

# 1 Stability of a ferroelectric phase with electrical domains in multilayers

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5 Multilayer BaTiO<sub>3</sub>–SrTiO<sub>3</sub> and PbTiO<sub>3</sub>–SrTiO<sub>3</sub> structures with different electrical domain states  
6 are studied using a Landau–Ginzburg–Devonshire free energy. Polarizations in the layers are  
7 computed for multidomain and single-domain states where the paraelectric-to-ferroelectric  
8 volumetric layer ratio is varied. It is shown that the ferroelectric layers with electrical domains are  
9 thermodynamically more stable than the single-domain ferroelectric state. High domain wall  
10 energies result in the stabilization of the paraelectric state in the ferroelectric layers for large  
11 depolarizing fields. It is concluded that the stability of single-domain state ferroelectric layers  
12 correspond to a very small paraelectric-to-ferroelectric ratio after which multidomain ferroelectric  
13 state is favored. © 2009 American Institute of Physics. [DOI: 10.1063/1.3129872]

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15 Ferroelectric (FE) thin heterostructures have been the fo-  
16 cus of both the industry and the scientific community owing  
17 to their attractive electrical properties that could be tailored  
18 as functional components in new generation devices. Within  
19 the past two decades, possibility of growing FE structures  
20 together with another functional component either in a bi-  
21 layer or a multilayer form on a misfitting substrate has been  
22 demonstrated. This has opened the gate to new possibilities  
23 where the properties of the entire multilayer system can be  
24 tuned toward a desired application through component frac-  
25 tions. Enhancement of the electric polarization,<sup>1–3</sup> a giant  
26 dielectric response at critical component fractions and alter-  
27 ation of the Curie points ( $T_C$ ) of the constituent layers were  
28 among the reported and predicted.<sup>4–13</sup>

29 In a series of articles, Bratkovsky and Levanyuk<sup>14–16</sup>  
30 theoretically demonstrated that a FE thin film with 180° elec-  
31 trical domains is more stable when in the form of a capacitor  
32 sandwiched between electrodes if there are depolarizing  
33 fields (DFs) due to either ferroelectrically dead layers near  
34 the FE-electrode interface or if there is imperfect electrode  
35 screening. As the DFs scale with  $1/\epsilon_0$  where  $\epsilon_0$  is the per-  
36 mittivity of free space ( $\epsilon_0 = 8.85 \times 10^{-12}$  F/m, in SI units), a  
37 slight polarization variation  $\Delta P$  (C/m<sup>2</sup>) normal to a surface  
38 or an interface can create very strong electric fields, close to  
39 a form  $\Delta P/\epsilon_0$ , that is sufficient to suppress ferroelectricity  
40 when there are no free charges. Keeping in sight the magni-  
41 tude of the order of the polarization energy in FEs such as  
42 BaTiO<sub>3</sub> (BT), PbTiO<sub>3</sub> (PT) or solid solutions of Ba, Sr, TiO<sub>3</sub>  
43 and Pb, Zr, TiO<sub>3</sub>, even a  $10^{-5}$  or  $10^{-6}$   $\Delta P$  can introduce an  
44 additional energy to the system comparable to polarization  
45 energy sufficient to destabilize the ferroelectricity and the  
46 system will want to lower its energy by existing in the  
47 paraelectric (PE) state.

48 All what is explained until now can happen well below  
49 the  $T_C$  of the FE. The debate at this point has been whether  
50 the FE really switches to the PE state to lower its energy due  
51 to the DF or it splits into electrical domains that lead to a  
52 globally zero DF, stabilizing a FE state within each domain.  
53 Thermodynamically, it is now well established that the latter  
54 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 180°  
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 con-  
sequences of the competition between DWs and the system's  
tendency to compensate for DF as the film thickness is re-  
duced (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 FE layers in FE-PE multi-  
layers are analyzed using a Landau–Ginzburg–Devonshire  
free energy where the strain effects, electrostatic coupling,  
and 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 multidomain (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 assign-  
ing the FE layer two degenerate polarization states, similar to  
the approach in Ref. 9. The approach is applied to the  
BT-SrTiO<sub>3</sub> (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<sup>17</sup> with  
short-circuit boundary conditions (Fig. 1). Neglecting spatial

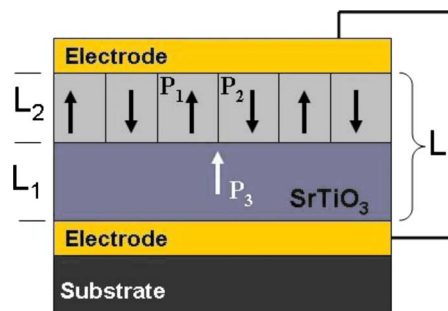


FIG. 1. (Color online) The schematic for the system considered in this study for the FE and PE layers.

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84 fluctuations other than short range variations of polarization  
 85 at DWs, the free energy of a FE-PE multicomponent system  
 86 can be written as

$$87 \quad F = F_1 + F_2 + F_{EL} + F_{ELASTIC} + F_{DW}, \quad (1)$$

$$88 \quad F_1 = (1 - \alpha)\{(1 - \beta)[aP_1^2 + bP_1^4 + cP_1^6 - EP_1] + \beta[aP_2^2$$

$$89 \quad + bP_2^4 + cP_2^6 + EP_2]\}, \quad (2)$$

$$90 \quad F_2 = \alpha[dP_3^2 + eP_3^4 + fP_3^6 - EP_3], \quad (3)$$

$$91 \quad \text{and} \quad F_{EL} = \frac{1}{2}\alpha(1 - \alpha)[(1 - \beta)P_1 + \beta P_2 + P_3]^2, \quad (4)$$

92 where  $\alpha$  is the volumetric layer fraction of the PE component  
 93 ( $\alpha = (L - L_1)/L$ , see Fig. 1),  $\beta$  is the fraction of FE domains  
 94 that have negative vector sign (taken as 0.5 in this study  
 95 assuming degeneracy).  $P_{1,2}$  are the degenerate polarization  
 96 states in the  $180^\circ$  domains of the FE,  $P_3$  is the polarization of  
 97 the PE,  $E$  is the externally applied field (zero in this work).  $a$ ,  
 98  $b$ ,  $c$  are the misfit strain-modified free energy coefficients of  
 99 the FE layer,  $d$ ,  $e$ ,  $f$  are the free energy coefficients of the PE  
 100 layer that were published elsewhere,<sup>18</sup>  $F_{EL}$  is the electrostatic  
 101 coupling energy responsible for the depolarization effect in  
 102 the FE component,  $F_{ELASTIC}$  is the elastic energy of the lay-  
 103 ers in the form  $u_M^2/(S_{11} + S_{12})$  where  $u_M$  is the pseudocubic  
 104 misfit,<sup>17</sup>  $S_{ij}$  are the elastic compliances of the layers in Voigt  
 105 notation.<sup>18</sup>  $F_{DW}$  is the DW energy in the FE approximated as  
 106  $A(P_1 - P_2)^2$  where  $A$  scales the volumetric DW energy den-  
 107 sity cost to the system.<sup>19</sup> Value of  $A$  normally depends on  
 108 additional material parameters<sup>19</sup> but is varied here to demon-  
 109 strate the competition of this term with  $F_1$  when the FE is  
 110 allowed to split into domains (i. e., when  $\beta > 0$ ). Note that  
 111  $\beta = 0$  imposes a SD state in the FE layer and no DW term  
 112 exists.

113 The total free energy in Eq. (1) is minimized with re-  
 114 spect to  $P_1$ ,  $P_2$ , and  $P_3$  for  $\beta = 0$  and  $\beta = 0.5$  and simulta-  
 115 neously solved using a Newton–Raphson iterative scheme  
 116 for the BT-ST and PT-ST system with  $\alpha$  values ranging from  
 117 0 (pure FE) to 1 (pure PE). The polarization solutions as a  
 118 function of  $\alpha$  for the BT-ST and PT-ST systems are given in  
 119 Fig. 2 for different magnitudes of DW energy as well as SD  
 120 states. As expected, for zero DW energy ( $A = 0$ ), the FE layer  
 121 can exist in a MD state until very small fractions (large  $\alpha$ ) in  
 122 the continuum limit. With increasing DW energy density  
 123 ( $A > 0$ ), there exists a critical  $\alpha$  beyond which the FE layer is  
 124 forced to exist in the PE state dictated by the strength of DF.  
 125 On the other hand, as seen in Figs. 2(a) and 2(b), when there  
 126 is electrical domain stabilization in the FE, the ST remains  
 127 macroscopically at zero polarization. Examining the polar-  
 128 ization profile for  $\beta = 0$  in Figs. 2(c) and 2(d), the PE layer  
 129 has to exist at values well beyond its bulk (zero for ST at RT)  
 130 to compensate for the DF due to the polarization jump at the  
 131 interface (see Fig. 2). In both SD, BT-ST and the PT-ST,  
 132 there is a critical  $\alpha$  beyond which the system is either en-  
 133 tirely PE or has very small values of remnant polarization.  
 134 This point has sometimes been discussed to be the critical PE  
 135 fraction beyond which electrical domains are stabilized in  
 136 the FE. In order to verify this, one has to compare the free  
 137 energies of the systems in SD and MD states. Figure 3 gives  
 138 the free energies for BT-ST and PT-ST using the polarization  
 139 solutions of MD and SD states given in Fig. 2.

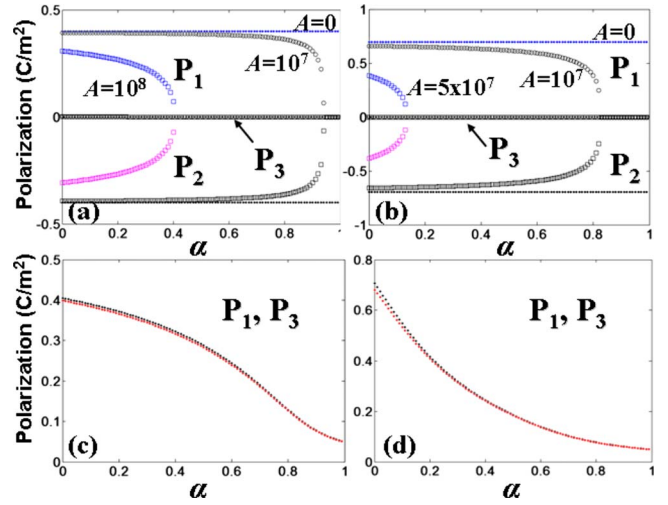


FIG. 2. (Color online) Polarization solutions in the FE layers as a function of  $\alpha$  when electrical domains are allowed ( $\beta = 0.5$ ) in (a) BT-ST, (b) PT-ST,  $P_1$  and  $P_3$  only when a SD state is imposed ( $\beta = 0$ ) in (c) BT-ST and (d) PT-ST. Note the impact of volumetric DW energy 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.

140 Figures 3(a) and 3(b) shows that the free energies of the  
 141 MD states, despite the DW energy, are much lower than the  
 142 SD states. Besides, the full SD state energy exhibits a broad  
 143 hump with  $\alpha$  in both Figs. 3(a) and 3(b) (partly visible as red  
 144 dots). This happens due to three reasons: First, the FE layer  
 145 is not in the polarization state corresponding to the minima  
 146 of the free energy. Second, the PE layer is forced to exist in  
 147 a FE state which again is not the minimum free energy of  
 148 itself. And third, there is still a polarization jump at the in-  
 149 terface resulting in a large, nonzero DF energy. Note that PE  
 150 state has lower energy than a SD-FE state nearly in the entire  
 151  $\alpha$  range. In addition, the PT-ST system prefers the PE state in  
 152 a wide range of  $\alpha$  for large DW energy density when  $\beta$   
 153 = 0.5. The very reason for this is the strain where ST sub-  
 154 strate induces a slight tensile in-plane strain on  $c$ -axis ori-  
 155 ented PT, reducing  $T_C$  with respect to its bulk counterpart,  
 156 raising the  $F_1$  value beyond that of the PE state. Also note  
 157 that the formation of elastic domains to relax the self-strain  
 158 of the PE-FE phase transformation in form of  $a1/a2$  or  $a/c$   
 159 configurations, depending on the extent of misfit dislocation  
 160 formation and thermal strains, is not considered in this work.

161 In order to determine the  $\alpha$  until which a SD state could  
 162 exist, one has to zoom into the small  $\alpha$  region to compare the  
 163 free energies of the MD and SD states of BT-ST and PT-ST  
 164 in Figs. 3(a) and 3(b). It can immediately be realized that the  
 165 transition from the SD to the MD state occurs at very small  
 166  $\alpha$  values and the corresponding PE layer thickness can  
 167 hardly be resolved from Fig. 3, at the order of  $10^{-4}$ . This  
 168 result is entirely consistent with the findings of theoretical  
 169 studies of pure FE thin film capacitors and recent findings for  
 170 superlattices.<sup>16,20,21</sup> Moreover, the PE state is stabilized for  
 171 high DW energy densities for  $\beta = 0.5$  as seen in the enlarged  
 172 insets of Fig. 3. Such a picture could of course change when  
 173 there is an internal bias field resulting from asymmetric FE-  
 174 electrode interfaces or other secondary effects such as fields  
 175 due to defects and etc. In the presence of strong DFs due to,  
 176 for instance, thin layers (small  $\alpha$ ), the system cannot accom-

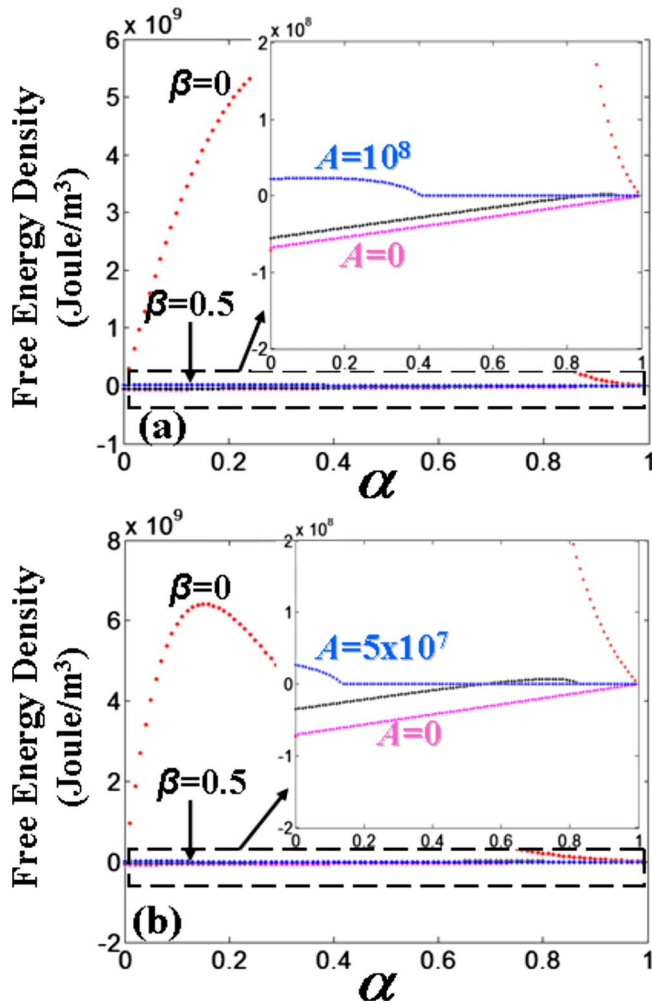


FIG. 3. (Color online) Free energies of (a) the BT-ST system and (b) the PT-ST system for various magnitudes of DW energy ( $\beta=0.5$ ) and SD state ( $\beta=0$ ). Region inside the dashed line is enlarged for better visualization of the free energies of different states. The MD and PE states have 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  $A=10^8$  ( $5 \times 10^7$  for PT-ST) are denoted here for brevity and space limitations.

moderate 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 Figs. 2(a) and 2(b). 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.<sup>16,22</sup>

Assuming a multilayer system that consist of FE components instead of a FE and PE, the SD state can be maintained for  $\alpha$  larger than what is shown in this work. This critical  $\alpha$  for MD formation in a FE-FE system, however, will still not be substantially greater than the  $\alpha$  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.*<sup>9</sup>

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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- <sup>17</sup>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. 236
- <sup>18</sup>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); 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.). 237
- <sup>19</sup>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  $\delta$  is the correlation length, also expressed as  $(a\delta^2/\Delta x^2)(P_i - P_{i-1})^2$  in a discretized form.  $\Delta x$  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. 240
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- #1 Au: Please check the changes made in Ref. 10.
- #2 au: please check Ref. 18b for accuracy