

Surface polarization, rumpling, and domain ordering of strained ultrathin BaTiO₃(001) films with in-plane and out-of-plane polarization

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At the surface of a ferroelectric material, out-of-plane polarization leaves non-zero surface charge which induces a depolarizing field. Complex screening mechanisms can take place to suppress this field. On the one hand, electrochemical surface charge compensation such as external adsorbates or internal defects can suppress the depolarizing field, stabilizing the polarization. On the other hand, due to the long-range character of the dipole-dipole interactions, the ferroelectric polarization can order into domains of opposite polarization such that the resulting surface charge of each domain screens the depolarizing field of the neighboring domains.

Ultrathin free-standing films (thickness ≈ 1.6 nm – 9 layers) of BaTiO₃ with in- and out-of-plane polarization are studied by first-principles calculations [1], with the ABINIT code, by building tetragonal supercells exhibiting alternating up (P^+) and down (P^-) polarization oriented along [001] (Fig. 1a, c phase) [2] or orthorhombic supercells with polarization oriented along [110] (Fig. 1a, aa phase) [3,4]. The substrate misfit strain is modelled by varying the in-plane lattice constant a within a compressive to tensile strain range of ≈ -3.8 to $\approx +1.3\%$ with respect to the LDA lattice constant of cubic BaTiO₃ ($a = 3.949$ Å). Different supercell widths ($N = 2, 4$ or 6 unit cells along y) allow to investigate the multiplicity of the polarization domains in the c phase under periodic boundary conditions. Ferroelectric c and aa phases are compared to the paraelectric tetragonal centrosymmetric p phase. It has been carefully checked that the results are perfectly converged with the vacuum thickness.

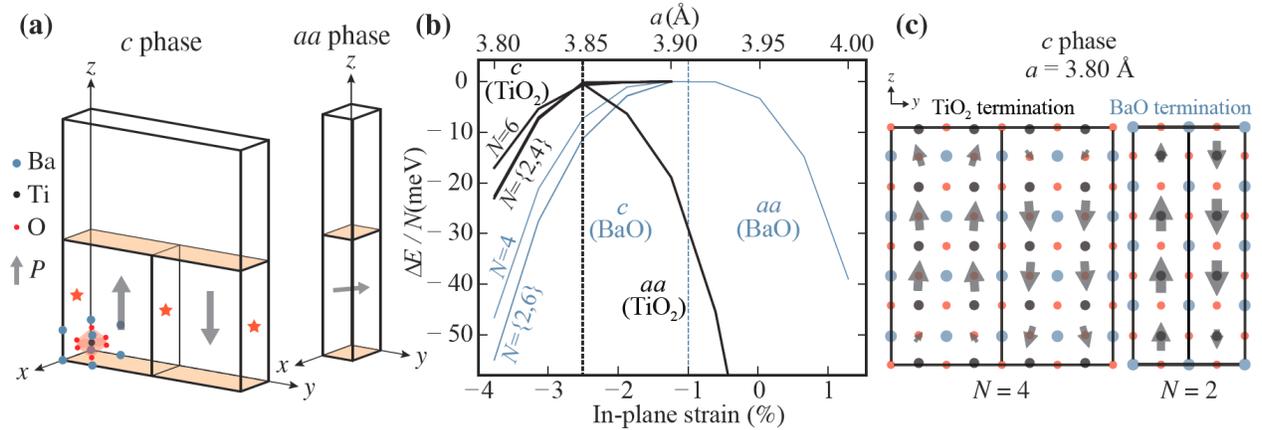


Figure 1. (a) (left) Out-of-plane polarized c phase and (right) in-plane polarized aa phase configurations. (b) Energy (meV) of the c and aa phase relative to that of the p phase as a function of misfit strain. (c) Polarization pattern in the fundamental state in c phase for $a = 3.80$ Å for the (left) TiO₂-terminated and (right) BaO-terminated film.

Out-of-plane polarization (c phase) is stabilized under compressive strain whereas in-plane polarization is stabilized under tensile strain, although the strain at the transition between c and aa depends on the surface termination ($\approx -2.5\%$ and $\approx -0.5\%$ for TiO₂ and BaO termination, respectively) (Fig. 1b). This demonstrates a strong surface effect on the value of the lattice constant of the phase transition when compared to that of the bulk (at 0%). The structures of lowest total energy are found with domains 1 to 2 unit cells wide for the TiO₂ termination (Fig. 1c, left) and with domains of 1 unit cell wide for the BaO termination (Fig. 1c, right). Ferroelectric induced displacements at the surface in c phase are found to

modify the natural surface rumpling in the corresponding p phase, with oxygen atoms outwards and cations inwards in all cases.

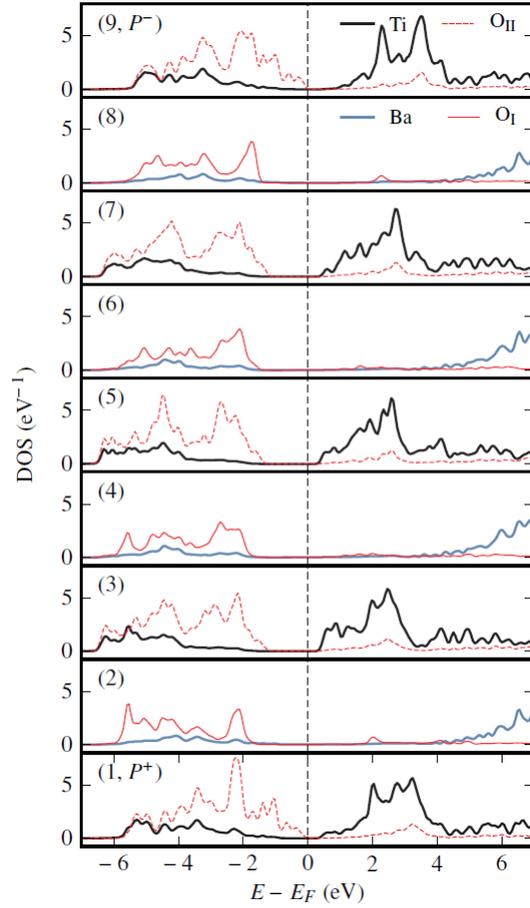


Figure 2. Electronic density of states of the c phase projected on each of the nine atomic layers of one domain of the TiO_2 -terminated film. $N = 6$, $a = 3.80 \text{ \AA}$.

Electronic density of states (DOS) calculations confirmed the presence of polarization dependent surface states (Fig. 2) that depend on the surface termination. All the surfaces studied are found to be insulating, for both c and aa phases, even though a strong reduction in the Kohn-Sham band gap (by $\approx 1 \text{ eV}$) is predicted for the TiO_2 surface termination in the c phase.

Atom-projected density of states on the (001) atomic planes of a single domain in the case of the TiO_2 termination reveals the combined effects of a microscopic and a macroscopic potential due to the presence of the surface.

Surface states are observed at the top of the valence band of both P^+ and P^- (atomic plane numbers 1 and 9, respectively). A clear effect of band bending can also be observed by following the band edges, mostly produced by a difference in the Madelung potential between the oxygen sites at the surface and in the bulk. This microscopic potential is higher in the c phase than in the aa phase as a consequence of the ferroelectric distortions.

A potential difference of $\approx 0.2 \text{ eV}$ between the top of the valence band at P^+ and P^- in the c phase is assigned to imperfect screening of the depolarizing field. This is evidenced by the observation of a residual macroscopic potential computed as a double average over (001) atomic planes and then along [001]. Nevertheless, the microscopic Madelung potential at the surface is predicted to play a more prominent role in modifications of the surface electronic structure at this ultrathin film thickness.

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