

Compositional symmetry breaking in ferroelectric bilayers

S. Zhong and S. P. Alpay^{a)}

Department of Materials Science and Engineering and Institute of Materials Science,
University of Connecticut, Storrs, Connecticut 06269

J. V. Mantese

Delphi Research Laboratories, Shelby Township, Michigan 48315

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Compositional variations across ferroelectric bilayers result in broken spatial inversion symmetry that can lead to asymmetric thermodynamic potentials. For the case of insulating materials, ferroelectric multilayers will self-pole due to the electrostatic coupling between the layers. Polarization-graded ferroelectrics with smooth composition, temperature, or stress gradients are viewed as bilayer structures in the limit of the ever-increasing number of bilayer couples, thus permitting us to conclude that the unconventional hysteresis associated with “up” and “down” polarization graded structures are real phenomena, and not artifacts associated with free charge or asymmetric leakage current. © 2005 American Institute of Physics. [DOI: 10.1063/1.2039990]

It has been more than ten years since an unconventional form of hysteresis was first observed and characterized from polarization-graded ferroelectrics (FEs).¹ Subsequently, it was concluded that the offsets observed from “up” and “down” graded materials were the result of “built-in” potentials due to the polarization gradients; much analogous to the potentials that account for the asymmetric conduction observed from semiconductor junction devices.² Successive theoretical refinements of these concepts; starting first with a simple Slater model,³ followed by a transverse Ising model,^{4,5} electrostatic analysis,⁶ and finally detailed thermodynamic modeling^{7–9} have yielded progressively better descriptions for these internal potentials, the latter of which can completely account for most of the experimental observations related to the structures without any free “fitting” parameters. However, despite a long succession of theoretical and experimental papers^{10–14} aimed at conclusively showing that the observed properties are a direct result of the polarization gradients, controversy still persists as to the role of free charge or asymmetric leakage current in determining the hysteretic response of polarization graded structures.^{15,16}

Thus, in this letter, we examine the simplest of constructs, FE bilayers having differing levels of intrinsic polarization and permittivity. We specifically show that even in the absence of free charges, a polarization difference between the two layers skews the otherwise symmetric potentials of the constituent FE materials, thereby breaking the spatial symmetry of the potentials and making it more energetically favorable for the FE bilayers to self-pole. Our findings are entirely consistent with first principles calculations that also revealed asymmetric potentials from inhomogeneous ferroelectric structures.^{17,18}

Consider a bilayer consisting of two FE layers with equal lateral dimensions sandwiched between electrodes as shown in Fig. 1(a). A FE superlattice consisting of sets of identical bilayers with the same short-circuit conditions can be treated analogously. In its most general form, the energy

density of Layers 1 and 2 in their uncoupled unconstrained state can be expressed as:

$$\begin{aligned} F_1 &= F_{0,1} + \frac{1}{2}aP_1^2 + \frac{1}{4}bP_1^4 + \frac{1}{6}cP_1^6, \\ F_2 &= F_{0,2} + \frac{1}{2}dP_2^2 + \frac{1}{4}eP_2^4 + \frac{1}{6}fP_2^6, \end{aligned} \quad (1)$$

where $F_{0,i}$ is the energy of layer i in its high-temperature paraelectric state, P_i are the polarizations of Layers 1 and 2, and $a, b, c, d, e,$ and f are Landau coefficients. a and d are temperature dependent with their temperature dependency given by the Curie–Weiss law, i.e., $a=(T-T_{C,1})/\epsilon_0C_1$ and $d=(T-T_{C,2})/\epsilon_0C_2$ where ϵ_0 is the permittivity of free space, $T_{C,i}$ and C_i are the Curie–Weiss temperature and constant of Layer i . The other coefficients for both materials are assumed to be temperature independent. The spontaneous polarization for each layer ($P_{0,i}$) is given by the condition of thermodynamic equilibrium, $\partial F_i/\partial P_i=0$.

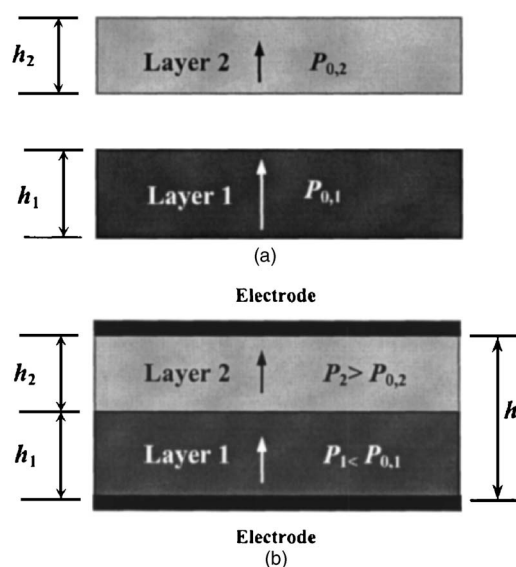


FIG. 1. (a) Freestanding FE bilayer with equal lateral dimensions. The initial polarization in Layers 1 and 2 are $P_{0,1}$ and $P_{0,2}$, respectively, and $P_{0,1} > P_{0,2}$. (b) A FE bilayer constructed by joining the layers in (a), sandwiched between metallic top and bottom electrodes. Due to interlayer coupling the polarization in Layer 1 (P_1) is less than its uncoupled value $P_{0,1}$ and the polarization in Layer 2 (P_2) is larger than $P_{0,2}$.

^{a)} Author to whom correspondence should be addressed; electronic mail: p.alpay@ims.uconn.edu

Suppose Layer 1 with thickness h_1 is joined together with Layer 2 with thickness h_2 and the bilayer is sandwiched between metallic electrodes [Figure 1(b)]. The relative volume fraction of Layer 2 is $\alpha = h_2/h$. We will assume that both h_1 and h_2 are much larger than the characteristic correlation lengths of each layer. Before Layers 1 and 2 are brought together, their polarizations are equal to their bulk values $P_{0,1}$ and $P_{0,2}$. Obviously, when these layers are coupled, the actual polarization of each layer is expected to be different from its “decoupled” value due to the electrical interaction between the layers. The internal electric fields $E_{D,1}$ and $E_{D,2}$ in Layers 1 and 2 due to the polarization mismatch essentially establish new polarization states, i.e., P_1 and P_2 in Layers 1 and 2, respectively, see Fig. 1(b). The internal electric fields \mathbf{E}_D are related to the difference in polarization of each layer and can be determined through the Maxwell relations $\nabla \times \mathbf{E}_D = 0$ and $\nabla \cdot \mathbf{E}_D = (1/\epsilon_0)(\rho_f - \nabla \cdot \mathbf{P})$, where ρ_f is the free charge density. For perfectly insulating bilayers, the internal fields in each layer are given by¹⁹

$$E_{D,1} = -\frac{1}{\epsilon_0}(P_1 - \langle P \rangle) = \frac{\alpha}{\epsilon_0}(P_2 - P_1), \quad (2)$$

$$E_{D,2} = -\frac{1}{\epsilon_0}(P_2 - \langle P \rangle) = \frac{1-\alpha}{\epsilon_0}(P_1 - P_2), \quad (3)$$

where $\langle P \rangle = (1-\alpha)P_1 + \alpha P_2$ is the average polarization.

The role of the internal fields is different for Layers 1 and 2. $E_{D,2} > 0$ serves to enhance the polarization of Layer 2. On the other hand, $E_{D,1}$ attempts to decrease the polarization of Layer 1 since it lies antiparallel to the polarization vector ($E_{D,1} < 0$). Therefore, in equilibrium, it is expected that $P_1 < P_{0,1}$ and $P_2 > P_{0,2}$ so as to decrease the polarization difference, $\Delta P = P_1 - P_2$.

The total free energy functional incorporating the potential energies of the internal fields $E_{D,1}$ and $E_{D,2}$ is given by:

$$\begin{aligned} F_\Sigma &= (1-\alpha) \left[F_1(P_1) - \frac{1}{2} \xi E_{D,1} P_1 \right] \\ &+ \alpha \left[F_2(P_2) - \frac{1}{2} \xi E_{D,2} P_2 \right] + \frac{F_S}{h}, \\ &= (1-\alpha) F_1(P_1) + \alpha F_2(P_2) + \frac{1}{2} \alpha (1-\alpha) \frac{\xi}{\epsilon_0} (P_1 - P_2)^2 \\ &+ \frac{F_S}{h}, \end{aligned} \quad (4)$$

where F_S is the energy per unit area of interlayer interface. This additional contribution may arise, for example, due to the compositional inhomogeneity, the polarization discontinuity, and internal stresses. The effect of the interface extends over very small length scales²⁰ and since the surface energy scales with the total bilayer thickness, its contribution to the total free energy can be neglected for a relatively thick bilayer. In Eq. (4), we have introduced a coefficient ξ which is essentially a measure of the free charge density with respect to the bound charge at the interlayer interface such that $\xi = 1 - \rho_f/\rho_b$, where ρ_b is the bound charge density. The two limiting values, $\xi = 1$ and $\xi = 0$ correspond to perfect insulating and semiconducting FE bilayers, respectively. The latter condition implies that there are sufficient free charges with high mobility to compensate for the internal fields due to the

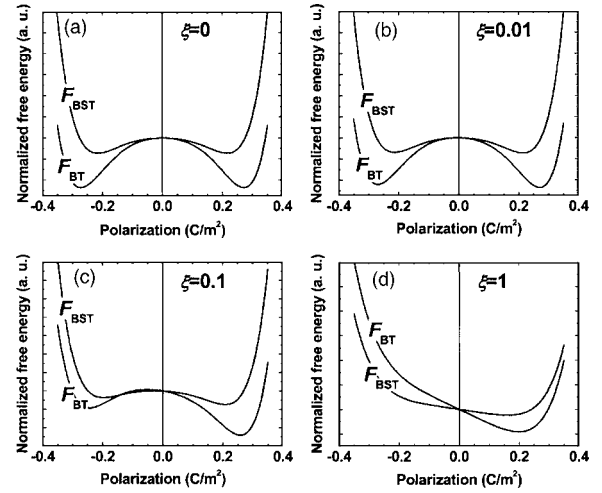


FIG. 2. Free energy potentials as a function of polarization for an equal-fraction BaTiO₃ (BT)–Ba_{0.9}Sr_{0.1}TiO₃ (BST 90/10) bilayer: (a) $\xi=0$, (b) $\xi=0.01$, (c) $\xi=0.1$, and (d) $\xi=1$.

polarization mismatch. Thus, for $\xi=0$ (and for $\xi < 0$), there is no electrostatic contribution to the total free energy due to the internal electrical field.

The equilibrium polarization of each layer is given by the simultaneous solution of the equations of state $\partial F_\Sigma / \partial P_1 = 0$ and $\partial F_\Sigma / \partial P_2 = 0$. The thermodynamic potential for each layer can be extracted from the total free energy as:

$$F_1(P_1) = F_{0,1} + \frac{1}{2} a P_1^2 + \frac{1}{4} b P_1^4 + \frac{1}{6} c P_1^6 - \frac{1}{2} \xi E_{D,1} P_1, \quad (5)$$

$$F_2(P_2) = F_{0,2} + \frac{1}{2} d P_2^2 + \frac{1}{4} e P_2^4 + \frac{1}{6} f P_2^6 - \frac{1}{2} \xi E_{D,2} P_2. \quad (6)$$

It is clear that the electrostatic energy of the internal fields in Eqs. (5) and (6) serves to introduce a symmetry-breaking element in the otherwise symmetric Landau potentials having even powers of the polarization. Consider the example of an equifraction ($\alpha = 1/2$), stress-free BaTiO₃–Ba_{0.9}Sr_{0.1}TiO₃ (BT–BST90/10) bilayer. In Fig. 2, we plot the normalized free energy as a function of the net polarization of each layer. The “degree” of symmetry-breaking strikingly varies with the variations in the density of free charges in the bilayer. For instance, for $\xi=0$ [Fig. 2(a)], the two layers are electrically screened from one another and can act essentially independent and are unrelated entities. This is due to the complete compensation of the electrical field resulting from bound charges at the interlayer interface through free charges. An equivalent construction of this condition would be two ferroelectric layers with a metallic electrode between them, i.e., two dielectrics with a series connection. Both layers display typical symmetric double well potentials, whose minima correspond to two energetically identical FE ground states. The equilibrium polarizations of the layers assume their values in single-crystal form. Due to the free charges, a relative large polarization difference, ΔP , can be maintained between the two layers, where, for instance, $\Delta P \approx 0.056$ C/m² for BT–BST90/10 bilayer.

The electric coupling between layers due to the polarization mismatch is evident for nonzero values of ξ where this coupling is enhanced with increasing ξ , i.e., a reduction in the free charges. Figures 2(b)–2(d) show that the otherwise symmetric double wells of BT and BST90/10 are skewed toward one FE equilibrium state with $P > 0$. The other FE

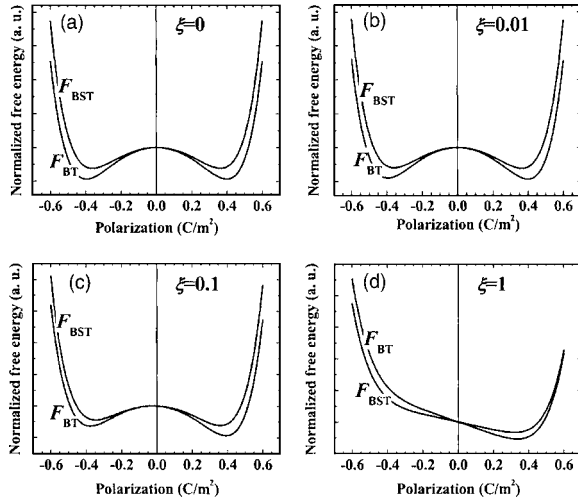


FIG. 3. Free energy potentials as a function of polarization for an equal-fraction (001) BT-BST90/10 bilayer on a (001) (ST) substrate with in-plane strains $x_{BT} = -2.6\%$ and $x_{BST} = -2.2\%$: (a) $\xi = 0$, (b) $\xi = 0.01$, (c) $\xi = 0.1$, and (d) $\xi = 1$.

ground state with $P < 0$ becomes *metastable*. The strongest value of electrical coupling between the layers corresponds to a bilayer made up of two completely insulating FEs, i.e., no free charges, $\xi = 1$. This results in only one stable FE ground state in both layers and a small polarization difference between two layers ($\Delta P = 0.037 \text{ C/m}^2$). The other FE ground state becomes *unstable* due to the electrical interaction between the layers. This shows that the initial “uncoupled” polarization gradient in insulating graded FEs becomes smoother due to the electrostatic interactions between the layers thus resulting in a smaller polarization difference that seeks to minimize the internal electric field.

The analysis can be extended to a heteroepitaxial bilayer grown on a thick cubic substrate by incorporating the elastic energy of the internal stresses that results in renormalized Landau coefficients:²¹

$$\bar{a} = a - x_1 \frac{4Q_{12,1}}{S_{11,1} + S_{12,1}}, \quad \bar{b} = b + \frac{4Q_{12,1}^2}{S_{11,1} + S_{12,1}}, \quad (7a)$$

$$\bar{d} = d - x_2 \frac{4Q_{12,2}}{S_{11,2} + S_{12,2}}, \quad \bar{e} = e + \frac{4Q_{12,2}^2}{S_{11,2} + S_{12,2}}, \quad (7b)$$

where $S_{ij,i}$ and $Q_{ij,i}$ are the elastic compliances at constant polarization and electrostrictive coefficients of material i , respectively. $x_i = (a_S - a_i)/a_S$ are the (polarization-free) misfit strains of layer i with respect to substrate, where a_i are the unconstrained equivalent cubic cell constants of layer i and a_S is the lattice parameter of the substrate. For a pseudomorphic bilayer with $h < h_\rho$ where h_ρ is the critical thickness for misfit dislocations, these misfit strains are not independent and the relation between them is given by $x_2 = 1 - [a_2(1 - x_1)/a_1]$.

As an example, we consider a heteroepitaxial, equifraction (001) BT-BST90/10 bilayer on a (001) SrTiO₃ (ST) substrate. The lattice parameters of ST, BT, and BST are 0.3905 nm, 0.4005 nm, and 0.3999 nm, respectively, and thus the in-plane strains in each layer are $x_{BT} = -2.6\%$ and $x_{BST} = -2.2\%$. The equilibrium polarizations of the BT and BST90/10 thin films at these strain levels are $\sim 0.39 \text{ C/m}^2$ for BT and $\sim 0.36 \text{ C/m}^2$ for BST. Similar to the behavior of unconstrained system, we plot the normalized free energy of

both layers as function of polarization in Figs. 3(a)–3(d). Due to the small initial polarization difference, the electrostatic coupling effect is not as strong as stress-free layers (Fig. 2) but it still displays electrostatic coupling that induces symmetry breaking.

The above results are consistent with both the *ab initio* and density functional theory calculations carried out by Sai *et al.*,^{17,18} wherein they also concluded that compositional variations result in a broken inversion symmetry that likewise leads to asymmetric thermodynamic potentials. As discussed in the present analysis, we show that whenever the free charge density is less than the bound charges density, an internal potential arises from the compositional inhomogeneity always resulting in asymmetric potentials. Moreover, our present work expands beyond these studies by further including the effects of internal stresses in epitaxial films as well as the effects of free charge within the material systems. A more detailed study extending our analysis to the electrical and electromechanical properties of multilayer and graded FEs incorporating formation of misfit dislocations at the inter-layer interfaces will be presented elsewhere.

Finally, these results lead to the inescapable conclusion that insulating FE multilayers are self-poled due to the electrostatic coupling between the layers. Hopefully, the present analysis will finally lead to a consensus as to the nature of polarization-graded FEs.

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