APPLIED PHYSICS LETTERS **91**, 022911 (2007)

Space charge contribution to the apparent enhancement of polarization in ferroelectric bilayers and multilayers

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(Received 14 February 2007; accepted 19 June 2007; published online 11 July 2007)

The authors study the effect of interfacial space charge in ferroelectric multilayers through a thermodynamic formalism. Using an electrostatic approach that takes into account the presence of trapped charges between the layers, the authors show that considerable modification in electrical properties can be exhibited, giving rise to polarization enhancement depending on the type of dopants and configuration of the layers. Space charge effect becomes more pronounced in structures with smaller ferroelectric layer fractions. It is shown that built-in polarization due to space charge can stabilize a switchable ferroelectric polarization at small fractions of the ferroelectric layer in a paraelectric matrix. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2757127]

Artificially fabricated ferroelectric superlattices and multilayers have promising electrical properties that make them candidates for applications requiring a highly stable polarization, large dielectric constant, and dielectric tunability. Out of these, the spontaneous polarization or tetragonality enhancement in these structures is often pronounced and has been the focus of extensive scientific research.[1–10] For example, keeping the volume fractions of the layers constant on adjusting the frequency of the compositional modulation was shown to promote enhanced polarization values.[3–5] Studies have revealed evidence that remnant polarization values can exist in ferroelectric(FE)-paraelectric(PE) layers even at fractions of a few FE layers.[1,2,8,9]

Dawber *et al.*[1] have published experimental observations that show the recovery of tetragonality in $PbTiO_3/SrTiO_3$ (PT/ST) multilayers at ratios of PT/ST less than 1/2. However, an electrostatic model combined with a first principles approach predicted the PT/ST structure to be ferroelectrically inactive at a ratio smaller than approximately 50% of FE fraction. Tian *et al.* have investigated the $BaTiO_3/SrTiO_3$ (BT/ST) superlattice structures both experimentally and theoretically and concluded that the enhanced polarization in the BT layers was mainly resulting from the inadequate relaxation of the BT that had a higher tetragonality than the bulk.[8] The $PbZrO_3/PbTiO_3$ (PZ/PT) system was shown to exhibit enhanced dielectric response by increasing the frequency of the layers while keeping the volume fractions of the layers constant.[9] With all coherent and commensurate interfaces,[1,2,7–9] one is compelled to explain the observed phenomena through strong electrostatic interactions between layers.

In this letter, we investigate the ferroelectric polarization in the presence of interfacial charges using a thermodynamic approach.[11,12] The configuration is schematically shown in Fig. 1. We basically consider a planar charge density σ trapped between layers of FE and PE components inducing piecewise[12] built-in polarization values P_{b_i} in the FE and PE layers and a piecewise ferroelectric polarization P_{f_i} that is coupled to it. The equations of state for a bilayer under the field of a planar charge density σ situated between the FE and PE layers of thickness L_1 and L_2 and polarizations P_1 and P_2, respectively, can be written as

$$E_1 = 2aP_1 + 4bP_1^3, \tag{1a}$$

$$E_2 = 2dP_2 + 4eP_2^3 \tag{1b}$$

for which the fields E_1 and E_2 due to σ are approximated from the two equations:

$$V_1 + V_2 = V_{\mathrm{App}}, \tag{2}$$

$$\varepsilon_0 E_2 + P_2 - \varepsilon_0 E_1 - P_1 = \sigma, \tag{3}$$

where $V_1=E_1L_1$ and $V_2=E_2L_2$ with $L_1+L_2=L$ and $V_{\mathrm{App}} = E_{\mathrm{App}}L$ with E_{App} being the applied field, taken as zero in this study. The coefficients in Eq. (1) are

$$a = \frac{(T - T_{C_1})}{2\varepsilon_0 C_1} - \chi_m^1 \frac{2Q_{12}^1}{S_{11}^1 + S_{12}^1},$$

$$d = \frac{(T - T_{C_2})}{2\varepsilon_0 C_2} - \chi_m^2 \frac{2Q_{12}^2}{S_{11}^2 + S_{12}^2},$$

$$b = \alpha_{11}^1 + \frac{(Q_{12}^1)^2}{S_{11}^1 + S_{12}^1},$$

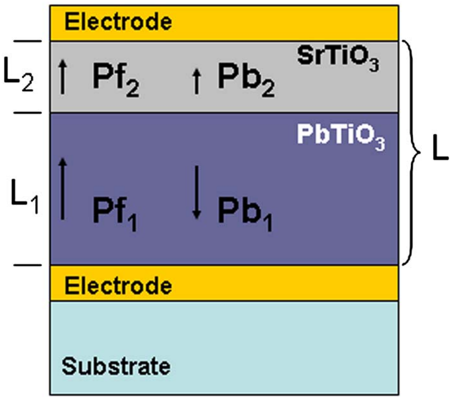

FIG. 1. (Color online) Schematic of the planar charge geometry between FE (PT) and PE (ST) layers. The directions of the built-in polarizations are also given.

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$$e = \alpha_{11}^2 + \frac{(Q_{12}^2)^2}{S_{11}^2 + S_{12}^2}. \tag{4}$$

where T is temperature, T_{C_i} are the Curie points of layers in bulk, C_i are the Curie constants of each layer, χ_m^i are the pseudocubic misfits of the two layers with the substrate, Q_{jk}^i are the electrostrictive constants for a cubic crystal with i indicating the layer, S_{jk}^i are the elastic constants of layer i in the Voigt notation, and α_{11}^i are the free energy coefficients for the fourth power of polarization in layers 1 and 2 for bulk. In the entire study, $(100)_{\text{Substrate}} \| (100)_{\text{Film}}$ epitaxial relation is assumed with equal misfit along $[100]_{\text{Film}}$ and $[010]_{\text{Film}}$ and zero stress along out-of-plane and traction-free surface inducing zero shear. To express the relative fractions of the layers, we introduce $\alpha = L_2/L$ for layer 2 and $(1-\alpha) = L_1/L$ for layer 1. Solution of the equations in Eqs. (1)–(3) for P_i with the imposition that $P_1 - P_2 = \sigma$ yield the unstable roots that comprise the built-in polarization in the layers, written as P_{b_1} and P_{b_2} from this point onward. Hence, $\sigma = \Delta Pb_i$ in the rest of the letter. To find the ferroelectric polarizations in the layers, we write the energy of the system as the following:

$$F = F_1 + F_2 + F_{\text{EL}}, \tag{5a}$$

$$F_1 = (1-\alpha)[a(\bar{P}_1)^2 + b(\bar{P}_1)^4 + c\bar{P}f_1^6 - E_{App}\bar{P}_1], \tag{5b}$$

$$F_2 = \alpha[d(\bar{P}_2)^2 + e(\bar{P}_2)^4 + f\bar{P}f_2^6 - E_{App}\bar{P}_2], \tag{5c}$$

$$\text{and } F_{\text{EL}} = \frac{1}{2\varepsilon_0}\alpha(1-\alpha)[P_{f_1} - P_{f_2} - \Delta P_{b_i}]^2, \tag{5d}$$

where F_1 and F_2 are the free energies of the two layers with thickness, F_{EL} is the electrostatic coupling energy[11] that takes into account the difference between the dielectric displacement in the layers, $\bar{P}_i = P_{f_i} + P_{b_i}$ where P_{f_i} are the ferroelectric polarizations in the layers. In Eqs. (5a)–(5d), a, b, d, and e, are the same as in Eq. (4), c and f are coefficients to the sixth power of polarization in bulk, respectively, for 1 and 2.[13] We proceed by writing the equations of state from which P_{f_i} can be calculated as follows:

$$\frac{dF}{dPf_1} = (1-\alpha)[(2a + 12bPf_1Pb_1)(Pb_1 + Pf_1) + 4b(Pf_1^3 + Pb_1^3) + 6Pf_1^5 + \alpha(Pf_1 + Pb_1 - Pf_2 - Pb_2)],$$

$$\frac{dF}{dPf_2} = \alpha[(2d + 12ePf_2Pb_2)(Pb_2 + Pf_2) + 4e(Pf_2^3 + Pb_2^3) + 6Pf_2^5 - (1-\alpha)(Pf_1 + Pb_1 - Pf_2 - Pb_2)]. \tag{6}$$

As one can notice, P_{f_i} will be a function of P_{b_i} together with misfit and α. Values we obtain for P_{b_i} from Eqs. (1)–(3) are given in Fig. 2 for FE and PE layers when $\sigma = 0.025\ \text{C/m}^2$ as a function of α for the PT/ST system.

We applied our methodology to the PT/ST (Ref. 13) system on ST substrates at room temperature in the presence of a pseudocubic misfit strain value of −1.69% for the PT on ST. Equation (6) is numerically solved for P_{f_i} in the FE and PE layers simultaneously in the presence of P_{b_i}, attaining values from Eqs. (1)–(3). For the case of multilayers, P_{b_i} in the midlayers will be zero due to the symmetry of the field[12] in a perfectly symmetric multilayer unless there are variations from interface to interface. P_{b_i} contribution is significant only at small FE fractions as the magnitudes of P_{f_i} and P_{b_i} become somewhat comparable for large σ. In addition, $\bar{P}_1 - \bar{P}_2$ is nearly zero in our results (not shown here) so as to minimize the internal electrostatic energy at all relative ST fractions.

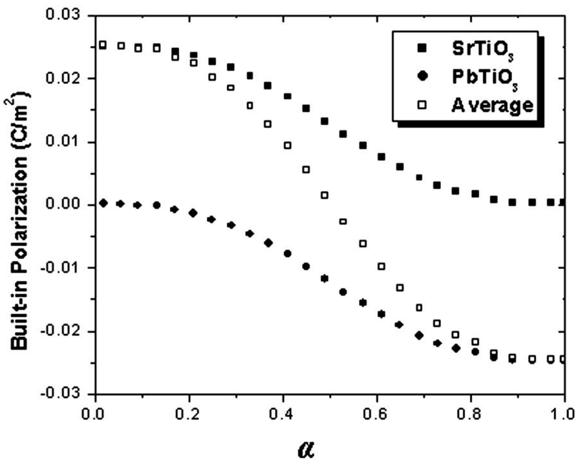

FIG. 2. Values of the built-in polarization for $\sigma = 0.025\ \text{C/m}^2$. Decreasing layer thickness makes the built-in polarization in that layer attain higher values.

Figure 3 shows the analysis for the PT-ST on ST substrate for different space charge densities at room temperature. For very small σ values (such as $1 \times 10^{-5}\ \text{C/m}^2$), the change is hardly distinguishable where the strain and the depolarization effects dominate. For higher densities, such as $0.025\ \text{C/m}^2$, the structure exhibits a small but finite ferroelectricity until around 95%–98% ST fraction, first exhibiting a drop and a slight recovery after ~60% ST. P_f in PT at relatively high ST fractions follows a nearly flat trend that resembles the P_b in this layer. For very small fractions of PT at the order of a few percent, however, results for P_{f_i} presented in our study may not reflect reality as the solution of Eq. (6) becomes strongly dependent on P_{b_i} which was *pre-introduced* and may pose an unreal situation in the numerical analysis. It is worth to note that the P_f in PT is insensitive to σ when the structure is mainly PT but becomes very suscep-

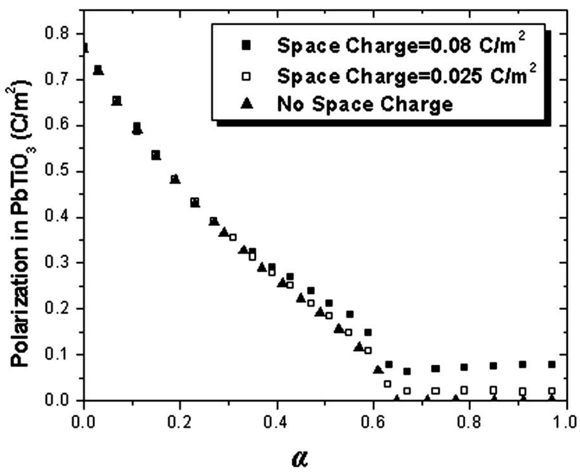

FIG. 3. Switchable ferroelectric polarization in the PT layer at various interface charge densities.

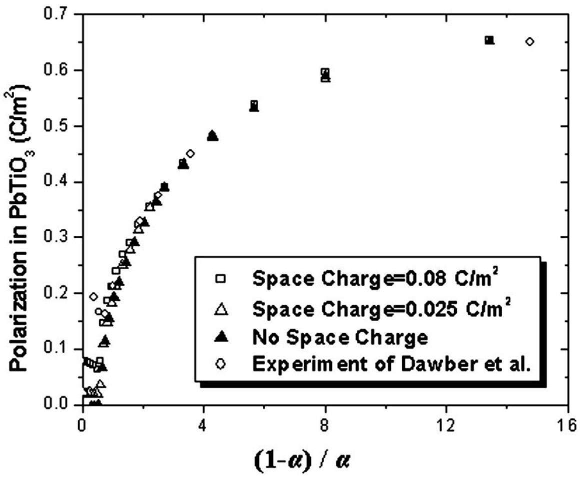

FIG. 4. Comparison of the results of the methodology in this article with the data extracted from Ref. 1 (see Fig. 4 in Ref. 1).

tible to values of σ at low fractions through Pb_i. P_f in the layer that has negative P_b is enhanced, even if the other layer was also PT instead of ST, alike stated in Ref. 12. This enhancement is higher when σ attains larger values, as seen in Fig. 3. Space charge influence on P_f becomes distinguishable when the structure is dominated by ST. Strain has little impact on the stability of ferroelectricity at high ST fractions despite the high tetragonality of the PT. We also note that the small-signal dielectric constant of PT for high ST fractions when $\sigma > 0$ attains values at the order of 300–400 which is much higher than the bulk PT.

In the light of the above statements, the existence of switchable polarization in thin layers (at the order of a few monolayers) embedded in paraelectric matrices that was observed by several groups could be a consequence of the interface space charge (Fig. 4). In Fig. 4, the polarization data of Dawber *et al.* is extracted approximately using published tetragonality in this reference for comparison. The charge mentioned in our study is space charge[14] which is assumed to exist at or very close to the interface. A charge distribution in the layers that is position dependent would, of course, complicate the problem. Furthermore, we also note that regardless of the value of σ, the polarization states always remain coupled to each other due to the depolarizing fields.

Clearly, the presence of an interfacial charge might have different origins, other than the ferroelectric polarization jump at the interface. An analysis on graded structures has shown the possibility of obtaining built-in potentials due to intrinsic polarization gradients other than space charge.[15] Stoichiometric deviations at the interface such as vacancies, nonstoichiometric termination planes, and band bending, due to the semiconductor nature of the perovskite FE, to adjust to a common Fermi level in an attempt to satisfy local electrostatic neutrality[16,17] could result in a release of charge as much as $10^{17}-10^{20}$ carriers/cm^3. The covalent nature of PT and the ionic nature of ST could also result in the formation of a charge layer at the interface due to local electrostatic imbalance.[18] Trapped charge densities in BT films as high as 0.05 C/m^2 have been reported.[19] It was also shown that a thermodynamically driven 180° domain formation may be favored if a large internal electrostatic energy persists due to different P_{f_i} values in the layers, even in the case of single composition FE films to minimize the ferroelectric polarization difference.[12,20]

In this preliminary analysis, we show that ferroelectric polarization in a multilayer can be influenced by the presence of an interfacial charge other than the depolarization effect which can enhance or degrade polarization depending on the layer configuration and dopant type. This mainly arises from the interaction of the interfacial charge with the polarization difference between the layers. It becomes more pronounced with decreasing FE fractions and might explain the existence of remnant polarization in very thin FE layers embedded in a PE matrix in previous reports. The presence of such a charge at the interface can also impact the switching characteristics of ferroelectric superlattices as it will create local deviations from overall equilibrium characteristics.

One of the authors (I.B.M.) wishes to thank the Alexander von Humboldt Foundation for funding his stay in Germany. They also would like to thank their reviewer for his/her suggestions to improve the methodology.

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