Dielectric anomaly due to electrostatic coupling in ferroelectric-paraelectric bilayers and multilayers

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(Received 18 March 2005; accepted 5 July 2005; published online 22 August 2005)

A thermodynamic model is presented that describes the polarization and the dielectric response of ferroelectric-paraelectric bilayers and multilayers. It is shown that a strong electrostatic coupling between the layers results in the suppression of ferroelectricity at a critical paraelectric layer thickness. The bilayer is expected to have a gigantic dielectric response similar to the dielectric anomaly near Curie–Weiss temperature in homogeneous ferroelectrics at this critical thickness. A numerical analysis is carried out for a pseudomorphic (001) $BaTiO_3/SrTiO_3$ heteroepitaxial bilayer on (001) $SrTiO_3$ and a stress-free $BaTiO_3/SrTiO_3$ bilayer. Complete polarization suppression and a dielectric peak are predicted to occur at approximately 66% and 14% of $SrTiO_3$ in these two systems, respectively. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2032601]

Ferroelectric (FE) multilayers, superlattices, and graded ferroelectrics have attracted considerable interest in recent years due to their dramatically different behavior compared to their constituents in bulk form.[1–9] Indeed, multilayer and graded FEs exhibit many striking phenomena and properties, including substantial variations in phase transition characteristics, an enhancement in remnant polarization, and a large dielectric response.[2–7] Experimental observations and theoretical studies[10–20] clearly suggest that there is a strong interlayer coupling of the layers that must be considered to account for the properties of FE heterostructures. However, there are no systematic investigations of the effect of electrostatic interactions on the interlayer coupling. In this letter, we present the thermodynamic analysis explicitly taking into account electrostatic interactions between FE-FE and FE-paraelectric (PE) bilayers. For a FE-PE bilayer, the analysis predicts the presence of a critical relative thickness at which a gigantic dielectric response, similar to the λ-type response at transition temperature, is expected.

Consider a bilayer of two FE layers between electrodes on a substrate much thicker than the bilayer (Fig. 1). A multilayer consisting of sets of identical bilayers on a thick substrate with the same short circuit conditions can be considered analogously. The free energy density of the bilayer (or the multilayer) can be presented as follows:

$$F = (1-\alpha)[F_1(P_1) - EP_1] + \alpha[F_2(P_2) - EP_2] + \frac{1}{2}\alpha(1-\alpha)\frac{1}{\varepsilon_0}(P_1 - P_2)^2 + \frac{F_s}{h}, \quad (1)$$

where $\alpha = h_2/h$ $(h = h_1 + h_2)$ is the relative thickness of the layers, P_i is the polarization of layer i normal to the interlayer interface, and E is an applied electrical field parallel to the polarization. The third term with the coefficient $\alpha(1-\alpha)$ expresses the electrostatic coupling between the layers. $F_i(P_i)$ are the uncoupled free energies of the layers that can be determined by a Landau expansion, such that

$$F_i(P_i) = F_{0,i} + \frac{1}{2}a_i P_i^2 + \frac{1}{4}b_i P_i^4 + \frac{1}{6}c_i P_i^6. \quad (2)$$

The normalized coefficients a_i and b_i are used to take into account the misfit between the layers and substrate and the two-dimensional clamping effect of the substrate[21]

$$a_i = a_i^0 - x_i \frac{4Q_{12,i}}{S_{11,i} + S_{12,i}}, \quad b_i = b_i^0 + \frac{4Q_{12,i}^2}{S_{11,i} + S_{12,i}}, \quad (3)$$

where $S_{ij,i}$ and $Q_{ij,i}$ are the elastic compliances at constant polarization and electrostrictive coefficients of layer i, respectively; $x_i = (a_S - d_i)/a_S$ is the in-plane misfit strain of

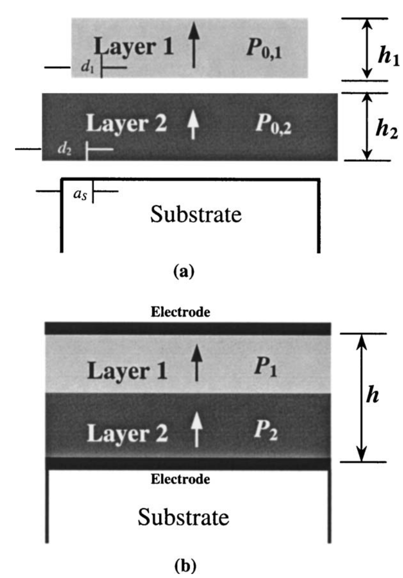

FIG. 1. (a) Freestanding FE layers and substrate. The lattice parameters of the FE layers are d_1 and d_2 and a_S is the lattice parameter of the substrate. The initial polarization in layers 1 and 2 are $P_{0,1}$ and $P_{0,2}$, respectively. (b) An epitaxial bilayer constructed by joining the layers in (a), sandwiched between metallic top and bottom electrodes and deposited on a thick substrate. Due to interlayer coupling, $P_1 < P_{0,1}$ and $P_2 > P_{0,2}$.

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layer i with respect to substrate, where d_i is the unconstrained equivalent cubic cell constants of layer i and a_S is the lattice parameter of the substrate. For a pseudomorphic bilayer, these misfit strains are not independent and the relation between them is given by $x_2 = 1 - [d_2(1-x_1)/d_1]$; a_i^0 and b_i^0 are Landau coefficients of bulk material with $a_i^0 = (T - T_{C,i})/\varepsilon_0 C_i$ 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 spontaneous polarization in the FE layers $(P_{0,i})$ is given by the equation of state $\partial F_i / \partial P_i = 0$

The last term in Eq. (1) is the energy of the interfaces between the layers. We assume that the layers are relatively thick compared to the correlation length of ferroelectricity which is of the order of 1 nm.[22] Therefore, we can neglect the interface energy F_S/h even for thin bilayers with thickness of about 100 nm. The polarization is given by the continuity of the normal component of the electrical displacement across the interfaces in each layer.[23] The polarizations beyond the interface area are constant in each layer. Similarly, the internal stresses arising from the misfit between the films and the substrate are homogeneously distributed throughout the volume of the individual layers if these layers are free of dislocations and other defects.[24]

The polarizations in the coupled layer are determined by the equation of equilibrium $\partial F / \partial P_1 = \partial F / \partial P_2 = 0$

$$\frac{dF_1}{dP_1} = E + \frac{\alpha}{\varepsilon_0}(P_2 - P_1), \quad \frac{dF_2}{dP_2} = E + \frac{1-\alpha}{\varepsilon_0}(P_1 - P_2), \quad (4)$$

where the second terms in the right part of Eq. (4) are the depolarizing fields in the layers, $E_{D,1}$ and $E_{D,2}$, which arise due to mismatch of the equilibrium polarization of constrained and uncoupled layers, $P_{0,1} - P_{0,2}$ $(P_{0,1} > P_{0,2})$.

The role of the internal fields is significantly different for layers 1 and 2. In layer 2 $E_{D,2} > 0$ enhances the polarization and increases stability of a FE state. On the other hand, $E_{D,1}$ is negative, meaning that the field is directed opposite to the spontaneous polarization and thus decreases stability of the FE state in layer 1. Destabilization effect of depolarizing field in layer 1 is maximum if $P_{0,2} = 0$, i.e., for a FE-PE bilayer.

We have solved Eqs. (4) for this particular case taking as an example $BaTiO_3$ (BT) and $SrTiO_3$ (ST) as the FE and PE layers, respectively. The Landau coefficients[21,25] and elastic constants[21] for BT and ST are well established and allow us to carry out a numerical quantitative study. We consider a heteroepitaxial (001) ST-BT bilayer on a thick (001) ST substrate such that $x_{ST} = 0\%$ in Eq. (3) at RT. The lattice parameters of ST and BT are 0.3905 and 0.3994 nm, respectively, and thus the strain in the BT layer is $x_{BT} = -2.28\%$. The equilibrium polarization of a BT film at this strain level is 38 $\mu C/cm^2$. The spontaneous polarization in the BT layer in the ST-BT bilayer for $E = 0$ decreases from this value with increasing volume fraction of the ST layer until it completely vanishes at a critical relative thickness of $\alpha_{ST} = 0.66$ [Fig. 2(a)]. Figure 2(b) plots the difference between polarizations in the coupled BT and ST layers $\Delta P = P_{BT} - P_{ST}$. ΔP is small (typically less than 1% of the polarization of BT) indicating that the induced polarization in the ST layer almost equals the polarization in BT layer. As the relative fraction of the ST layer increases, there is a commensurate rise in the depoling field in the BT layer as well as a drop in the internal field in the ST layer that induces polarization. Eventually, a critical

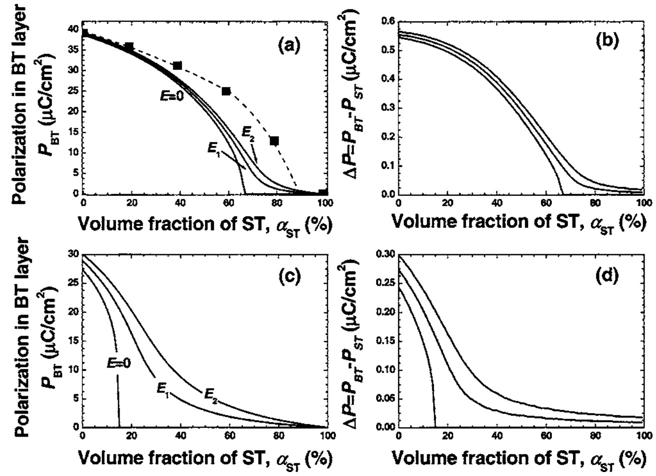

FIG. 2. Dependence on ST fraction, α_{ST}, of polarization in BT layer under different external fields ($E=0$, $E_1 = 100$ kV/cm, $E_2 = 200$ kV/cm) and the polarization difference, $\Delta P = P_{BT} - P_{ST}$: (a) and (b) for constrained BT-ST bilayer; $x_{BT} = -2.28\%$ and $x_{ST} = 0\%$ (solid squares: first-principles results from Ref. 19); (c) and (d) for unconstrained BT-ST bilayer.

relative thickness is reached at $\alpha_{ST} = 0.66$ which corresponds to $P_1 = P_2 = 0$, the only solutions of Eqs. (4) for $\alpha_{ST} \geqslant 0.66$. The equilibrium polarization in BT layer and the polarization difference between two layers for a completely relaxed system has similar behavior as shown in Fig. 2(c) and 2(d). Without the biaxial internal stress, the polarization in the BT is ~ 27 $\mu C/cm^2$ for $\alpha_{ST} \approx 0$ and disappears at a critical relative thickness $\alpha_{ST} = 0.14$.

The (small-signal) average dielectric response of the bilayer is

$$\langle \varepsilon_R \rangle \cong \frac{1}{\varepsilon_0}\frac{d\langle P \rangle}{dE} = \frac{1}{\varepsilon_0}\left[(1-\alpha)\frac{\delta P_1}{E} + \alpha \frac{\delta P_2}{E}\right], \quad (5)$$

where $\langle P \rangle = (1-\alpha)P_1 + \alpha P_2$ is the average polarization, $\delta P_i = P_i(E) - P_i(E=0)$ as $E \to 0$, and P_i satisfying Eqs. (4). The dielectric response of the heteroepitaxial and unconstrained BT-ST bilayers are presented in Fig. 3 that display an anomaly at the critical relative thicknesses.

To explain the behavior of polarization and dielectric constant of a bilayer, we considered analytical solutions of Eqs. (4). Using a linear approximation for internal field of layer 2 such that $dF_2/dP_2 = -2a_2(P_2 - P_{0,2})$ for $a_2 < 0$ (FE

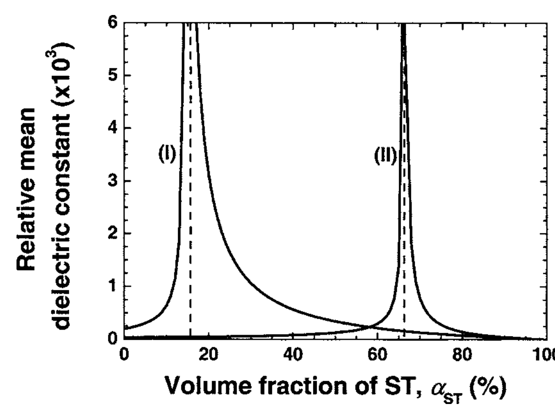

FIG. 3. Relative mean dielectric constant as a function of volume faction, α_{ST}: (I) for unconstrained BT-ST bilayer; (II) for strained heteroepitaxial BT-ST bilayer, $x_{BT} = -2.28\%$ and $x_{ST} = 0\%$.

state) or $dF_2/dP_2=a_2P_2$ for $a_2>0$ (PE state) together with the approximation

$$dF_1/dP_1 = a_1P_1 + b_1P_1^3 \quad (6)$$

transform Eq. (4) into

$$\frac{1}{2\varepsilon_1}\left[-P_1\left(1-\frac{2\varepsilon_1\alpha}{1+(1-\alpha)\varepsilon_2}\right)+\frac{P_1^3}{P_{0,1}^2}\right]=\frac{\alpha P_{0,2}}{1+(1-\alpha)\varepsilon_2}, \quad (7)$$

where $P_{0,1}^2=-a_1/b_1$, $\varepsilon_1=-1/(2\varepsilon_0 a_1)$ and $\varepsilon_2=-1/(2\varepsilon_0 a_2)$ [or $\varepsilon_2=1/(\varepsilon_0 a_2)$ in the PE state] are the dielectric constants of the constitutive layers. For a FE-PE bilayer $P_{0,2}=0$ and thus

$$P_1 = \pm P_{0,1}\sqrt{1-\frac{2\varepsilon_1\alpha}{1+(1-\alpha)\varepsilon_2}}, \quad (8)$$

which vanishes at a critical relative thickness $\alpha^*=(1+\varepsilon_2)/(2\varepsilon_1+\varepsilon_2)$ that results in $\langle P\rangle=0$. For a FE-FE bilayer P_1 decreases but does not disappear for all fractions of layer 2 since $P_{0,2}>0$.

The analogy with temperature dependence of polarization and dielectric response as well as with smearing of the dielectric anomaly under an applied electric field is obvious (Fig. 2). However, the effect of the depolarizing field is not equivalent to the effect of temperature. Therefore, using the expansion of free energy [Eq. (6)] does not mean that the phase transition in bulk ferroelectrics is a second order transformation. For example, BT in constrained layer undergoes a second order phase transformation, while in bulk BT the transformation is first order. Although a single-domain state near the transformation temperature is unstable with respect to the formation of 180° domains,[15] it can be metastable far from this temperature, especially for thin constrained FE films. Comparison of results of our scale independent analysis in bilayers with results of first principal calculations for superlattices allows one to conclude that the effects of electrostatic interactions considered above should be observed in thin films as well. The polarization of superlattices with period equaling five atomic planes[19] shown in Fig. 2(a) demonstrates a similar dependence on the layer fraction as a macroscopic FE-PE bilayer. A critical fraction of ~0.9 can be expected on the basis of extrapolation of microscopic data to the zero polarization [dashed line in Fig. 2(a)]. It is clear that increasing the period of the superlattices should decrease the deviation between the results of macroscopic and microscopic analysis.

The stability of single domain states in films obviously warrants further theoretical consideration. However, there are several experimental results supporting the results of this study. Experimental observations where an average relative dielectric response of ~500 was reported for a BT-ST superlattice with $\alpha_{ST}=0.5$ and one stacking period[26] can be related to the properties of a partially relaxed bilayer. Extremely high dielectric permittivities in $PbTiO_3-Pb_{1-x}La_xTiO_3$[3] and $SrZrO_3-SrTiO_3$ superlattices[8] have been reported in the literature that is in agreement with the conclusions of this work.

Free charges that may be present in bilayers in thin-film form result in a similar effect as the misfit dislocations as they "relax" (or compensate for) bound charges at the interlayer interfaces. Their contribution can be included in the thermodynamic model using a "correction factor," the ratio of the free charge to bound charge density at the interlayer interface, in the internal fields of Eqs. (4).

The electrostatic interlayer coupling has obviously significant technological implications. First, an extremely high dielectric response can be achieved in the vicinity of a critical layer fraction. In addition, below the critical layer fraction it is possible to induce almost as much polarization in the PE layer as the FE layer and the bilayer displays FE behavior in the absence of an applied electric field. The leakage and loss characteristics of FE devices could, therefore, be controlled by depositing thin PE or dielectric buffer layers that would not result in a decrease in the overall polarization and the dielectric response. This is in agreement with recent results where the loss of ferroelectric memory elements have been shown experimentally to be reduced by growing top and bottom dielectric buffers before they were metallized.[27]

A.L.R. thanks the National Science Foundation (NSF) for support under Grant Nos. DMR-0210512 and DMR-0407517. The work at UConn was supported by the NSF under Grant No. DMR-0132918.

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