ATOMIC-LEVEL SIMULATION OF FERROELECTRICITY IN BaTiO$_3$ ULTRATHIN FILMS

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The question of how the ferroelectric phase transitions of bulk BaTiO$_3$ are modified in ultrathin films is investigated using an atomic-level simulation approach based on a model with parameters obtained from first-principles calculations. This model correctly reproduces the ferroelectric phase behavior of the bulk material and its static surface properties. The phase transition sequence in the film is investigated through molecular dynamics simulations. The effect on ferroelectricity produced by the film-substrate lattice mismatch is investigated by simulating strained epitaxial films grown on cubic substrates.

Keywords: thin films, domain structure, atomistic modeling

Ferroelectric (FE) thin films can display a wide range of dielectric, ferroelectric, piezoelectric, electrostrictive, and pyroelectric properties. The potential utilization of these properties in a new generation of devices has driven the large amount of research worldwide on the synthesis and characterization of FE thin films. The determination of the minimum film thickness (critical thickness) with switching polarizations in ABO$_3$ ferroelectric perovskites is a crucial point for the development of new devices, such as the fabrication of high-density Non-Volatile Random Access Memories [1]. Recently, high quality films of PZT grown on Nb-doped (001) SrTiO$_3$ single-crystal substrates have been observed to exhibit ferroelectricity down to a thickness of 4 nm [2]. However, what is the thinnest ferroelectric layer that can still yield stable polarization remains as an
unsolved question.

Although Landau-Devonshire type theories play an important role in the understanding of FE thin film properties [3, 4, 5, 6], these approaches are based on the continuous medium approximation and, therefore, they are not applicable for ultrathin films where an accurate atomic-level description is necessary. The indispensability of an atomic-level approach was borne out by recent first-principles calculations on BaTiO₃ slabs [7, 8], which demonstrated that the surface relaxation energies are many times larger than the bulk ferroelectric well depth, which would indicate that the surface relaxation is capable of acting as a strong perturbation on the ferroelectric order. Recently, an effective hamiltonian approach [9] showed that PbTiO₃ films as thin as three unit cells exhibit a perpendicularly polarized ground state, with significant enhancement of the polarization at the surface. However, this model does not include surface relaxation effects.

In this work we investigate the ferroelectric phase transitions and surface effects of BaTiO₃ ultrathin films using atomic-level simulations. Since the epitaxial effect can strongly influence ferroelectricity, we also investigate the strain effect produced by the film-substrate misfit. The variation of the polarization as a function of depth into the ferroelectric film and the critical thickness are determined.

For the simulations we used an atomistic model for BaTiO₃ developed by mapping first-principles underlying potential surfaces (details of the modelling approach are presented elsewhere [10]). This model describes accurately several bulk properties of BaTiO₃, such as energy instabilities, lattice dynamics, phase transition sequence, structural parameters, thermal expansivity, etc [10], in good agreement with first-principles and experimental data. The drawback is, however, that the theoretically determined transition temperatures tend to be too small compared with experiment. Later on, we showed that this model, developed for the bulk material, proves also successful for describing static surface effects [11], such as surface energy, atomic relaxation patterns and relaxation energies which are in very good agreement with "state of the art" first-principles
Figure 1: Phase diagram of the BaTiO₃ ultrathin film.

calculations [7, 8].

In the present study we chose a stress-free (001) TiO₂-terminated slab of 28Å width to perform constant-pressure molecular dynamics (MD) simulations. Periodic boundary conditions over 6x6x7.5 primitive cells (1368 atoms) were considered. To minimize the interaction between periodic images, a vacuum region of 20Å separates the periodic slabs. We tested the sensibility of the results with respect to the vacuum region size: by increasing the vacuum gap by 20%, the resulting polarization profiles changed by less than 0.5%.

In Fig. 1 we show the three components of the mean polarization of the stress-free slab obtained by MD simulations as a function of temperature. Pₓ and Pᵧ are the polarization components parallel to the slab surface, while Pₜ is the one perpendicular to the surface. While Pₜ is zero at all temperatures, the behavior of the other two components indicates a sequence of transitions which leads to the appearance of ferroelectric phases with in-plane polarization.

In order to clarify the description we have divided the phase diagram, shown in Fig. 1, into four temperature ranges. At high temperatures (stage A), the polarization components are all very close to zero indicating a paraelectric phase. As the system is cooled down (stage B), Pₓ acquires a value clearly different from zero while Pᵧ ≈ 0, and the structure presents
a considerable in-plane strain. When the temperature is further reduced to stage C the two mentioned features of stage B are magnified. In both stages, B and C, the slab has a net polarization along the (100) direction. Finally, in stage D, $P_x \approx P_y$ different from zero, and the slab has a net (110) polarization.

The cell-by-cell in-plane polarization profiles across the slab are shown in Fig. 2. All profiles show increments of the local polarization in the two unit cells nearest to the surface, at both sides of the slab. This surface polarization enhancement arises from the fact that we are simulating a TiO$_2$-terminated slab. On the contrary, we find a decrease of the surface polarization for a BaO-terminated slab. So, the in-plane polarization behavior near the surface depends on the surface termination, a fact which is in agreement with static surface properties obtained from first-principles calculations [8].

The local polarizations of the inner cells display a rather flat plateau. The magnitude of the electric polarization for these cells in stages C and D, and the transition temperatures coincide with the bulk results. These observations lead to the conclusion that ferroelectric phase transitions involving in-plane electric polarization are practically unperturbed by the presence of the surface. One important difference with the bulk is, however, the appearance of a surface phase transition at stage B, where the
two unit cells nearest to the surface are polarized, while the inner cells are not (see Fig. 2). So, in this temperature range, the slab is composed by a ferroelectric surface layer on both sides of a paraelectric bulk material.

To understand the nature of the microscopic dynamics leading to the presence of this ferroelectric surface layer, we analyzed, in the high temperature paraelectric phase, the time evolution of local polarizations for a surface and an inner cell. For both we observe in Fig. 3 that fast oscillations around finite polarization values coexist with much slower polarization reversals. Therefore, as in the bulk material [12], a relaxational slowing-down process is responsible for the appearance of the in-plane polarized phase in the film. Since the relaxation time of the surface cells is \( \approx 10 \) times larger than the one for the inner cells, the polarization “freezes” first in the surface, in such a way that the surface orders at a higher temperature than the interior of the film. We observed that local polarizations at the surface correlate forming chain-like precursor domains, as it was observed for the bulk material [12].

Although the mean polarization perpendicular to the surface is zero at all temperatures, it is interesting to analyze its profile across the slab which is presented in Fig. 4 (see the case \( \eta = 0 \)). It is clear that the two unit cells nearest to the surface are polarized, while the inner cells are
not. The local polarization of the surface cells, at both sides of the slab, are pointing inwards towards the bulk, so the net polarization vanishes and a FE state has not been stabilized. This inward direction of the local surface polarization is just a consequence of the surface atomic relaxation pattern [11]. This surface relaxation could also lead to a surface tension effect, i.e. as a consequence of the inwards movement of the surface layers, the interior of the slab could be denser than the bulk material inhibiting ferroelectricity. To address this point, we have measured the interlayer distance between two consecutive TiO$_2$ planes at the surface and in the interior of the slab. While this distance is 3.89 Å at the surface, indicating that the surface layers contract substantially, it reaches the value of 3.99 Å at only two unit cells from the surface. So, the interior of the slab is not considerably denser than the bulk material.

An important factor which can influence ferroelectricity is the effect produced by the lattice mismatch between a given substrate and the ultrathin film [5]. Experimental data on BaTiO$_3$ films deposited on SrTiO$_3$ substrates [13] showed a shift of $T_c$ towards higher temperatures. They conclude that this effect should be due to epitaxial strain, showing that the lattice parameter $a$ of a 10 ML-thick film is exactly the same as that of the substrate. So, if the substrate is sufficiently thick, the in-plane strains of the film at the interface are totally controled by the thick substrate, which produces a two dimensional clamping and straining of the film. We assume that these internal elastic fields are homogeneous, so the 2D clamping holds throughout the ultrathin film. Considering a commensurate interface between a cubic substrate and the film, we can define the misfit strain as $\eta = (b - a)/b$, where $b$ is the substrate lattice constant and $a$ is the lattice parameter of the stress-free film. We show in Fig. 4 the $P_2(z)$ profile (T=0K) of a randomly chosen chain perpendicular to the slab surface for different misfit strains. It is clear from the figure that an out-of-plane orientation of polarization is stabilized by the negative strains. On the other hand, all the profiles display a considerable reduction of the polarization at the surface cells, indicating that the surface produces a weakening of ferroelectricity, in agreement with a
Figure 4: Cell-by-cell out-of-plane polarization profiles of a randomly chosen chain perpendicular to the slab surface for different misfit strains ($\eta$) at $T=0$K.

Although the individual chains shown in Fig.4 display a perpendicular nonvanishing polarization, the net out-of-plane polarization of the slab is zero due to the development of polarized domains, as it is shown in Figure 5 for $\eta = -2.5\%$. In this case the ground state is a c-phase where $P_x = P_y = 0$, so $180^\circ$ polarized domains are developed. However, when the strain is lower, the net in-plane polarization is not zero and the domain configuration is more complex. We can describe the behavior of the polarization vector under strain in the following way. The stress-free film is polarized only along the (110) direction. When the film is strained, the polarization vector start rotating towards the $z$ axes. In this case a domain configuration is developed because the polarization vector rotates towards the positive $z$ axis in one domain, while for the other it rotates in the opposite direction. Finally, at a given value of $\eta$ the polarization vector of each domain lies along $z$ axis, giving arise to $180^\circ$ polarized domains. In all cases the domain wall is not charged. So, we demonstrate that ferroelectricity with domain structure is indeed stable in ultrathin films, in disagreement with an earlier phenomenological result [3].
Figure 5: Top view of the out-of-plane polarization pattern for the case \( \eta = -2.5\% \). The symbols \( \times \) or \( \cdot \) on each chain denote opposite polarization directions.

It is known that domains are favored by the reduction of the depolarizing field energy in spite of the increased surface energy of the domain walls. So, if electrodes are deposited on the film surfaces cancelling out the depolarizing field, a single-domain structure is expected to become more stable.

It is easy to visualize from Fig.5 that the antiparallel domain configuration is of stripe type. It is important to remark, however, that the equilibrium value of the domain width can not be determined from the present simulations, since this magnitude is constrained by the dimension of the simulation cell. In spite of that, we are able to provide another valuable microscopic information: the 180° domain wall is centered on a Ba-O plane, i.e. the atomic displacements have odd symmetry across (and vanish on) the BaO plane, which indicates that the domain boundary is indeed very sharp, its width being of approximately one lattice constant, in agreement with domain walls simulations in bulk [14].

We have chosen the case \( \eta = -2.5\% \), which model an ultrathin film of \( \text{BaTiO}_3 \) deposited on a thick substrate of \( \text{SrTiO}_3 \), to perform finite temperature simulations. In this case, as was already mentioned, the ground state is a c-phase. The para-ferroelectric transition temperature obtained
by the MD simulations is ≈ 240K (this was determined by monitoring the polarization of each domain), which lies above that of stress-free bulk BaTiO$_3$ ($T_c=190K$). To find out the minimum film thickness ($d_c$) with stable out-of-plane polarization we have done simulations on slabs of different widths. From this study we predict $d_c = 20\AA$. Although thinner films also display polarized profiles at $T=0K$, their polarizations are washed out at finite temperature.

In conclusion, we have shown that ferroelectric phase transitions involving in-plane electric polarization are unperturbed by the presence of the surface in ultrathin films. However, surface atomic relaxations act as a strong perturbation on the ferroelectric order perpendicular to the surface. In spite of that, a strain induced polydomain ferroelectric state with an out-of-plane orientation of polarization is stabilized, in films as thin as 20 Å. $P_z(z)$, which is a key information for Landau-Devonshire type theories, displays a weakening of the polarization at the surface. Finally, we point out that the development of polarized domains in the film constitutes a promising starting point for a further investigation on the microscopic mechanism for the poling and polarization switching processes when an external electric field is applied. Moreover, the present atomistic approach is indeed very appropriate for the investigation of the effects of geometries on ferroelectric nano-capacitors, which are still largely unknown and are of extreme technological relevance.

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