

# Stabilization of highly polarized PbTiO<sub>3</sub> nanoscale capacitors due to in-plane symmetry breaking at the interface

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Stable ferroelectric (FE) phases in nanometer-thick films would enable ultra-high density and fast FE field effect transistors (FeFETs), and the stability of ferroelectricity in ultrathin films has been under intense theoretical and experimental investigation. Here we predict, using density functional theory calculations, that the low-energy epitaxial PbTiO<sub>3</sub> (001)/Pt interface strengthens the electrode-oxide bonds by breaking in-plane symmetry and stabilizes a ground state with enhanced polarization in subnanometer oxide films, with no critical-size limit. Additionally, we show that such enhancement is related to large work function differences between the  $P^-$  and  $P^+$  PbTiO<sub>3</sub> surfaces, which gives rise to a net polarizing field in the oxide.

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## I. INTRODUCTION

Bulk ferroelectricity has multiple applications in technology, from actuators and sensors to catalysis and information storage.<sup>1-3</sup> In particular, due to the convenient control of polarization ( $P$ ) orientation with applied electric field, ferroelectricity can be useful in nonvolatile memory and other information processing devices. However, in these systems, the small thickness of the film gives rise to a depolarizing field ( $\varepsilon_{\text{dep}}$ ) caused by uncompensated surface charges.<sup>4</sup> In the case when the top and bottom electrodes are similar, and the potential drop in the material is smaller than the band gap,  $\varepsilon_{\text{dep}}$  is given by

$$\varepsilon_{\text{dep}} = -2 \frac{\lambda_{\text{eff}}}{d \epsilon_0} P \quad (1)$$

where  $\lambda_{\text{eff}}$  is the effective screening length of the system, and  $d$  and  $P$  are the thickness and polarization of the ferroelectric (FE) film, respectively.<sup>5</sup> The  $\varepsilon_{\text{dep}}$  becomes stronger as the thickness of the sample is decreased and can suppress polarization entirely. Optimal ways to overcome this deleterious effect and improve FE stability of films have been the focus of intense theoretical and experimental study.<sup>4-20</sup> It has been shown that the details of the chemical bonding at the interface play a critical role in determining the effectiveness of the screening and properties of films such as interface-induced polarization, ease of polarization switching, and FE stability in perovskite-based capacitors.<sup>18,20</sup> In addition, charge compensation by adsorbed molecules is also highly effective; it has been demonstrated to govern the magnitude and sign of the surface potential on FE surfaces and to stabilize ferroelectricity in ultrathin films and nanowires,<sup>12,17,21,22</sup> providing further evidence for the important role played by interfacial chemical bonding in determining FE stability.

Consideration of an idealized capacitor device consisting of a perovskite oxide insulator sandwiched between metal electrodes<sup>7</sup> demonstrates that symmetry-breaking polarization creates different chemical interactions at the positive and negative oxide/electrode interfaces. This gives rise to a difference in the work function at the two surfaces of the FE slab, which is of crucial importance for the screening of

the polarization surface charge.<sup>13,23</sup> However, while previous theoretical studies have examined the effects of interface interactions, they have primarily considered changes in the oxide structure perpendicular to the interface. Consequently, little is currently known about how atomic scale rearrangements parallel to the interface, for example, polarization-induced surface reconstructions or shifts of the metal layer with respect to the underlying oxide registry, can affect the behavior of FE capacitors. In this work, we use density functional theory calculations to elucidate the role of the latter in the classic Pt/PbTiO<sub>3</sub>/Pt metal/oxide nanocapacitors, exploring different registries of Pt atoms on the PbTiO<sub>3</sub> surface and optimizing all degrees of freedom. We find that the lowest-energy interface structure deviates significantly from that considered in previous works, exhibiting a net polarizing field that increases  $P$  with decreasing film thickness, in contrast to the expected behavior. Our analysis demonstrates that although the lateral relaxation reduces  $P$  enhancement with respect to the in-plane symmetric structures, it plays a vital role by creating more favorable bonding at the interface. This lowers the energy of the polarized state relative to the nonpolar state, making it the global minimum on the potential energy surface. These two factors (polarization enhancement and favorable bonding) are both important to attain globally stable FE polarization in an oxide thin film.

## II. METHODOLOGY

We performed density functional theory (DFT) calculations using the PBEsol exchange-correlation functional<sup>24</sup> as implemented in the QUANTUM ESPRESSO<sup>25</sup> DFT code. The PBEsol functional was shown by Perdew and collaborators to describe solids and surfaces accurately, and it recently has been used successfully to study PbTiO<sub>3</sub> bulk and thin films.<sup>26</sup>

A supercell slab method was used to describe the different FE thin film capacitors. The supercells consist of a PbTiO<sub>3</sub> oxide region sandwiched by Pt electrodes, with approximately 18 Å of vacuum separating images. The atoms were represented by norm-conserving pseudopotentials<sup>27</sup> generated using the code OPIUM<sup>28</sup> with a plane-wave cutoff

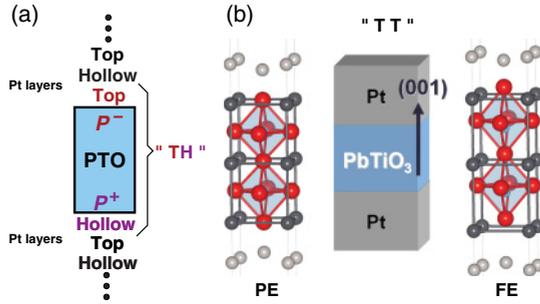


FIG. 1. (Color online) Nomenclature convention for the nanocapacitor systems. Names are based on the atomic arrangements at the interfaces, and Pt layers are assumed to follow FCC (001) stacking. (a) Schematic diagram and name of one of the interfaces studied here. (b) Model of relaxed TT capacitors in the PE and FE state. For clarity, only the interfacial Pt-electrode atoms are shown. Color labeling (online version): Pb = dark gray, Ti = cyan, O = red, and Pt = light gray.

of 50 Ry. We performed the structural relaxation at the theoretical in-plane lattice constant of tetragonal PbTiO<sub>3</sub>, attaining an optimized structure when forces are lower than 10 meV/Å on each atom. In addition to upper and lower interfaces with equivalent registries, we studied inequivalent registries of Pt electrodes on (001) PbTiO<sub>3</sub> FE surfaces. Figures depicting the different capacitor arrangements were created using the VESTA software.<sup>29</sup> In the presence of symmetry-breaking polarization, we consider four possible interfaces: Top/ $P^- \dots P^+$ /Top; Top/ $P^- \dots P^+$ /Hollow; Hollow/ $P^- \dots P^+$ /Top; and Hollow/ $P^- \dots P^+$ /Hollow (hereafter labeled as TT, TH, HT, and HH, respectively). Figure 1 depicts the naming scheme we use for the studied systems. Here, Top refers to registries in which the Pt atoms are directly above the oxide surface atoms (Pb and O), while Pt atoms in the Hollow registry are over unoccupied lattice sites on the surface.

We assess the stability of each of the different arrangements by comparing the energy per PbTiO<sub>3</sub> unit cell of a given polar structure with the paraelectric (PE) state in the TT registry

$$\Delta E = \frac{(E_{FE} - E_{PE^{TT}})}{N_{\text{PbTiO}_3 \text{ unit-cell}}}. \quad (2)$$

Analysis of the density of states (DOS) per PTO layer in the capacitors, Fig. 2, shows that the metallic behavior is localized at the interface, with exponential decay of the metallic states within the oxide region. Therefore, metallic layers at the interface are attributed to the chemical bonding between atoms (e.g., localized charge transfer at the interfaces); this effect is confined to the interface layers, and the bulk PTO layers remain insulating. This is in agreement with previous studies of other AO/Pt interfaces,<sup>13,14,18,23,26</sup> and it means that our system exhibits proper band alignment of the metal and oxide.<sup>30</sup> Also, supporting this conclusion, the cation displacements with respect to oxygen atoms in each layer [rumplings, Fig. 2(c)] show uniform enhancement of the polarization throughout the oxide film<sup>23,30</sup> for all the capacitor systems.

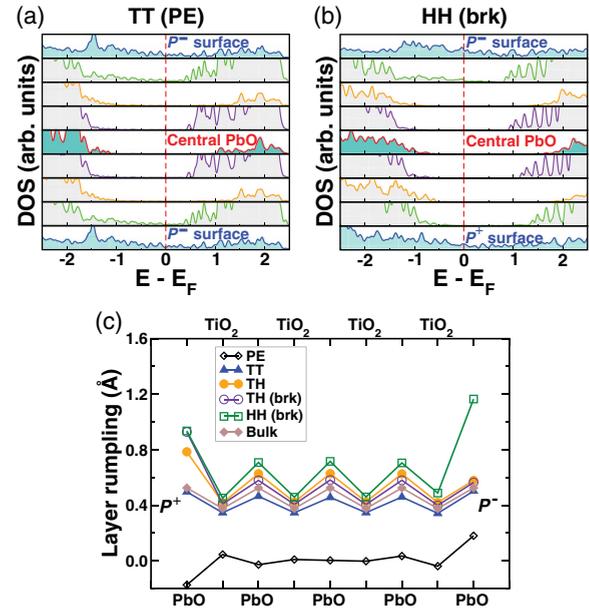


FIG. 2. (Color online) Density of states (DOS) in each oxide layer for the capacitor systems. The interfaces and central layer are labeled in the figure. Shown here are the DOS for the (a) TT-PE and (b) HH<sub>brk</sub>, four unit-cell PTO capacitors, note the local insulating character of the inner layers of the oxide film. (c) Average values of the layer rumpling [cation(z)-oxygen(z) displacement in the z axis].

### III. RESULTS AND DISCUSSIONS

#### A. Inequivalent Pt electrodes under the in-plane symmetry constraint

We first examined the structures and energetics of the various Pt/PbTiO<sub>3</sub>/Pt capacitors under the constraint of bulklike lateral ionic coordinates. For paraelectric (PE) PbTiO<sub>3</sub>, the TT interface registry that was used in previous theoretical studies is energetically preferred. For polar PbTiO<sub>3</sub> films, however, the polarization of the oxide influences the energetics of Pt on the (001) surfaces so that the top sites are preferred for the  $P^-$  surface while the hollow sites are preferred on the  $P^+$  surface. We find that epitaxial Pt electrodes in the TH registry stabilize a polar PbTiO<sub>3</sub> structure relative to the PE state. This is in contrast with previous studies<sup>14</sup> that found that at the theoretical lattice constant, the PE state is more stable for PbTiO<sub>3</sub> films less than six unit-cells thick. The HH and HT structures are least favorable and are metastable local minima with high energy. The strong enhancement of FE polarization in one particular direction (TH) while disfavoring the opposite polarization (HT), is analogous to the findings of Umeno *et al.*<sup>19</sup> for capacitors with an asymmetric combination of electrodes, SrRuO<sub>3</sub>/PbTiO<sub>3</sub>/Pt. Since our system has compositionally equivalent electrodes, our results emphasize the importance of the local atomic rearrangement at the interface.

Analysis of the structural differences between the T and H interfaces at the  $P^+$  and  $P^-$  surfaces sheds light on the Pt/PbTiO<sub>3</sub> interface energetics. In the T registry, one half of the Pt atoms sit on top of the Pb atoms and one half are on top of the O atoms. For the  $P^+$  surface, the Pb atoms lie higher than the surface O atoms, which relax inward. This makes

the Pt-Pb distances short and Pt-O distances long, indicating weak Pt-O bonds. Thus, for the  $\text{Top}/P^+$  case, one half of the Pt atoms are only weakly bound to the oxide surface. In contrast, for the H registry each Pt atom has two Pb and two O nearest neighbors. Consequently in the  $\text{H}/P^+$  case all Pt atoms can form strong Pt-Pb bonds, making this interface preferred over  $\text{T}/P^+$  and stabilizing the TH relative to the TT and PE (TT) capacitors.

The opposite preference is found for the  $P^-$  surface. For the  $\text{T}/P^-$  interface, the positively charged Pt atoms that form ionic bonds with surface O are located far away from the positively charged Pb atoms, minimizing the electrostatic repulsion. For the  $\text{H}/P^-$  surface, the short bonds between Pt and O would bring the positively charged Pt atoms close to the Pb cations and give rise to a strong electrostatic repulsion. Instead, the O atoms are extracted from the  $\text{PbTiO}_3$  surface and move up close to the Pt layer. As we show later, this is a key contribution for  $P$  enhancement in films with respect to the bulk. However, the breaking of the O-Ti and O-Pb bonds raises the energy of the  $\text{H}/P^-$  configuration, destabilizing HH relative to the TH and TT configurations.

### B. Fully relaxed broken symmetry interfaces

Interestingly, our calculations show that relaxation of all degrees of freedom for the nanocapacitors leads to an in-plane symmetry breaking at the interfaces, resulting in a large stabilization of the otherwise metastable HH capacitor. Figures 3(b) and 3(d) depict the lowest-energy, broken-symmetry structures along with their in-plane symmetry-preserved counterparts. We labeled the two lower-energy structures with broken in-plane symmetry as  $\text{TH}_{\text{brk}}$  and  $\text{HH}_{\text{brk}}$ . Due to in-plane relaxation, the high-energy  $\text{HH}_{\text{sym}}$  structure is stabilized by 250 meV/ $\text{PbTiO}_3$ -UC as it evolves into  $\text{HH}_{\text{brk}}$ , which is the lowest-energy arrangement, approximately 150 meV/ $\text{PbTiO}_3$ -UC more stable than the paraelectric TT capacitor. In contrast, the energy of the TH arrangement is

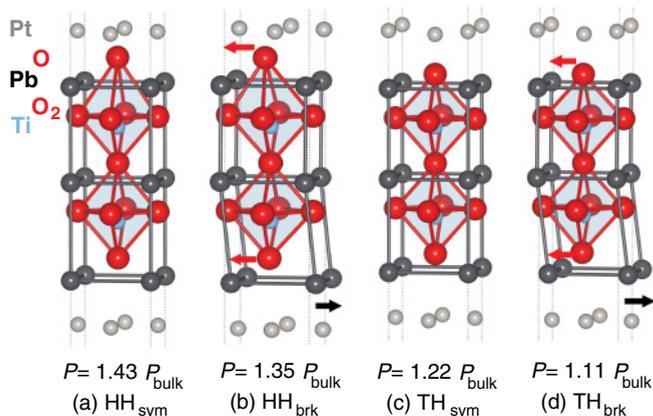


FIG. 3. (Color online) Fully relaxed two-unit cell  $\text{Pt}/\text{PbTiO}_3/\text{Pt}$  nanocapacitors. (a)  $\text{HH}_{\text{sym}}$ , (b)  $\text{HH}_{\text{brk}}$ , (c)  $\text{TH}_{\text{sym}}$ , and (d)  $\text{TH}_{\text{brk}}$ , only the interfacial Pt atoms are shown for clarity. The predominant structural changes are the displacement of the atoms at the  $P^+$  interface for TH, and at the  $P^-$  interface for HH, as indicated by arrows. The estimated polarization with respect to that of bulk is shown for each configuration.

only lowered by approximately 10 meV/ $\text{PbTiO}_3$ -UC when in-plane symmetry breaking is allowed (Table I).

Our findings imply that the TT in-plane-constrained structure previously considered as a model of the oxide/metal electrode interface is only a saddle point and not a local minimum of the full potential energy surface.

Comparison of the potential difference and structural features of the symmetric and asymmetric arrangements shows that the oxygen tilting occurring at the  $P^-$  interface makes the largest impact in the stabilization of broken-symmetry interfaces. For the  $P^-$  surface, the interfacial oxygen atoms move by  $\approx 0.3 \text{ \AA}$ , making short  $2.0 \text{ \AA}$  bonds with one of their Pt neighbors, while the oxygen atoms in the  $\text{TiO}_2$  layer stay nearly in their symmetric position. This atomic rearrangement favors the stability of the capacitor, as it creates stronger Pt-O bonds and compensates for the weakened bonds between the surface O and Pb atoms. On the other side of the film, the Pb atoms on the  $P^+$  surface move laterally in the  $xy$ -plane, decreasing the Pb-O distance by approximately  $0.3 \text{ \AA}$ , in conjunction with a small oxygen tilt ( $\approx 2.5^\circ$ ).

### C. Net polarizing field and Polarization enhancement in PTO films

To study the screening in the nanocapacitor, we decompose the system into its oxide and electrode components.<sup>31</sup> Analysis of the planar-averaged electronic charge density normal to the surface ( $\rho(z) = \int dx \int dy \rho(x, y, z) / A_{xy}$ , where  $A_{xy}$  is the cross-section area of the cell)<sup>6,32</sup> for the capacitors (Fig. 4) shows that it is essentially just a sum of the charge densities of the bare oxide and Pt electrode fixed in their respective capacitor geometries. Therefore, the screening in the nanocapacitor can be modeled as the metal electrode screening of the electrostatic potential profile of the bare oxide in the nanocapacitor geometry.

Analysis of the  $\text{PbTiO}_3$  cation displacements shows that  $P$  values for the nanocapacitors previously presented in Fig. 3 are greater than those of bulk  $\text{PbTiO}_3$ .<sup>33</sup> This is in contrast with the  $\text{TT}_{\text{sym}}$  structure, for which  $P$  is reduced compared to the bulk value. A comparison of HH and TH  $P$  magnitudes shows that  $P_{\text{HH}} > P_{\text{TH}}$  for both the in-plane constrained and the broken symmetry structures.

The enhancement of  $P$  above the bulk value suggests the presence of a polarizing field. To confirm this and to understand the origin of the enhancement, we plot the macroscopic-averaged electrostatic potential of each capacitor and compare it to the potential of their corresponding bare  $\text{PbTiO}_3$  film (removing all the Pt atoms from the calculation and freezing the  $\text{PbTiO}_3$  ions in the relaxed geometry of the  $\text{Pt}/\text{PbTiO}_3/\text{Pt}$  heterostructure). The electrostatic potential profiles clearly show that the enhanced  $P$  values of the nanocapacitors are due to a net polarizing field in the film, as evidenced by the change in the sign of the slope in the presence of electrodes with respect to the frozen freestanding film (Fig. 5). For instance, in the case of the  $\text{TT}_{\text{sym}}$  geometry the net remnant field is depolarizing (the frozen bare oxide and the capacitor have the same sign of the slope in the electrostatic potential); although drastically reduced to  $\approx -10 \text{ mV/\AA}$ , it is not eliminated entirely. On the other hand, for  $\text{HH}_{\text{brk}}$ , for example, we find

TABLE I. Energetics and electrostatic potential data. Energy differences per unit cell with respect to the four unit-cell PE-PTO, 5TT5 capacitor.  $E$  fields (mV/Å) are calculated from DFT and our modified Thomas-Fermi screening model. Potential drops (mV),  $\Delta_1$ , and  $\Delta_2$ , are obtained from DFT for a frozen freestanding film. The field inside the FE region in the capacitor system is strongly influenced by  $\Delta_2 - \Delta_1$ : The larger this difference is, the more positive the net  $\epsilon_{FE}$  field in the capacitor is.

System	$\Delta E$ (meV/UC)	$\epsilon_{FE}$ Field (mV/Å)			$\Delta$ (mV)		$\lambda$ (Å)
		Free slab	Thomas-Fermi	DFT	$\Delta_1$	$\Delta_2$	
TT <sub>sym</sub>	-50.0	-123.8	-10.2	-11.6	-1680	-2740	0.040
TH <sub>sym</sub>	-129.0	-105.4	15.4	23.8	-1470	-2750	0.064
TH <sub>brk</sub>	-136.0	-104.6	11.5	17.8	-1390	-2800	0.068
HH <sub>sym</sub>	+106.4	-57.7	64.0	61.5	-1020	-3850	0.134
HH <sub>brk</sub>	-151.4	-56.7	42.1	44.9	-890	-3810	0.131

the appearance of a polarizing field of  $\approx 40$  mV/Å (note the change of the sign of the slope).

The differences in the screening properties of the nanocapacitors can be directly related to the differences in the work functions on the positive and negative bare-PbTiO<sub>3</sub> surfaces. Previous work<sup>13</sup> has shown that for polar PbTiO<sub>3</sub>, this difference is the variation between the two vacuum potentials for the frozen bare slab ( $\Delta_2$ ) and it is greater than the potential drop inside the film ( $\Delta_1$ ) [see Figs. 5(a) and 5(b)]. Thus, screening of the difference in the work functions at the two surfaces in the oxide by the electrodes can overscreen the potential drop due to polarization and create a polarizing field. Similarly, the importance of Schottky barrier heights (SBHs) for the screening in ferroelectric oxides has also been analyzed in detail by Stengel *et al.*<sup>23</sup> using constrained displacement-field calculations. Examination of the electrostatic potential plots shows that for the bare slab in the HH<sub>brk</sub> geometry, the work function difference is larger ( $-3.8$  V for HH<sub>brk</sub> vs  $-2.7$  V for TT<sub>sym</sub>). This is due to the much stronger PbO surface rumpling at the HH interface. The separation between the O and the Pb atoms is greater for the HH interface, with the O atom rising out of the surface by  $\approx 0.7$  Å more than in the TT case. This makes the electrostatic

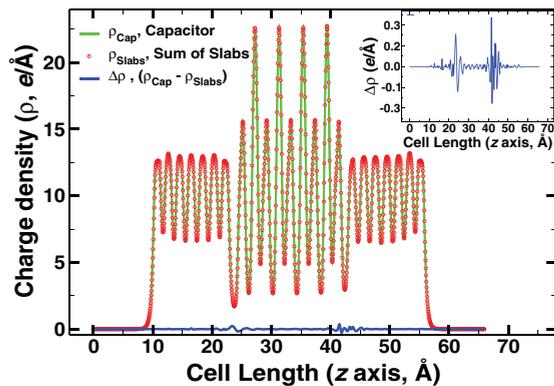


FIG. 4. (Color online) Electron charge density along  $z$  in the unit cell [ $\rho(z)$  in units of  $e/\text{Å}/(\text{cell cross-section})$ ]. DFT-obtained electronic charge density for the TT capacitor system compared with the sum of the isolated metal and oxide charge densities calculated separately frozen in the respective capacitor geometries. The small difference between the two (inset) means that the capacitor systems can nearly be split into their individual isolated oxide and metal components.

potential more repulsive for electrons and increases the work function difference magnitude.

The screening can be described by a standard depolarizing field equation, generalized to the case of different work functions at the surfaces of the FE. In this case, the net electric field inside the FE is given by

$$\epsilon_{FE} = \frac{P}{\epsilon_0} \left( \frac{2\lambda}{d} \right) + \frac{(\Delta_2 - \Delta_1)}{d} \left( 1 - \frac{2\lambda}{d} \right). \quad (3)$$

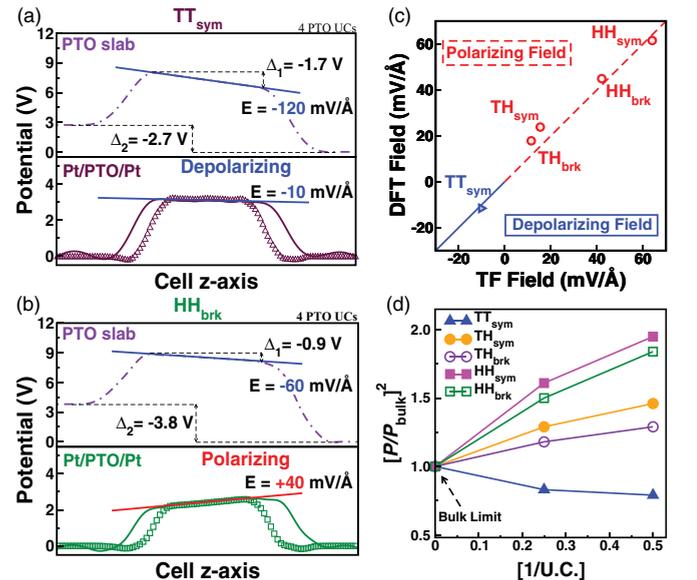


FIG. 5. (Color online) Macroscopic averaged electrostatic potential [ $\bar{V}(z)$ ] plots. (a), (b) Potential in the frozen freestanding PbTiO<sub>3</sub> film (upper panel, dot-dashed line), their corresponding capacitors (solid line) and potential from our Thomas-Fermi model (open symbols). Polarization points ( $P^+ \leftarrow P^-$ ) in the plot. A net polarizing field can develop in the oxide film, indicated by the flip in the sign of the slope, if the screening of  $\Delta_2$  overscreens  $\Delta_1$ , as in the case of HH<sub>brk</sub>. (c) A comparison of the electric field calculated values in the PbTiO<sub>3</sub> films ( $\epsilon_{FE}$ ) for all registries, shows that the Thomas-Fermi model accurately reproduces the trends found by DFT, as long as  $\Delta_2 - \Delta_1$  is included. (d) Relationship between  $P^2$  and the inverse PbTiO<sub>3</sub> film thickness. The TT capacitor shows decreasing  $P$  as film thickness is decreased. By contrast, the low-energy broken-symmetry structures, follow the opposite trend. Hence, there is no intrinsic critical size limit for these capacitors, due to the broken symmetry and enhanced screening.

Inspection of Eq. (3) suggests that a large  $\Delta_2 - \Delta_1$  would play a crucial role in the screening and can result in a polarizing field, equivalent to a negative effective screening length in Eq. (1). We use our DFT-computed values of  $\epsilon_{\text{FE}}$ ,  $P$ ,  $\Delta_1$ , and  $\Delta_2$  to solve Eq. (3) for the  $\lambda$  values (which are due to electronic screening only) in the different capacitor arrangements. The corresponding values are shown in Table I and range from 0.04 Å to 0.13 Å. Note that for the TT<sub>sym</sub> interface, which most closely resembles the bulk PbTiO<sub>3</sub> and Pt structures, the  $\lambda$  value is the smallest, while the HH interfaces exhibit values that are three times larger than those. According to the classic theory, which assumes equivalent electrostatic potentials at the  $P^-$  and  $P^+$  surfaces of the oxide, the poorer screening at the HH interface would lead to larger depolarizing field, in stark contrast to the strong polarizing field found by DFT calculations.

To show that the combination of simple metallic screening and a large difference in the surface electrostatic potential drops at the  $P^-$  and  $P^+$  surfaces ( $\Delta_2 - \Delta_1$ ) in the FE slab is sufficient to account for the results found by our DFT calculations, we use a simple Thomas-Fermi model for the electrode electrons in the nanocapacitor. The Thomas-Fermi equation is solved iteratively to obtain the total electrostatic potential due to screening by the free electrons in the electrodes. The nanocapacitor electrostatic potentials, and their associated  $\epsilon_{\text{FE}}$ , are obtained from direct DFT calculations and from the Thomas-Fermi model applied to the DFT-extracted bare-oxide potentials [Figs. 5(a), 5(b) and Table I]. The close quantitative agreement between these results [Fig. 5(c)] indicates that our model can capture the essential features of all the charge compensation mechanisms that contribute to the stability of ferroelectricity in ultrathin films, and thus highlights the importance of the  $\Delta_2 - \Delta_1$  difference as the main contributor to the interface-induced modifications in the depolarizing field. Furthermore, our results provide a straightforward guideline for stabilizing FE in ultrathin films: since  $\Delta_2$  is created by vertical separation between the surface cations and anions, the strongest reduction of the depolarizing field will occur for interfaces that create larger rumpling in the surface layer of the FE oxide.

The presence of enhanced polarization is not sufficient on its own to guarantee that ferroelectricity is energetically stable relative to the PE phase. As shown in Fig. 5(d),  $P^2$  scales as  $1/d$  reaching the highest values for the ultrathin film systems. This trend shows that  $P$  enhancement for the Pt/PbTiO<sub>3</sub>/Pt capacitors in the TH- and HH-related systems, in principle, has no critical size limit. However, a comparison of the in-plane constrained and relaxed nanocapacitor energies and  $P$  values shows that there are two criteria for stability in ultrathin perovskite films. First, the electrode must screen the surface charges well enough to remove the depolarizing field. This makes the FE state a local minimum on the potential energy surface. Such a minimum could still be higher in energy than the PE state due to a less favorable bonding at the interfaces. Hence, the second requirement is that the bonding energy of the metal-oxide interface for the polarized state must be equal to or greater than the metal-oxide bonding energy of the paraelectric state. That is, in films where the FE state is the global minimum, an interface with larger vertical rumplings reduces the depolarizing field while in-plane relaxation provides the

favorable interface chemistry that lowers the energy of the rumplings.

To illustrate these criteria, consider the HH<sub>sym</sub> and the HH<sub>brk</sub> nanocapacitors. In the HH<sub>sym</sub> system, the overscreening leads to a 37% increase in  $P$  for the FE state. Nonetheless, the metal-oxide bonding is significantly weaker than for the paraelectric case, making the HH<sub>sym</sub> FE state a high-energy local minimum. When the in-plane symmetry is broken, the screening is not quite as efficient, leading to a  $P$  enhancement of only 24% for the HH<sub>brk</sub> structure. However, the metal-oxide bonding is stronger. This lowers the energy of the HH<sub>brk</sub> nanocapacitor making it the global minimum on the potential energy surface.

To describe these two criteria in the language of the Landau-Ginzburg-Devonshire (LGD) theory, we introduce additional order parameters to represent the surface deformation and the bonding interaction at the interface<sup>34</sup> and write

$$U_{\text{tot}} = n\left(-\frac{1}{2}AP^2 + \epsilon_{\text{FE}}P + \frac{1}{4}BP^4\right) + aS_{\text{top}} + \frac{1}{2}bS_{\text{top}}^2 - aS_{\text{bot}} + \frac{1}{2}bS_{\text{bot}}^2 - kS_{\text{top}}P - kS_{\text{bot}}P, \quad (4)$$

where  $U_{\text{tot}}$  is the total energy of the system,  $n$  is the thickness of the oxide film in unit cells,  $P$  is the polarization of the oxide,  $S_{\text{top}}$  and  $S_{\text{bot}}$  are the surface order parameters relating to the structural changes at the surface due to the metal-oxide bonding and  $A$ ,  $B$ ,  $a$ ,  $b$ , and  $k$  are constants parameterizing the oxide ferroelectricity, surface bonding and the interplay between  $P$  and structural changes due to the metal-oxide bonding. The presence of the additional order parameters makes the potential energy surface complex and allows for the existence of metastable states.

Minimizing the energy with respect to all three order parameters shows that three minima are present on the potential energy surface. For a paraelectric state,  $S_{\text{top}} = -S_{\text{bot}} = -a/b$ ; here, the interfaces are symmetrically deformed, as we indeed find for the PE capacitor where both surfaces are locally  $P^-$  with the oxygen atoms sticking out from the surface. For the FE state, the surface deformation will be different at the two surfaces, as found by DFT calculations, with one surface forced away from its preferred state by the coupling of the surface atom displacements to the film  $P$ .

To illustrate the impact of the oxide-metal bonding on the relative stability of the FE and PE states and the critical thickness, we compare the energy of the PE state and the energy of the FE state at  $P = P_0$  (polarization of the oxide bulk). For convenience, we use a case where the constant  $k$  that scales the strength of the coupling between the surface order parameter and the bulk  $P$  is such that  $kP_0 = a$ .

The energy of the PE state is given by

$$U_{\text{tot}}^{\text{PE}} = 2U_{\text{int}}^0 = -a^2/b. \quad (5)$$

For the FE state with  $P = P_0$  and  $kP_0 = a$ ,  $S_{\text{top}}$  and  $S_{\text{bot}}$  are 0 and  $2a/b$  respectively. In this case, the interface energy for the top and bottom surfaces is 0 and the energy of the system is given by

$$U_{\text{tot}}^{\text{FE}} = nU_{\text{bulk}}^{\text{FE}} - 2a^2/b, \quad (6)$$

where  $U_{\text{bulk}}^{\text{FE}}$  is the energy due to ferroelectric polarization in the oxide unit cell at  $P = P_0$ . Setting the PE and FE cases to

the same energy and solving for  $n$ , we get

$$n_{\text{crit}} = (a^2/b)/U_{\text{bulk}}^{\text{FE}}. \quad (7)$$

Thus, due to the effect of the interface, it is possible to have a high  $n_{\text{crit}}$ , even for the case where the depolarizing field has been eliminated by a full compensation of the surface charge or even in the presence of a polarizing field. We emphasize that the  $n_{\text{crit}}$  here is the critical thickness at which the FE state is the ground state of the system, not the one at which the  $P$  can be metastable but only as a local minimum, higher in energy than the PE state. These effects are independent of the depolarizing field, as illustrated by the comparison between the  $\text{HH}_{\text{sym}}$  and the  $\text{HH}_{\text{brk}}$  systems above.

#### IV. CONCLUSION

We conclude that even for simple surfaces with bulk stoichiometry, energy minimization with respect to lateral degrees of freedom is necessary to find the correct ground state structure of FE/metal nanocapacitors. We find that the ground state for the classic  $\text{Pt/PbTiO}_3/\text{Pt}$  systems exhibits a strong polarization enhancement due to the polarizing field. This leads to  $P$  increase as the film size decreases. There are two requirements for stable, FE  $\text{PbTiO}_3$  ultra-thin films with no critical size limit: (i) overscreening of depolarizing field, caused by strong surface rumpling and large oxide work function differences; this allows a

minimum energy state with  $P > 0$  to exist, and (ii) favorable chemical bonding at the interface, allowed by ionic in-plane relaxation, which then ensures that the FE state is a global minimum.

We hope that our findings will encourage development of experimental techniques that allow for a better controlled epitaxial growth of FE films and the use of characterization techniques such as x-ray photoelectron diffraction (XPD), low-temperature Raman scattering using UV illumination or grazing incidence x-ray diffraction (GIXD) to reveal surface structure features (i.e., intracell atomic-displacement distributions or symmetry-lowering due to surface O-Ti bond tilts) and to advance the understanding of the impact of surface structure on the screening properties of the interface.

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