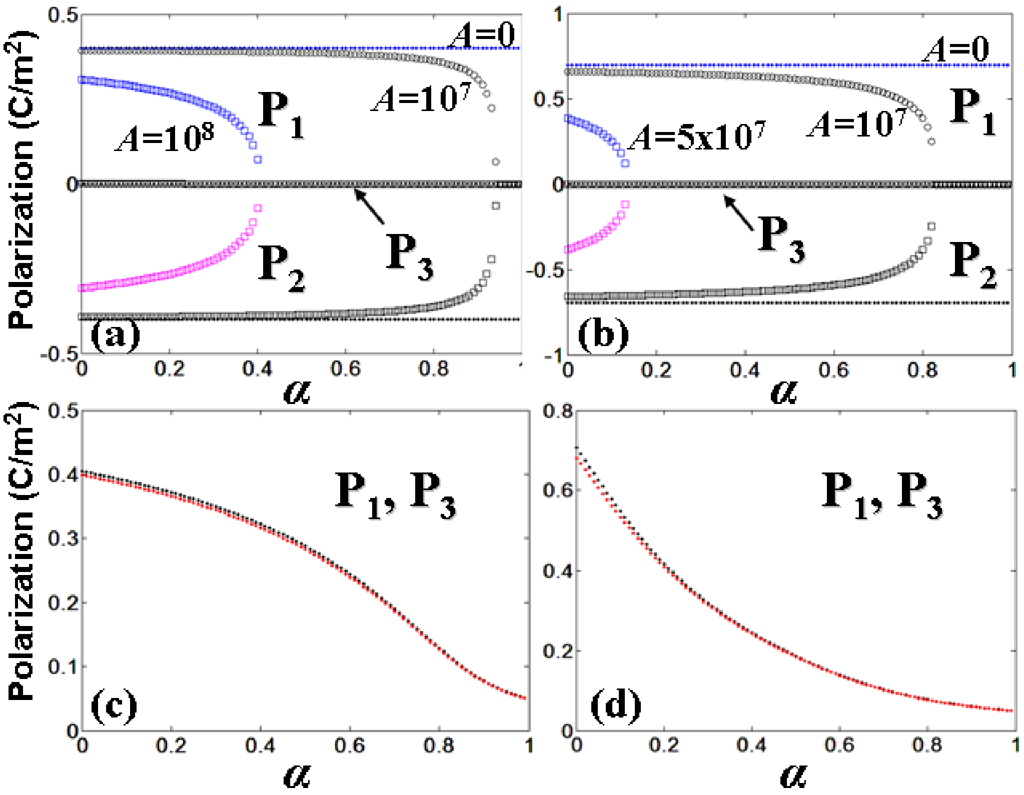

Figure 2. Misirlioglu, APL

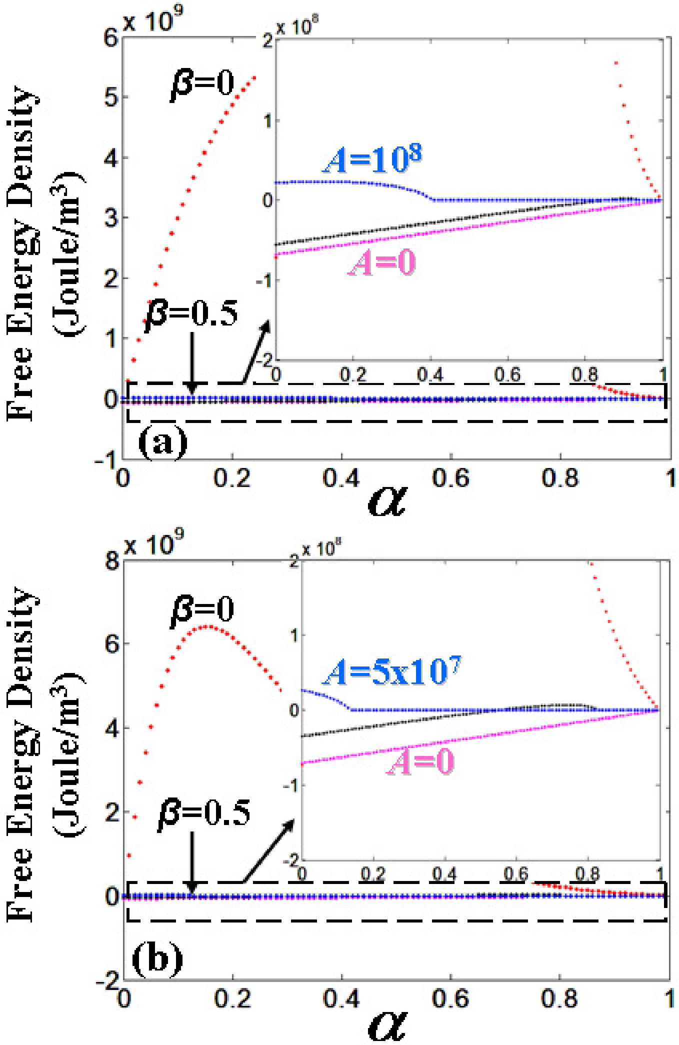

Figure 3. Misirlioglu, APL