Surface and Substrate Effects on the Ferroelectric Properties of PbTiO₃ Ultrathin Films

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The effects of the antiferrodistortive surface reconstruction and the interface with a SrTiO₃ substrate on the ferroelectric properties of PbTiO₃ ultrathin films are investigated using an interatomic potential approach with parameters determined from first-principles results. First we show that a shell model developed for the bulk describes properly the surface properties of PbTiO₃, in particular the antiferrodistortive surface reconstruction recently observed from x-ray scattering. We investigate also the effects of the surface reconstruction on the polarization behavior of ultrathin films under open-circuit electrical boundary conditions, showing that the surface layer participates in the ferroelectricity. Finally, film-substrate interface effects on the ferroelectric properties are investigated simulating PbTiO₃ ultrathin films on a SrTiO₃ substrate.

Keywords Thin films; theory; atomic-level mode

Introduction

With the rapidly advancing miniaturization of ferroelectric (FE) devices and the use of thin films, attention is focusing on the role played by surfaces and interfaces in the overall performance of the materials. Size dependent effects on the structural phase transitions have become an issue of significant importance because the surface can affect the structural behavior of the perovskites by modifying the strength of various instabilities. Lead titanate is a clear example. In PbTiO₃(PT), ferroelectricity is due to the condensation of a $\Gamma_{15}$ unstable phonon in which the oxygen octahedra shift against the Pb sub-lattice. The ground state consists of shifts along (001) accompanied by a tetragonal lattice strain which stabilizes this direction [1]. However, complete phonon dispersions for the ideal perovskite structure of PT show ferroelectric ($\Gamma_{15}$) and also rotational AFD ($R_{25}$ type) instabilities [2]. In bulk, the FE and AFD instabilities compete with each other and the FE lattice distortion suppresses the AFD distortion, but the proximity to a surface modifies that balance. Recently, an AFD reconstruction of the PT (001) surface has been found using grazing incidence x-ray scattering. The atomic structure of the surface consist of a single layer of an AFD structure with oxygen cages rotated by 10° around the [001] axis through the Ti ions [3]. Latter on, the AFD reconstruction at the PbO-terminated (001) surface was reproduced by Bungaro and Rabe using ab-initio calculations [4]. They also found for in-plane polarized
films that the FE and AFD distortions coexist in the proximity of the surface. Regarding device applications, out-of-plane polarized films are more relevant, and surface modify the ferroelectric character in thin films. For example, there is critical size below which no ferroelectric ordering occurs [5]. Therefore, it is worth investigating also the effects of the surface reconstruction on the out-of-plane ferroelectricity.

The realistic simulation of PT thin-films is a theoretical challenge due to the interplay of polar and non-polar instabilities at the surface. Although first-principles methods are extremely precise, they are quite computer demanding. So, other methods are necessary to handle larger system sizes. During the last years, the effective Hamiltonian approach has been used for the investigation of thin film properties [6–9]. However, for the simulation of Pb-based perovskite thin-films the coexistence of rotational and FE distortions should be explicitly considered [10]. Atomistic simulations based on interatomic potentials can account naturally for the presence of competing instabilities because they describe all degrees of freedom of the crystal. However, the validity of any atomistic simulation study depends to considerable extent on the quality of the potentials used. The shell model approach has proved to be a computationally efficient and confident methodology for the simulation of ferroelectric perovskites, including bulk properties of pure crystals [11–13], solid solutions [14] and superlattices [15], and also surfaces and thin films properties [16]. In this model, each atom is represented by a massive core coupled to a massless shell, and the relative core-shell displacement describes the atomic polarization. In this paper we investigate the ferroelectric properties of PT thin films using a shell model. We investigate first if the model developed for the bulk describes properly surface properties. Then the ferroelectric behavior of ultrathin films under open-circuit electrical boundary conditions is investigated. Finally, we analyze the effects of a SrTiO3 substrate on the ferroelectric properties of the film.

Model and Computational Details

The model used in the present work to describe PT was developed in a previous study on bulk properties [13], and the model parameters were fitted to reproduce extensively first principle results for bulk. The model contains 4th order core-shell couplings, long-range coulombic interactions and short-range interactions described by two different types of potentials. A Rydberg potential \( V(r) = (a + br) \exp(-r/\rho) \) is used for the Pb-Ti, Pb-O and Ti-O pairs, and a Buckingham potential \( V(r) = a \exp(-r/\rho) - cr^{-6} \) is used for O-O interactions. The input information corresponded to extensive LDA results for PT. The resulting model was able to reproduce delicate properties of PT, including the ferroelectric (at \( \Gamma \)) and rotational (at \( R \)) instabilities from the phonon dispersion curves in the cubic structure. However, as a consequence of the LDA, volume and volume dependent properties were underestimated with respect to experimental values. For example, the model gave a tetragonal ground state with a lattice parameter \( a = 3.859 \) Å, a tetragonal distortion \( c/a = 1.043 \), and a spontaneous polarization \( P = 54 \) \( \mu \)C/cm\(^2\), while the experimental data are \( a = 3.90 \) Å, \( c/a = 1.065 \), and \( P = 75 \) \( \mu \)C/cm\(^2\). The underestimation of the static structural properties is translated via the adjusted model to the finite temperature behavior, with a cubic-tetragonal transition at \( T_c = 450K \), 300K below the experimental value. Nevertheless, the qualitative temperature behavior of lattice parameters and polarization was correctly reproduced.

The investigation of the surface properties is carried out using an isolated slab geometry with periodic boundary conditions in the x-y plane. The long ranged electrostatic energy and forces are calculated by a direct sum method [17]. The equilibrated zero-temperature
structure of the slabs was determined by a zero-temperature quench until the force on each individual ion was less than 0.001 eV/Å. To mimic the two dimensional clamping and straining of the film due to the presence of a substrate, we force the simulation cell to be square in the x-y plane.

Surface Effects in Non-Polar Slabs

In order to check if the model developed for the bulk is able to describe surface properties we take first-principles calculations as benchmark results to compare with. In particular, we consider two first-principles studies for (001) surfaces of cubic PT on a c(1 × 1) surface periodicity using ultrasoft-pseudopotential [18] and a hybrid DFT calculation [19] as reference. To this end we determined the atomic equilibrium position for both PbO- and TiO- symmetrically terminated 7-layer periodic slabs. We set the in-plane lattice parameter to the cubic equilibrium value yielded by the model in bulk, a = 3.887 Å, and we relaxed the atomic positions from the ideal positions only in the direction perpendicular to the surface. The results obtained for the atomic relaxations for both slabs are listed in Table 1, and ab-initio results are shown also as reference. The model reproduces satisfactorily the relaxation direction of the atoms and related magnitudes such as the change in the interlayer distance and atomic rumpling. For the case of the PbO surface, which is the equilibrium termination for PT [18], the numerical values are in very good agreement with the ab-initio ones. Also, the average surface relaxation energy obtained with the model ΔE_{relax} = 0.237 eV is also in quite good agreement with the ab-initio result of 0.210 eV [18].

A recent pseudopotential study of the AFD surface reconstruction in PbTiO_3 slabs [4] provides reliable additional information to validate the model. In Table 2, we show structural parameters of the relaxed c(2 × 2) 11-layer PbO terminated slab. The overall agreement with the ab-initio results is very good. The model reproduces the main differences between the c(2 × 2) and c(1 × 1) surface periodicity, that is the presence of an AFD reconstruction with a reduction of rumpling and interlayer distances. Regarding the AFD surface reconstruction, the rotation angles are slightly overestimated with respect to the pseudopotential calculations; the experimentally determined rotation angle for the surface layer is 10° [3]. The energy gain associated with the octahedra rotations is 0.32 eV per surface unit cell, which is approximately one order of magnitude larger than the bulk ferroelectric well depth.

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<tbody>
<tr>
<td>Pb(1)</td>
<td>3.45</td>
<td>4.36</td>
<td>3.82</td>
<td>Ti(1)</td>
<td>4.17</td>
<td>3.40</td>
<td>2.81</td>
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<td>O_{III}(1)</td>
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<td>0.46</td>
<td>0.31</td>
<td>O_{I-II}(1)</td>
<td>2.94</td>
<td>0.34</td>
<td>0.31</td>
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<tr>
<td>Ti(2)</td>
<td>3.19</td>
<td>2.39</td>
<td>3.07</td>
<td>Pb(2)</td>
<td>1.58</td>
<td>4.53</td>
<td>3.07</td>
</tr>
<tr>
<td>O_{I-II}(2)</td>
<td>1.65</td>
<td>1.21</td>
<td>2.30</td>
<td>O_{III}(2)</td>
<td>0.34</td>
<td>0.43</td>
<td>2.30</td>
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<tr>
<td>Pb(3)</td>
<td>0.78</td>
<td>1.37</td>
<td>0.98</td>
<td>Ti(3)</td>
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<td>0.27</td>
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<tr>
<td>O_{III}(3)</td>
<td>0.33</td>
<td>0.20</td>
<td>0.56</td>
<td>O_{I-II}(3)</td>
<td>0.56</td>
<td>0.27</td>
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Table 2
Change in the interlayer distance ($\Delta d$), layer rumpling ($\nu$), and rotation angle ($\Theta$) of oxygen octahedral for the PbO terminated $c(2 \times 2)$ surface at $d_{bulk}$ in a 11-layer nonpolar PbTiO$_3$ slab. For comparison, ab initio results are shown in parentheses.

<table>
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<tr>
<th>Interlayer distance</th>
<th>Rumpling</th>
<th>Rotation angle</th>
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<tbody>
<tr>
<td>$\Delta d_{12}$</td>
<td>$-3.3$ (-3.4)</td>
<td>$\nu_1$ -1.4 (-1.4)</td>
</tr>
<tr>
<td>$\Delta d_{23}$</td>
<td>$+2.1$ (+2.9)</td>
<td>$\nu_2$ +1.3 (+0.9)</td>
</tr>
<tr>
<td>$\Delta d_{34}$</td>
<td>$-0.1$ (-0.9)</td>
<td>$\nu_3$ -1.8 (-2.0)</td>
</tr>
<tr>
<td>$\Delta d_{45}$</td>
<td>$+0.3$ (+0.4)</td>
<td>$\nu_4$ +0.5 (+0.4)</td>
</tr>
<tr>
<td>$\Delta d_{56}$</td>
<td>$+0.1$ (-0.1)</td>
<td>$\nu_5$ +0.2 (-0.2)</td>
</tr>
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</table>

We have shown that a shell model can mimic at the atomic level the tendency of Pb to move off-center and enhance the AFD distortion at the PbO surface. The AFD surface reconstruction is due to the formation of strong covalent Pb—O [4]. In the less-sophisticated model approach, it obtained just as a result of the change in the balance of long-range Coulombic and short-range interactions at the surface. In conclusion, the shell model parameters fitted to describe bulk properties of PT is able to describe surface properties in good agreement with ab-initio and experimental results.

Ferroelectric Behavior in Polar Slabs
The agreement with first-principle results makes the model reliable to explore zero-temperature ferroelectric properties in PT ultrathin films. For this case, we consider only PbO-terminated surfaces because they are the most stable ones [18]. The in-plane lattice parameter was set and clamped to the model equilibrium value for the tetragonal bulk $a = 3.859$ A. Since this value is close to the lattice parameter of SrTiO$_3$, this clamped condition simulates the strain effect of a SrTiO$_3$ substrate. The simulation cell contains $10 \times 10$ unit cells with periodic boundary conditions along the x-y plane, and we have performed standard-atomic relaxation methods to determine the zero temperature structure in slabs from 2 to 10 unit cells thick. To analyze the results, we define the cell parameter $c$ as the distance between two consecutive PbO planes, and the local polarization is defined as the polarization of a Ti-centered unit cell.

In the film, the presence of the surface produces a diminution in their tetragonality respect to bulk. Figure 1 provides detailed microscopic information about the average cell-by-cell tetragonal distortion $c/a$ for a 10-unit cells thick slab. It can be seen that the tetragonality of all unit cells in the slab is considerable lower than in the bulk ($c/a = 1.043$ for the bulk). The strongest reduction is observed for the surface cells which are practically cubic ($c/a = 1.005$) while the tetragonality increases towards the interior of the slab reaching the value $c/a = 1.032$. As the imposed in-plane lattice parameter corresponds with the one of ferroelectric bulk PT, we can expect that the tetragonality gradually converges to the bulk value when the film thickness increases. In fact, we can roughly estimate by extrapolation a slab thickness of 86 Å ($\approx 22$ unit cells) so that the center of the film reaches the tetragonality of the bulk. The strong thickness dependence of tetragonality is in qualitative agreement with recent experimental measurements which showed that the average $c/a$ ratio decreases substantially for films thinner than 200 Å [20].
Out-of-plane ferroelectricity manifests above a critical thickness through the formation of stripe domains of alternating polarity in free-standing slabs. The observation of stripe domains below the ferroelectric transition in epitaxial PbTiO\textsubscript{3} ultrathin films on SrTiO\textsubscript{3} substrates was reported from x-ray scattering [21], and the ferroelectric phase was found to be stable for thickness down to 3 unit cells [5]. Figure 2 shows the cell-by-cell out-of-plane polarization profile of a chain perpendicular to the surface of slabs of 4 and 5 unit cell width.
It is clear that under the imposed stress and electrical boundary conditions, the model gives a critical thickness \( (d_c) \) for ferroelectricity of 4 unit cells \( (d_c \) is defined as the maximum thickness at which polarization is zero). In the 4-cell slab the surface cells develop a small inward polarization of \( \approx 3 \, \mu C/cm^2 \) due to surface atomic relaxations (see Table 1) while the polarization of the two inner cells is practically zero. In the 5-cell slab, individual chains have a net out-of-plane polarization but the average polarization of the slab is zero due to the development of stripe domains. The inner cells display a local polarization of \( \approx 18 \, \mu C/cm^2 \), that is 0.33 of the bulk value. The surface cells present an even stronger reduction of polarization. It is very important to point out, however, that the polarization of the surface cells in the 5-cell ferroelectric slab is considerably larger than in the 4-cell non-ferroelectric one, it increases from \( \approx 3 \, \mu C/cm^2 \) to \( \approx 10 \, \mu C/cm^2 \). This polarization enhancement indicates that the surface layer, which forms an AFD reconstruction, also participates in the ferroelectricity. We note that the value of \( d_c \) obtained with the model is two unit cells larger than the experimental one reported in Ref. [5]. One possible explanation of this difference could arise from the fact the model was developed to reproduce the LDA ground state of bulk PT, and consequently the ferroelectric instability is underestimated. Another possibility is we are not explicitly simulating the substrate.

Polar slabs not only present the AFD surface reconstructions but they also show an unexpected in-plane polarization component because the in-plane lattice parameter corresponds to the tetragonal bulk value. In films, the decrease in tetragonality favors the stabilization of a phase with a non-vanishing in-plane polarization component along the (110) direction, above and also below the critical thickness. The reduction of tetragonality produces that the in-plane polarization increases when the film thickness decreases. Locally, there is a strong increment of the in-plane polarization at the surface, and it decreases towards the interior of the slab. For thick enough films, it is expected that the interior of the slab reaches the vanishing in-plane polarization of the bulk. On the other side, polar slabs show a surface reconstruction with a rotation angle similar to the non polar ones. However, one difference is that neighboring planes of octahedra along the rotation axis rotates in-phase instead of out-of-phase. In fact, for the polar slabs, \( \Theta_2 = 13.5^\circ \), \( \Theta_4 = 4.5^\circ \) and \( \Theta_6 = 7.3^\circ \) for the first, second and third layers, respectively. We note that unstable modes at the M and R points, which are associated with oxygen rotation instabilities, have similar frequencies and compete with each other in the cubic bulk [3]. The presence of the polarized surface affects these two competing structural instabilities stabilizing M-type distortions at the surface. Also, the AFD surface reconstruction produces a peculiar effect on the in-plane polarization profile. Although the average in-plane polarization is oriented along the (110) direction, unit cells are not uniformly polarized along that direction. This can be visualized by the top view of the surface showed in Fig. 3.

To make the description simpler, consider the displacements of the Pb atoms. It is clear from the figure that they displace mainly along (100) directions (see the arrows) in such a way that half of the Pb atoms are displaced along a (100) direction, and the other half along a (010) direction. Although the effect is much stronger at the surface, this local behavior is observed throughout the ultrathin film. This polarization profile, which produces an average in-plane polarization along the (110) direction, is a consequence of the oxygen octahedra rotation plus the tendency of Pb to move off-center shortening Pb—O bonds.

**Film-Substrate Interface Effects**

The value for the critical thickness of the PT film determined by the model is greater than the experimental one [5]. A possible explanation for the discrepancy arises from the
fact that theoretical simulation of the free-standing film does not reproduce appropriately the experimental situation of the film deposited on the substrate. Although we previously considered the effect of the substrate fixing the in-plane lattice parameter of the film, other effects were not simulated explicitly. For example, the film-substrate interaction was not taken into account. The presence of a substrate modifies the boundary condition on one of the film surfaces and, as consequence; it could produce significant effects on the ferroelectric properties of the film. We have simulated the presence of a SrTiO$_3$ substrate by a shell model. The model for SrTiO$_3$ (ST) was obtained from the PT model. The difference between the two lies in the different A–Ti and A–O interactions and the different polarizability parameters for Sr and Pb. The input data to develop the ST model correspond to LDA results of the energy as function of volume and phonon frequencies. As result the ST model displays a cubic lattice parameter $a = 3.860$ Å that agrees with the LDA value of 3.861 Å. On the other hand, the ferroelectric mode is stable (77 cm$^{-1}$) at the theoretical volume and unstable (1113 cm$^{-1}$) at the experimental one, in agreement with the LDA behavior (68 cm$^{-1}$ and 944 cm$^{-1}$ at both volumes respectively). In addition, the cubic structure presents an antiferrodistortive instability that leads to a small rotation of the oxygen octahedra.

The properties of PT films deposited on the ST substrate were investigated using a semi-infinite crystal geometry, where the substrate is divided in two regions. The first region corresponds to the part of the substrate near the PT film, here the atoms can relax without

**Figure 3.** Top view of the antiferrodistortive surface reconstruction. The arrows indicates the displacements of Pb atoms that produce an average (110) in-plane polarization.
any restriction. A thickness of 10 cells was taken for this region, which is thick enough to not produce significant changes in the final results. The second region corresponds to the part of the substrate which is away from the film, and it simulates the interior of the substrate non disturbed by the presence of the interface. Atoms in this region are fixed to the ideal cubic positions. The interface between both compounds consists of a TiO plane common to PT and ST. Relaxed zero-temperature structures were determined as in the case of the isolated slab.

The polarization perpendicular to the surface of the film deposited on the ST substrate is qualitatively similar to the free-standing case. That is, polar domains are formed, and the polarization in each domain grows from the interfaces (the free surface and the film-substrate interface) towards the interior of the film. However, the values of $P_z$ in the film on the substrate are substantially larger than in the slab. Figure 4 shows the polarization profile of a chain perpendicular to the surface of a film-substrate system with 5 PbO planes, which corresponds to a 5-cell thick film since we considered that the cell centered at the interface ($z = 0$), limited by the last PbO plane and the first SrO, belongs to the film. In the figure, negative values of $z$ indicate the PT film while positive values indicate the ST substrate. The large increment of the film polarization indicates the importance of selecting appropriate boundary conditions to simulate the experimental set up. At the interface, for example, $P_z = 1.2 \, \mu\text{C/cm}^2$ in the case of the free surface while $P_z = 20 \, \mu\text{C/cm}^2$ when the substrate is present, and $P_z$ at the inner cell varies from 18 $\mu\text{C/cm}^2$ to 41 $\mu\text{C/cm}^2$ respectively. The effect of the boundary condition is also reflected in the substrate, where a induced polarization is developed in the paraelectric compound.

It is clear that the ST substrate favors the ferroelectricity of the PT film, so it is expected that films thinner than 5-cell thick still present ferroelectric behavior. Simulations to determine the critical thickness of the PT film deposited on ST substrate are in progress.

Figure 4. Out-of-plane polarization profile for a chain perpendicular to the surface in a film-substrate system with 5 PbO planes.
Conclusions

We have shown that an interatomic potential approach with parameters adjusted from first-principles results is able to reproduce the observed tetragonal ground-state of bulk PbTiO₃ and the AFD structure of the surface. In ultrathin films, there is a remarkable decrease in tetragonality that leads to a phase with non-vanishing in-plane polarization. The model predicts a critical thickness ($d_c$) of four unit-cells for ferroelectricity in a free-standing slab. However, the presence of a ST substrate enhances the polarization of the film, and it could reduce $d_c$.

References

