

Interface effects in ferroelectric bilayers and heterostructures

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We study the role of interlayer interfaces on the polarization response of ferroelectric-paraelectric bilayers using a nonlinear thermodynamic model. We carry out a numerical analysis for prototypical BaTiO₃-SrTiO₃ bilayers ranging from 40 to 800 nm total thickness as a function of SrTiO₃ fraction. There exists a critical fraction of SrTiO₃ at which the polarization is suppressed due to the depolarization field arising from the interlayer coupling and a large dielectric response is predicted. It is shown that this critical fraction decreases with decreasing total bilayer thickness, indicating that the interfacial effects are more pronounced in thinner bilayers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2433766]

Artificial ferroelectric (FE) heterostructures such as bilayers, superlattices, and graded films have attracted a great deal of interest due to their unusual behavior compared to their constituents in bulk or single-crystal form. Increases in the remnant polarization and extremely high dielectric response have been reported in a variety of FE-paraelectric (PE) and FE-dielectric (DE) systems.¹⁻⁸ It was also shown experimentally that lower losses and leakage can be achieved in ferroelectric memory elements by growing dielectric buffers before the growth of the metallic electrodes.⁹ Theoretically, the observed phenomena in these heterostructures have been explained through an interlayer coupling using a parametric coefficient or via electromechanical coupling that arises from internal stresses.¹⁰⁻¹³ The large dielectric response has also been attributed to Maxwell-Wagner effects where defect-related transport plays a major role.¹⁴ Recently, we have shown theoretically that the behaviors of FE-PE and FE-DE bilayers and multilayers are due to the electrostatic coupling between the layers through internal electric fields that are set up to minimize the polarization difference between the layers.^{15,16} The interplay between the internal fields results in the suppression of polarization in FE and PE (or DE) layers at a critical layer fraction. At this critical fraction, a gigantic dielectric response is also predicted.

The developed theoretical model of interlayer coupling in ferroelectric heterostructures was based on continuum relations and holds for relatively thick bilayers with layer thickness much larger than the correlation length of ferroelectricity and defect-free, morphologically smooth interlayer interfaces.¹⁵ Potential applications of these heterostructures as high-capacity stacks for on-chip charge storage devices or as memory elements would require a scaling down of the layer thicknesses and it is clear that the interlayer structure and interface defects would play a significant role in such heterostructures. In this letter, building upon our prior results, we employ a thermodynamic approach for a

FE-PE bilayer that incorporates the presence of polarization gradients at the interface to show that the interface plays a significant role on the properties of thin bilayers. The analysis shows that although the interfacial effects influence the critical fraction of the PE layer at which a huge dielectric response is expected, this transition from a polarized bilayer is still there for heterostructures with a thickness larger than the correlation length. For ultrathin films, the polarization gradients that emanate from the interlayer interfaces may completely suppress ferroelectricity.

Consider a single-domain FE layer and a PE layer with equal lateral dimensions between metallic electrodes. The thickness of the FE and PE layers are L_1 and L_2 , respectively, such that the total thickness $L=L_1+L_2$. The spontaneous (and induced) polarization is along a z axis normal to the interlayer interface located at $z=0$. The free energy density of such a configuration can be expressed as¹⁷⁻²¹

$$F = F_p + \int_{-L_1}^{L_2} \left[a_i P^2 + b_i P^4 + c_i P^6 + \frac{1}{2} A_i \left(\frac{dP}{dz} \right)^2 - \frac{1}{2} E_d P \right] dz + \frac{1}{2} \left(\frac{A_1}{\delta_1} P_{-0}^2 + \frac{A_2}{\delta_2} P_{+0}^2 \right), \quad (1)$$

where F_p is the combined polarization-free energy of the two materials in the paraelectric state and $P=P(z)$ is the polarization. In Eq. (1), a_i , b_i , and c_i are the dielectric stiffness coefficients of layer i ($i=1, 2$). a_i are temperature dependent via the Curie-Weiss law such that $a_i=(T-T_{C,i})/2\epsilon_0 C_i$, where $T_{C,i}$ and C_i are the Curie-Weiss temperature and constant of layer i , and ϵ_0 is the permittivity of space. A_i are the Ginzburg coefficients and they can be estimated as $A_i=|a_i|\xi_i^2$, where ξ_i is the correlation length of layer i .²⁰ $E_d(z)$ is the internal “built-in” electric field due to polarization variations such that

$$E_d(z) = - \frac{1}{\epsilon_0} [P(z) - \bar{P}], \quad (2)$$

where \bar{P} is the average polarization of the entire heterostructure. The last two terms of Eq. (1) describe the interfacial

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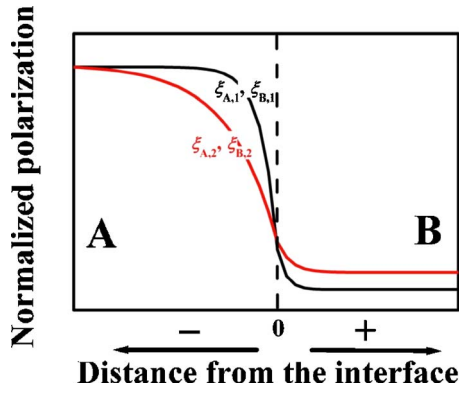


FIG. 1. (Color online) Normalized polarization change as a function of thickness in the vicinity of the interface for a bilayer consisting of two ferroelectrics, A and B: $\xi_{A,1} < \xi_{A,2}$, $\xi_{B,1} < \xi_{B,2}$; $\xi_{A,i}/\delta_{A,i} = \xi_{B,i}/\delta_{B,i}$, $i=1,2$.

energy where P_{-0} and P_{+0} are the polarizations of the two layers at the interface, i.e., at $z=-0$ and $z=+0$, respectively, and δ_i are the extrapolation lengths of layers i . We assume stress-free and unclamped layers throughout the calculations, although these contributions can be easily incorporated into the free energy functional using renormalized dielectric stiffness coefficients.²² We do so to assure that the effect of interfaces is clearly observable from the calculations since even small strains can modify the polarization of individual layers quite drastically. This also enables us to compare the properties of the layers to their bulk forms more clearly. Minimization of Eq. (1) with respect to P yields

$$A_i \frac{d^2 P}{dz^2} = 2a_i P + 4b_i P^3 + 6c_i P^5 + \frac{1}{\epsilon_0} (P - \bar{P}), \quad (3)$$

with the boundary conditions

$$\left. \frac{dP}{dz} \right|_{z=-L_1} = \left. \frac{dP}{dz} \right|_{z=+L_2} = 0, \quad (4)$$

corresponding to complete charge compensation at the electrode interfaces and

$$\left. \frac{dP}{dz} \pm \frac{1}{\delta_i} P \right|_{z=\pm 0} = 0, \quad (5)$$

which ensure that the polarization is continuous across the FE-PE interface.

We carry out a numerical analysis for bilayers consisting of BaTiO₃ (BT) as the FE layer and SrTiO₃ (ST) as the PE layer since the thermodynamic coefficients of BT and ST are well established.²² In our calculations, discrete elements (Δz) were taken 0.4 nm, corresponding approximately to the size of a BT unit cell. In order to illustrate the “strength” of the interfacial effect, two sets of values of the correlation lengths (ξ_i) for BT and ST were taken: 1 and 0.5 nm, and 3 and 0.8 nm, respectively, for BT and ST. The ratio δ_i/ξ_i was taken to be 1.41 for both cases.¹⁸ In Fig. 1 we show schematically the polarization variation in the vicinity of the interface which follows from Eq. (1). The polarization variation extends over a comparatively larger region in the case for the larger correlation length (which results in a smaller local polarization difference due to the increase in the strength of the depoling field). Thus, variations in this pa-

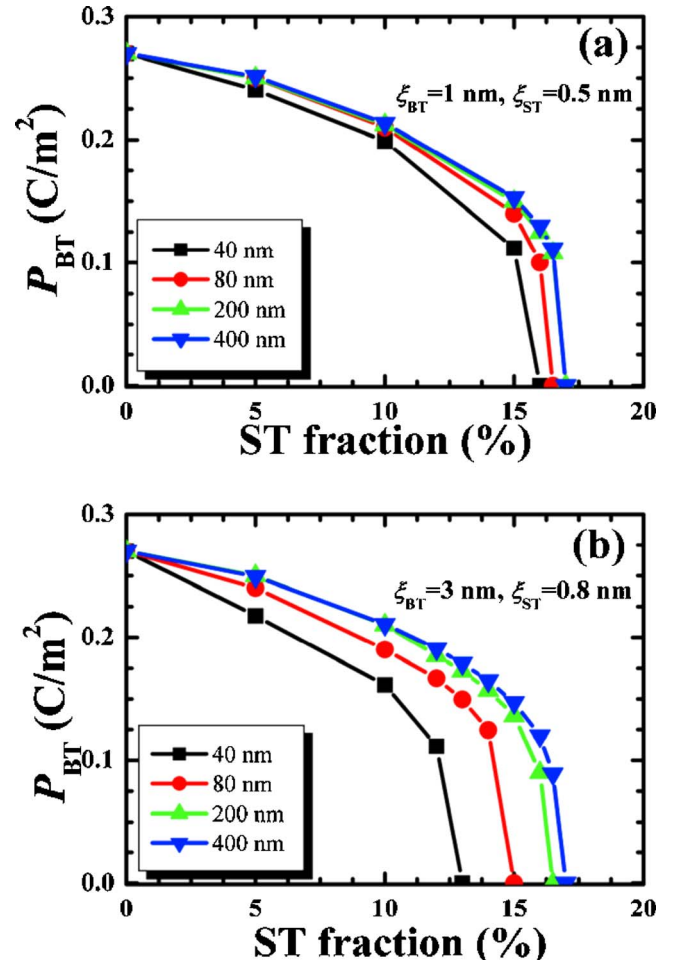


FIG. 2. (Color online) Polarizations in BT layer as a function of ST fraction for different thicknesses: (a) sharp interface ($\xi_{BT}=1$ nm, $\xi_{ST}=0.5$ nm) and (b) diffusive interface ($\xi_{BT}=3$ nm, $\xi_{ST}=0.8$ nm).

rameter allow the modeling of the role of the interface characteristics.¹⁸ Polarization and related electrical properties are a strong function of the correlation length as it describes the extent of fluctuations of the polarization and is a function of temperature (and internal/external stresses which alter T_C through Clausius-Clapeyron-type relations).²³ We note that defects in FE materials such as vacancies (which are invariably electrically charged) and interfacial dislocations²⁴ have highly localized nonlinear electrostatic fields around them that are created via the electrostrictive coupling of the eigenstrain of the defect and the spontaneous polarization. The strength of the electrostatic and elastic fields of the interface diminishes rapidly away from interface.²⁵ Thus, the analysis presented in this study provides an estimate to an extremely complicated problem since the exact variation of the polarization near the interface is unknown.

Figures 2(a) and 2(b) plot the polarization in the BT layer as a function of the ST fraction for four different total bilayer thicknesses and two sets of ξ_i . As L decreases, the polarization in the BT (as well as the ST layers, not shown) decreases due to the increase of the contribution of the interfacial energy to the total energy, i.e., the length scale of the polarization variation near the interface becomes comparable to L . For $L < 200$ nm, bilayers with larger correlation and

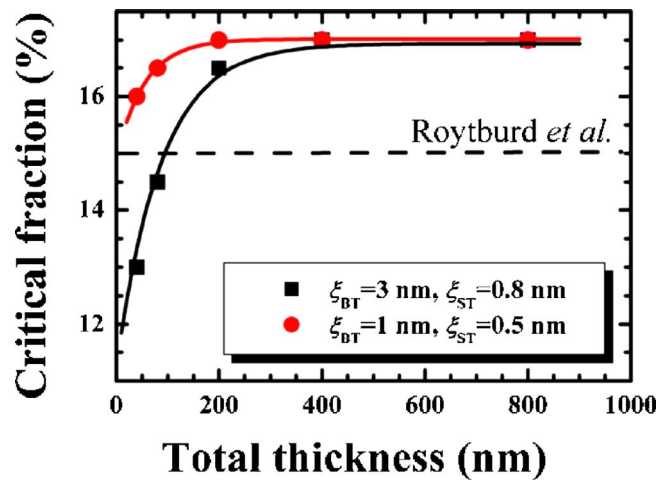


FIG. 3. (Color online) Critical fraction as a function of total bilayer thickness. The dashed line shows the continuum limit from Ref. 15 and the solid line is a guide for the eyes.

extrapolation lengths [Fig. 2(b)] have smaller polarizations compared to the same thicknesses with smaller correlation and extrapolation lengths [Fig. 2(a)], since the more diffuse interface introduces larger depolarization fields through the electrostatic coupling. Moreover, from Fig. 2, it is clear that the critical fraction of ST at which the polarization in the bilayer is suppressed due to the depolarization field arising from the interlayer coupling changes as a function of L .

To display the effect of the interlayer interface more clearly, we plot the critical ST fraction as a function of the total bilayer thickness in Fig. 3. The dashed line represents the result for thick bilayers in the continuum limit.¹⁵ The critical fraction increases as a function of L and levels off around 200 nm at $\sim 17\%$ for both sets of ξ_i . This is quite similar to the strain relaxation in epitaxial films with increasing film thickness via misfit dislocation formation.²⁶ For a “sharper” interface, the critical fraction decreases only slightly as L decreases from ~ 200 nm. On the other hand, for a more “diffuse” interface, the critical fraction drops markedly as L decreases. This is because the polarization varies along a larger length scale at the interface in comparison with the sharper interface. In either case, the impact of the interface becomes less prominent and can be neglected in bilayers for $L > 200$ nm. We note that the small difference between the critical fractions of the continuum limit calculations and the bilayer thicker than ~ 200 nm arises from the fact that in the previous model the equilibrium Ginzburg fluctuations in the polarization were ignored.^{15,16}

Results presented in this work have several implications. The thermodynamic model in the continuum limit clearly establishes that the internal electric field due to polarization mismatch between FE-FE, FE-PE, and FE-DE bilayers and heterostructures is the cause of unique electrical properties including polarization enhancement and high dielectric response.¹⁵ This is in accordance with our current approach where polarization gradients at the interlayer interfaces do not have much of an impact for relatively thick bilayers with

$L > 200$ nm. However, thinner bilayers typically with $L < 100$ nm should display a marked degradation in polarization with increasing ST fraction. This reduction occurs at much smaller ST fractions if the polarization variations at the interfaces persist at longer length scales away from the interface. For these cases, the polarization is controlled by the nature of the interface rather than the global thermodynamic driving forces. Therefore, the impact of the interface cannot be neglected in designing ultrathin bilayers as the interfacial region where polarization gradients exist due to defects that now represent a considerable volume of the material.

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