

Interface Effects in Ferroelectric PbTiO₃ Ultrathin Films on a Paraelectric Substrate

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Interface effects on the ferroelectric behavior of PbTiO₃ ultrathin films deposited on a SrTiO₃ substrate are investigated using an interatomic potential approach with parameters fitted to first-principles calculations. We find that the correlation of atomic displacements across the film-substrate interface is crucial for the stabilization of the ferroelectric state in films a few unit cells thick. We show that the minimum film thickness for the appearance of a spontaneous polarized domain state is not an intrinsic property of the ferroelectric film but depends on the polarizability of the paraelectric substrate. We also observe that the substrate displays an induced polarization with an unusual oscillatory behavior.

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The current high interest in ferroelectric thin films and nanostructures is due to the wide range of their potential applications in microelectronics. It is well known that the reduction of the characteristic size of ferroelectric structures in the nanoscopic regime may result in finite size effects. For instance, whether or not there is a critical thickness below which no ferroelectricity can occur is still under debate. Ferroelectricity is a cooperative phenomenon and, as such, it is expected to be strongly influenced by surfaces. Most active device applications eventually involve thin film forms and the understanding of the near-surface region becomes important. A ferroelectric thin film cannot be considered in isolation, but rather the measured properties reflect the entire system of films, interfaces, electrodes, and substrates. Although the effects of epitaxial strain and metal electrodes on film properties have been extensively investigated [1], almost nothing is known on how a paraelectric substrate modifies the ferroelectric properties of thin films.

Recently, Fong *et al.* showed that ferroelectric phases can be stable down to ≈ 12 Å (three unit cells) in PbTiO₃ films deposited on SrTiO₃ substrates by forming 180° stripe domains, suggesting that no fundamental thickness limit is imposed by intrinsic size effects in thin films [2]. This was directly confirmed by x-ray photoelectron diffraction studies [3]. Moreover, high-resolution electron density maps obtained by synchrotron x-ray scattering showed that thin ferroelectric films grown epitaxially on paraelectric substrates display a rich variety of structures and properties. It was shown that monodomain ferroelectricity can be stable when the samples are cooled sufficiently slowly, and details of the PbTiO₃/SrTiO₃ interface were obtained [4]. As for the origin of ferroelectricity in such ultrathin films, a mixed Pb_xSr_{1-x}TiO₃ interface has been suggested [5]. Despite these efforts, it is not clear why a polar state remains stable at such low thicknesses.

In this work we investigate the effects of a SrTiO₃ substrate on the ferroelectric behavior of PbTiO₃ thin films

using an atomic-level description. We find that the minimum film thickness for ferroelectricity is not an intrinsic property of the ferroelectric film, but depends on the polarizability of the paraelectric substrate. We show that the correlation of atomic displacements between film and substrate ions across the interface make possible the stabilization of the ferroelectric state in films up to 2 unit cells thick. We also find that a region of the SrTiO₃ substrate near the film polarizes in the opposite direction than the film.

The simulations are carried out using shell models with parameters fitted to first-principles calculations. That is, no explicit experimental data are used as input. The shell model offers a reliable atomic-level description of ferroelectric materials [6], and is a practical tool to investigate properties of systems where a large number of atoms are involved. The particular model for PbTiO₃ (PT) used here reproduces correctly the cubic-tetragonal phase transition of the bulk [7], and it is also able to describe properly surface properties, such as atomic relaxation patterns, change in the interlayer distances, layer rumpling, and the antiferrodistortive surface reconstruction observed experimentally [8]. The model for the SrTiO₃ (ST) substrate is developed following a similar procedure; that is the parameters are fitted to first-principles calculations. Moreover, to make the ST model compatible with the PT model, the only difference between both lies in the different A-Ti and A-O interactions and the different polarizability parameters for Sr and Pb. The input data correspond to local-density approximation (LDA) calculations of the energy as function of volume, lattice dynamics, and underlying potential energy surfaces as function of relevant distortions. The resulting model displays a cubic lattice parameter $a = 3.860$ Å that agrees with the LDA value of 3.861 Å (we note that LDA underestimates the lattice constant of perovskites by $\approx 1\%$, a better agreement with experiments is obtained with other functionals [9]). The ferroelectric soft-mode mode is stable (77 cm⁻¹) at the theoretical equilib-

rium volume and unstable ($i113 \text{ cm}^{-1}$) at the experimental one, in agreement with the LDA behavior (68 cm^{-1} and $i94 \text{ cm}^{-1}$ at the respective volumes).

We simulate coherently strained PT films on (001) ST substrates using a semi-infinite crystal geometry. The z axis lies along the growth direction of the film, and the x and y axes are chosen to be along the pseudocubic [100] and [010] directions. The simulation cell contains 10×10 unit cells with periodic boundary conditions in the x - y plane. The free surface is at the top and corresponds to a PbO-terminated surface, which is the equilibrium termination for PT [10]. The interface between the film and the substrate is chosen to be coherent, as it is observed in experiments [4], and consist of a common TiO_2 layer. We consider that a film with thickness of n unit cells corresponds to n PbO layers. The film-substrate system is described with a region I—region II strategy. Region I corresponds to the film and the nearby part of the substrate in interaction with the film. The second region corresponds to the part of the substrate which is away from the interface, and it simulates the interior of the non disturbed crystal. Whereas atoms in region I are allowed to relax, atoms in region II are held fixed at the ideal cubic positions. For the substrate, a thickness of 10 unit cells is taken for region I, which is thick enough to avoid significant changes in the final results. The long range electrostatic energy and forces are calculated by a direct sum method [11]. The equilibrated zero-temperature structures are determined by the standard atomic relaxation method until the force on each individual ion is less than $0.001 \text{ eV}/\text{\AA}$.

As the system is electrically neutral and there are no free charges to screen the depolarizing field, a ferroelectric state with polarization perpendicular to film surface manifests through the formation of 180° stripe domains with alternating polarity [12–16]. Atomic-level simulations provide detailed local information of the polarization across the film. Figure 1 shows the cell-by-cell out-of-plane polarization profile along the x axis, for successive layers from the free surface to the film-substrate interface, for a 5 unit cell film [17]. Positive polarization values correspond to polarization oriented towards the substrate. Stripe domains aligned along the y axis are formed. This stripe domain pattern forms naturally and does not depend on the initial configuration of the minimization procedure (a nonpolarized or uniformly polarized state). However, the domain period is imposed by the in-plane periodicity of the simulation cell. It is clear from that figure that the polarization is not uniform inside each nanodomain, and it increases with the distance to the interfaces: free surface, film-substrate interface, and domain walls. As a result, 180° domain walls in the film are not as sharp as in bulk.

Figure 2 shows the average layer-by-layer out-of-plane polarization profiles within a domain (P_z) for films 2 to 5 unit cells thick on the ST substrate. For comparison, the profile for the freestanding 5 unit cell film under the same

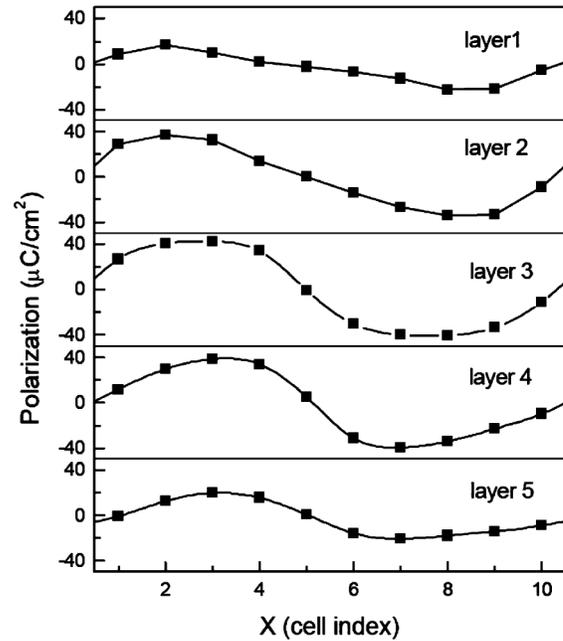


FIG. 1. Cell-by-cell out-of-plane polarization profile along the x axis, for successive layers from the free surface (top) to the film-substrate interface (bottom), for a 5 unit cell film.

in-plane condition is shown. In Fig. 2 positive values of z indicate the PT film region while negative values indicate the ST substrate region. The profiles for the films on the substrate are qualitatively similar to the one of the freestanding slab. However, the polarization in the last case is substantially lower. At the interface ($z = 0$), P_z is only $1.2 \mu\text{C}/\text{cm}^2$ in the freestanding slab and it increases to $14 \mu\text{C}/\text{cm}^2$ when the substrate is present. For the inner layer, P_z varies from $6 \mu\text{C}/\text{cm}^2$ to $28 \mu\text{C}/\text{cm}^2$, respectively. Since we take the same in-plane lattice parameter in

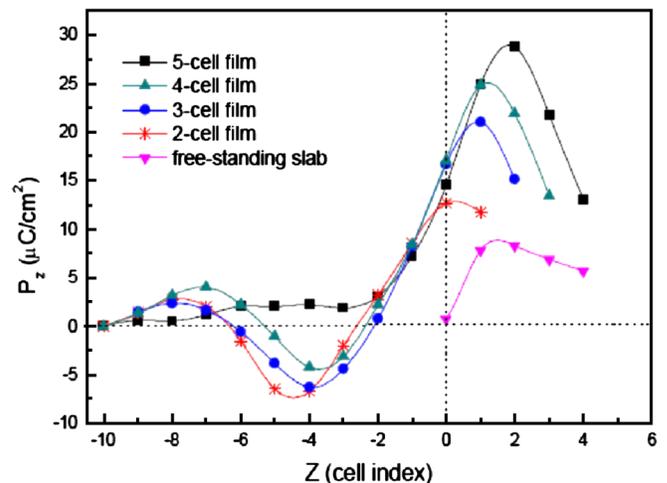


FIG. 2 (color online). Average layer-by-layer out-of-plane polarization profiles within a domain for films 2 to 5 unit cells thick on the ST substrate. For comparison, the profile for the freestanding 5-unit cell film is included.

both cases, the enhancement of the polarization is due to the presence of the paraelectric substrate. The larger P_z at the free surface ($z = 4$) of the film on the substrate indicates that the interaction between them manifests throughout the film. The effect of the film-substrate interaction is also reflected in the substrate region, where an induced polarization is developed in the nonpolar compound. In fact, Fig. 2 shows that in the paraelectric substrate, a region of ≈ 3 unit cells near the interface polarizes in the same direction as the film. These interface effects can be understood from the particular correlation of local dipole moments in perovskites. The so-called Lorentz field produces a significant mutual enhancement of the dipoles along the direction of polarization. As a consequence, strongly correlated chains of polarization tend to form. As ST is a highly polarizable substrate, the ionic displacements of the ferroelectric film correlate with the ones of the substrate across the coherent interface reinforcing the PT film polarization. As we will show later, this correlation is crucial for the stabilization of a ferroelectric state in films a few unit cells thick.

The large increment of the film polarization produced by the presence of the paraelectric substrate indicates the importance of selecting appropriate boundary conditions to interpret correctly the experimental results. The ST substrate favors the ferroelectricity of PT films and, as a consequence, it produces a decrement in the minimum thickness for ferroelectricity, in comparison with the free-standing slab. In fact, the minimum thickness decreases from 5 unit cells for the free-standing slab [8] to only 2 unit cells when the film is on the ST substrate [18]. The polarization profile of the 2 unit cell film (Fig. 2) shows that the film displays an average domain polarization of $\approx 12 \mu\text{C}/\text{cm}^2$. It should be noted that our theoretical calculations are at zero temperature while the experiments were performed above 120 K. This means that the 2-unit cell film predicted to be ferroelectric at 0 K might be expected to be paraelectric above 120 K. Moreover, the fit of the critical temperature as a function of film thickness predicted that the 2 unit cell thick film would be ferroelectric at low temperatures [13]. So, the substrate not only imposes an epitaxial strain on the film but generates a strong film-substrate coupling that plays an active role in the ferroelectric behavior of the film.

Another interesting effect observed in the substrate region is that the local polarization displays an unusual oscillatory behavior. The polarization profiles shown in Fig. 2 for the cases of 2 to 4 unit cell films indicate that a region of the ST substrate near the interface is polarized in the opposite direction than the film. The inversion of the induced polarization in the paraelectric material, which appears 3 cells from the interface, probably indicates that the depolarizing field has not been completely screened by the domain configuration and overcomes the effect of the correlation with the ferroelectric film. By extending the

relaxed ST region up to 20 unit cells from the interface, we observed that damped polarization oscillations continue beyond the relaxed 10 cells of Fig. 2. This fact, however, does not affect the polarization profiles of the PT films. A polarization inversion in the substrate region was obtained recently from estimations, under reasonable assumptions, of the dipole moment per unit cell using atomic positions determined by synchrotron x-ray scattering [4]. However, it was presumed that this feature is a consequence of the assumptions made in the calculations. We show here that this polarization inversion is indeed present when films are thin enough.

The above results raise the question of how the polarizability of the paraelectric substrate affects the minimum thickness for ferroelectricity in PT films. To answer this question we develop several ST-like hypothetical compounds with the following characteristics: they all have the same structure and lattice parameter of ST, they are paraelectric, but they have a different soft-mode frequency (i.e., different polarizability). We term these compounds soft, hard-1, and hard-2, with a soft-mode frequency of 19, 181, and 243 cm^{-1} , respectively, (the polar-mode frequency of the ST model is 77 cm^{-1}). We plot in Fig. 3 the polarization profile for a 3 unit cell film on the different hypothetical paraelectric substrates. It is clear that the film polarization increases when the substrate becomes softer (soft), and decreases when the substrate becomes harder (hard-1). If the substrate is hard enough (hard-2), no domain structure or ferroelectricity is found. So, not only the polarization of the film but the minimum film thickness for ferroelectricity depends on the dielectric properties of the substrate. Figure 4 shows the minimum thickness for the stabilization of a ferroelectric state as function of the substrate dielectric constant. For a dielectric constant higher than the one of ST, the minimum film thickness is

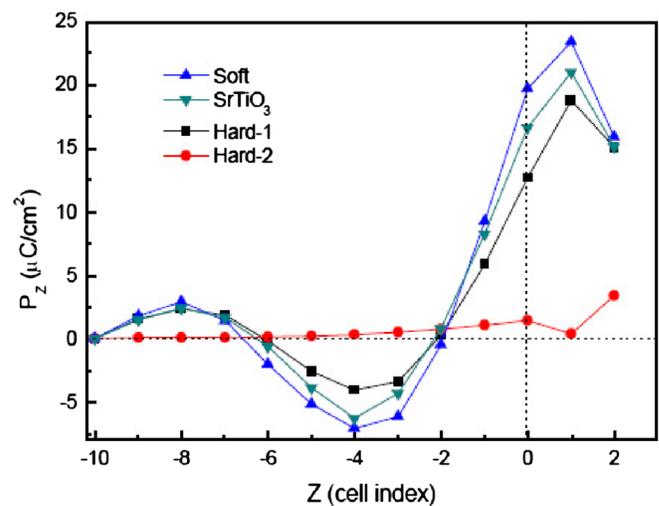


FIG. 3 (color online). Average layer-by-layer out-of-plane polarization profiles for a 3 unit cell film on hypothetical ST-like paraelectric substrates with different polarizabilities.

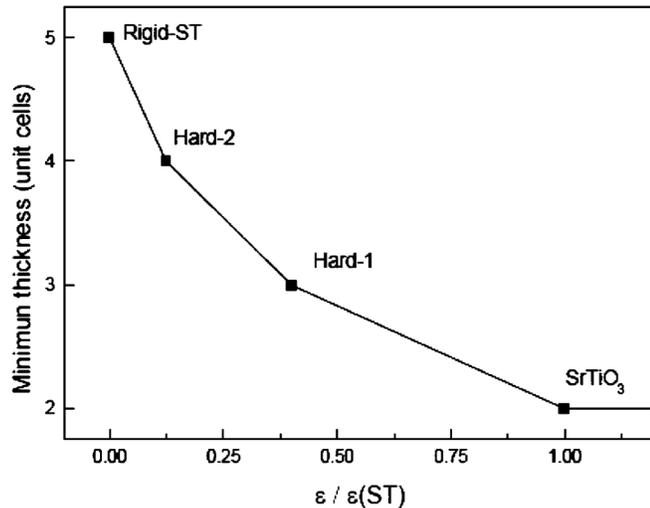


FIG. 4. Minimum thickness for the stabilization of a ferroelectric state as function of the substrate dielectric constant.

2 unit cells. This value increases when the substrate hardens its dielectric response. In the limiting case of a non-polarizable substrate, where the ions were held fixed at the equilibrium cubic positions, a minimum thickness for ferroelectricity of 5 unit cells is obtained, in concordance with the critical thickness of the freestanding slab. So, the critical thickness for the stabilization of a spontaneous polarized state is not an intrinsic property of the ferroelectric PT film but depends on the polarizability of the paraelectric substrate. For the thinnest film with ferroelectric properties observed in experiments, which is 3 unit cells on ST, a cooperative phenomenon between film and substrate ions across the interface is responsible for the stabilization of the ferroelectric state. That is, substrate atoms are part of the correlated region and contribute to the minimum correlation length necessary for ferroelectricity.

The effect of the ferroelectric-paraelectric coupling is even stronger when the PT film is coherently strained between two ST layers. In fact, we simulate PT ultrathin films of different thickness between two ST layers of 10 unit cells thick. The results indicate that, under such a boundary condition, even a single PbO plane polarizes in a stripe domain configuration, with a local polarization of $7 \mu\text{C}/\text{cm}^2$. This polarization is favored by the coupling to the surrounding highly polarizable media, which manifests by the extension of the polarized region over 5 unit cells. Interestingly, the paraelectric regions at both sides of the ferroelectric layer also display polarization oscillations, which might produce unexpected effects in superlattices with PT layers a few unit cells thick [19].

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- [1] M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
 - [2] D. D. Fong, G. G. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, *Science* **304**, 1650 (2004).
 - [3] L. Despont, C. Lichtensteiger, C. Koitzsch, C. Clerc, M. G. Garnier, F. J. Garcia de Abajo, E. Bousquet, Ph. Ghosez, J.-M. Triscone, and P. Aebi, *Phys. Rev. B* **73**, 094110 (2006).
 - [4] D. D. Fong, C. Cionca, Y. Yacoby, G. B. Stephenson, J. A. Eastman, P. H. Fuoss, S. K. Streiffer, Carol Thompson, R. Clarke, R. Pindak, and E. A. Stern, *Phys. Rev. B* **71**, 144112 (2005).
 - [5] M. D. Glinchuk, A. N. Morozovska, and E. A. Eliseev, *cond-mat/0504537*.
 - [6] M. Sepliarsky, M. G. Stachiotti, and S. Phillpot, in *Interatomic Potentials: Ferroelectrics, in Handbook of Materials Modeling*, edited by S. Yip (Springer, Dordrecht, 2005), p. 527.
 - [7] M. Sepliarsky, Z. Wu, A. Asthagiri, and R. E. Cohen, *Ferroelectrics* **301**, 55 (2004).
 - [8] M. Sepliarsky, M. G. Stachiotti, and R. L. Migoni, *Phys. Rev. B* **72**, 014110 (2005).
 - [9] E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier, and G. Borstel, *Phys. Rev. B* **64**, 235417 (2001).
 - [10] B. Meyer, J. Padilla, and D. Vanderbilt, *Faraday Discuss.* **114**, 395 (1999).
 - [11] D. Wolf, P. Keblinski, S. R. Phillpot, and J. Eggebrecht, *J. Chem. Phys.* **110**, 8254 (1999).
 - [12] S. Tinte and M. G. Stachiotti, *Phys. Rev. B* **64**, 235403 (2001).
 - [13] S. K. Streiffer, J. A. Eastman, D. D. Fong, C. Thompson, A. Munkholm, M. V. Ramana Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).
 - [14] M. G. Stachiotti, *Appl. Phys. Lett.* **84**, 251 (2004).
 - [15] Z. Wu, N. Huang, Z. Liu, J. Wu, W. Duan, L.-B. Gu, and X.-W. Zhang, *Phys. Rev. B* **70**, 104108 (2004).
 - [16] I. Kornev, H. Fu, and L. Bellaiche, *Phys. Rev. Lett.* **93**, 196104 (2004).
 - [17] We note that, as a consequence of LDA, we expect polarization values underestimated with respect to the experimental ones.
 - [18] The one unit cell thick film does not display a polar state, no domain structure or ferroelectricity is found. In this film, the surface cells develop a small inward polarization due to the relaxation and rumpling of the surface layers.
 - [19] M. Dawber, C. Lichtensteiger, M. Cantoni, M. Veithen, P. Ghosez, K. Johnston, K. M. Rabe, and J.-M. Triscone, *Phys. Rev. Lett.* **95**, 177601 (2005).