Ionic Polarizability of Conductive Metal Oxides and Critical Thickness for Ferroelectricity in $BaTiO_3$

G. Gerra,[1,*] A. K. Tagantsev,[1] N. Setter,[1] and K. Parlinski[2]

[1]*Ceramics Laboratory, Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland*
[2]*Institute of Nuclear Physics, Polish Academy of Science, 31-342 Cracow, Poland*

(Received 23 December 2005; published 17 March 2006)

We report a first-principles investigation of ultrathin $BaTiO_3$ films with $SrRuO_3$ electrodes. We find that the ionic relaxations in the metal-oxide electrode play a crucial role in stabilizing the ferroelectric phase. Comparison with frozen-phonon calculations shows that the degree of softness of the $SrRuO_3$ lattice has an essential impact on the screening of ferroelectric polarization in $BaTiO_3$. The critical thickness for ferroelectricity in $BaTiO_3$ is found to be 1.2 nm. The results of our calculations provide a possible explanation for the beneficial impact of oxide electrodes on the switching and dielectric properties of ferroelectric capacitors.

DOI: 10.1103/PhysRevLett.96.107603 PACS numbers: 77.55.+f, 68.35.−p, 77.22.Ej, 77.80.Fm

Ferroelectric oxides are essential components in a large number of applications, from ultrasound medical imaging [1] to nonvolatile random access memories [2] and microelectro-mechanical systems (MEMS) [3]. Following a general tendency towards miniaturization, ferroelectric-based devices are being shrunk to nanometer scale by growing thin-film capacitor structures. This procedure allows to achieve high electric fields from low-voltage sources, but it entails a size effect and ensuing degradation phenomena that limit the performance of the device [4]. The cause of this size effect is generally believed to be the depolarizing field produced by incomplete screening of the bound polarization charge at the ferroelectric-electrode interface. The presence of such interface is thus equivalent to adding an extra capacitor in series to the ferroelectric, thereby reducing the ability to vary the permittivity and hence the efficiency of the device. In memory applications, such a ‘‘surface-capacitor’’ effect is believed to lead to electrical overstress near the electrodes when cyclically switching the polarization, eventually degrading the switching ability of the film [a phenomenon known as *fatigue* [4]] and impairing the memory's performance.

Surface effects become more pronounced the thinner the film. The introduction of an extra capacitor between the metal and the ferroelectric produces a depolarizing field that suppresses the polarization and the permittivity of the film—an effect that grows stronger with decreasing film thickness. Such phenomenon has provoked speculation in recent years as to whether ferroelectrics have a critical thickness below which ferroelectricity disappears altogether, and whether this limit is intrinsic to the finite size of the system or whether it is imposed by the specific properties of the interface [5–12]. In light of the fundamental role played by the surface-capacitor effect in the physics of ferroelectrics and in the performance of coming applications, identifying its origin assumes a significance that goes beyond mere scientific curiosity.

There are two distinct possible explanations for the appearance of an additional capacitance at the ferroelectric-metal interface. The first possibility is related to the fact that when free charges in the electrode approach the ferroelectric-electrode interface to screen the bound charge of the ferroelectric, they form a layer of finite thickness (known as the Thomas-Fermi screening length) [13]. Therefore, the center of gravity of the free charges is displaced with respect to the interface, creating a capacitor. On the other hand, the polarization cannot drop abruptly in going from the ferroelectric to the metal (so-called Kretschmer-Binder effect) [14]. For this reason, the center of gravity of the bound charge is shifted away from the metal, creating another capacitor. These two mechanisms, shown schematically in Fig. 1(a), may act simultaneously as two back-to-back in-series capacitors.

In an effort to improve the performance of ferroelectric thin-film devices, it was found that the surface-capacitor

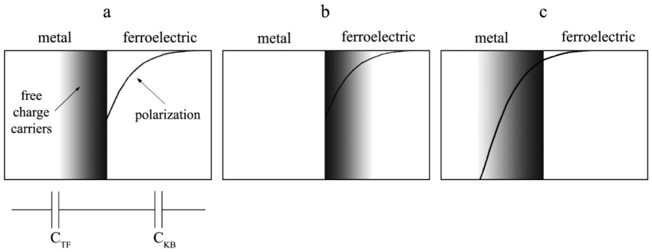

FIG. 1. The surface-capacitor effect. (a) Thomas-Fermi screening and Kretschmer-Binder effect, each being equivalent to the introduction of a capacitance (C_{TF} and C_{KB}) in series with the ferroelectric. (b) Compensation of the bound charge by the presence of free charge carriers in the ferroelectric, for example, as a result of doping or contact phenomena. (c) Penetration of the ionic polarization into the metal, for example, as a result of the mechanical relaxation of the electrode ions in response to the ferroelectric distortion of the adjacent lattice. The gradient in shading represents the concentration of free charge carriers, while the solid line represents the absolute value of polarization.

effect is much weaker when the electrodes are conductive metal oxides, such as RuO_2, IrO_2, or $SrRuO_3$. Unlike the case of simple Pt electrodes, for such materials no additional surface capacitor has been revealed by dielectric measurements [15]. This feature is in strong correlation with the essential suppression of degradation effects that is observed when oxide electrodes are used [2,4]. While the paramount importance of this phenomenon in view of the applications of ferroelectrics is universally recognized, the origin of the beneficial effects of conductive metal-oxide electrodes is still a matter of dispute [cf. reviews in Refs. [4,16]]. A reasonable approach to the problem is to look for a charge-compensation mechanism that makes the screening more efficient. One possibility is an enhanced concentration of free charge carriers in the first few layers of the ferroelectric [Fig. 1(b)], for example, as a result of doping [4] or of contact phenomena [17]. We can say that in this case the free charges move to where the bound charges are situated, so as to screen them "*in situ*." The second possibility is the penetration of the bound polarization charges into the electrode. In the case of oxide electrodes, this is made feasible by their ionic structure. We can imagine that the ionic displacements that produce the polarization in the ferroelectric might continue for some distance into the metal-oxide structure, leading again to *in situ* screening [Fig. 1(c)]. In this scenario, one can additionally profit from a weaker blocking of polarization at the interface [18]. It is worthy of note that whichever the mechanism behind it, *in situ* screening can essentially cancel out the destructive effect of the additional surface capacitor, thus explaining the enhanced performance of oxide electrodes.

In this Letter, we report a first-principles investigation of the second *in situ* screening scenario, which shows that the latter does indeed take place in $BaTiO_3$ thin films, hence significantly controlling the size effect. In the context of density functional theory calculations, we can compare the behavior of a ferroelectric-electrode system in which the electrode ions are blocked with a system in which they are free to move, thereby isolating the pure electrostatic effect due to Thomas-Fermi screening from the more complicated problem involving the mechanical relaxation of all the ions. In a recent work [5], Junquera and Ghosez have focused on the former aspect, modeling the impact of the Thomas-Fermi capacitor on ferroelectricity. Their work is based on the assumption that the ions of the electrode do not react at all to the ionic displacements in the ferroelectric, and that the latter displacements are homogeneous throughout the material. However, in order to check whether at a realistic interface the Thomas-Fermi capacitor fully exerts its effect, one can lift the aforementioned assumptions and let the ionic displacements penetrate into the electrode. Incidentally, the importance of allowing the atomic coordinates of the electrode to relax was recognized, but not further investigated, in Ref. [12]. If this penetration is important for polarization screening, one expects to find (i) significant ionic displacements within the electrode and (ii) an appreciable reduction of the critical thickness for ferroelectricity in the system. The latter effect arises because better polarization screening implies a reduction of the depolarizing field, which in turn is believed to kill ferroelectricity on decreasing the film thickness. In the present work, we have implemented this scheme, obtaining full confirmation of both expectations. We have found ionic distortions within the electrode lattice over a distance of 2–3 lattice constants, and approximately a twofold reduction of the critical thickness for ferroelectricity as a result of the lattice relaxations in the oxide electrode.

To have a clear comparison with previous results, we have modeled the ferroelectric state of a system identical to that treated by Junquera and Ghosez [5], and begun by calculating the total energy of the system as a function of the soft-mode distortion amplitude, in the so-called "frozen-phonon" approximation [19] (with the additional assumption that the electrode lattice is perfectly rigid with respect to ionic displacement). Specifically, we have considered $SrRuO_3/BaTiO_3/SrRuO_3$ sandwich structures, where the perovskite ferroelectric is intercalated between two slabs of the perovskite conductor, and assigned the $BaTiO_3$ ions a given fraction of the computed bulk soft-mode displacement of the relevant atomic species. The total-energy calculations were performed within the local density approximation, using the Vienna *Ab initio* Simulation Package (VASP) [20] and the projector augmented-wave method for the electron-ion interactions [21]. We have used a $6 \times 6 \times 1$ Monkhorst-Pack grid for k-point sampling [22], and a plane-wave energy cutoff of 400 eV. The $SrRuO_3$ and $BaTiO_3$ in-plane lattice constants were constrained to 3.94 Å [the bulk lattice constant—calculated from first principles for self-consistency—of the fictitious $SrTiO_3$ substrate [5] that is used to stabilize the tetragonal phase, with the polar axis normal to the interface [23]], while their equilibrium out-of-plane lattice constants were subsequently calculated by minimizing the total energy. The resulting structures were used as the building blocks of the supercell, which consisted of five unit cells of $SrRuO_3$ [24] and a variable number of $BaTiO_3$ unit cells. We have considered the simplest computational situation, where the supercell volume is fixed to its centrosymmetric equilibrium value. Such constraint should affect neither the qualitative considerations presented herein nor the obtained value of the critical thickness for ferroelectricity. The extent of the out-of-plane clamping imposed on the structure will somehow modify the absolute value of the spontaneous polarization, which was not, however, the subject of investigation here. The justification of our approach follows from the treatment of clamping effects reported in Ref. [23].

Figure 2 shows the change in energy effected by a given fraction of bulk soft-mode distortion for six different thicknesses of the $BaTiO_3$ layer. The presence of side minima on a particular curve indicates the existence of a ferroelectric instability at such thickness. The minima disappear at a

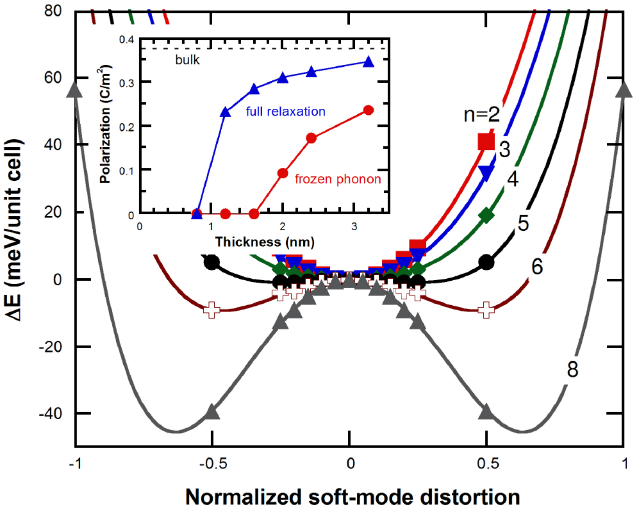

FIG. 2 (color online). The energy change (per unit cell of $BaTiO_3$) due to a given fraction of the computed bulk ferroelectric soft-mode distortion (in the frozen-phonon approach), for six different thicknesses of the ferroelectric layer (n is the number of unit cells of $BaTiO_3$). The total energy of the structure in the paraelectric phase is taken as a reference. Inset, average polarization of the ferroelectric layer as a function of thickness, for the frozen-phonon and the full-relaxation data. The polarization was calculated using the computed Born effective charges of bulk $BaTiO_3$ [26,27].

thickness of four unit cells, meaning that the critical thickness for ferroelectricity in this system is 2 nm, in good agreement with the result of Ref. [5].

As the next step, we have calculated the true ground-state ionic configuration of the six systems by letting all the ions (including those of the electrode) fully relax, until the Hellman-Feynman forces acting on each of them were less than 1 meV/Å. The profiles of the rumplings (i.e., the cation-oxygen relative displacements within each atomic layer) thus obtained are shown in Fig. 3.

The foremost result of the calculations is the fact that the ionic displacements penetrate into the metal over a distance of two or three unit cells. Furthermore, the ferroelectric distortions are hardly suppressed as we approach the interfaces, implying little or no surface reduction of polarization. In the case of the thinnest film (two unit cells of $BaTiO_3$), the rumpling pattern has a mirror-symmetry plane lying in the middle of the ferroelectric layer, and shows a clear antisymmetric poling effect of the two interfaces, which excludes the possibility of a ferroelectric bistability. Such poling effect of the interface is a consequence of its centrosymmetry-breaking action [25]. For thicknesses of three unit cells and greater, the mirror symmetry is broken: the rumplings are rather uniform within the ferroelectric film and yield a finite average polarization. This is clearly seen from the inset of Fig. 2, where, as an illustration, we have plotted the polarization as a function of thickness, using the computed Born effective charges [26,27] of bulk $BaTiO_3$. It follows that the critical thickness for ferroelectricity in $BaTiO_3$ is three unit cells (~1.2 nm), roughly half the value (~2 nm) found within the frozen-phonon approximation.

The striking observation of the "softness" of the oxide electrode sheds some light on a fundamental issue concerning ferroelectric thin films. If the ionic displacements associated with the polarization continue into the metal, then those long-range electrostatic effects associated with a nearby-electrode suppression of polarization are heavily reduced for this type of system. In other words, surface-capacitance effects are weaker in this case thanks to the partial screening of the bound polarization charge carried out *in situ* by the electrode's free charge carriers. That such screening is enhanced when the $SrRuO_3$ interfacial layers are allowed to relax is confirmed by an inspection of the macroscopically averaged [28] electrostatic potential of the system. By determining the potential drop across the ferroelectric film, we evaluated the depolarizing field E_d. Then, from the well-known relation [see e.g. Ref. [16]]

$$E_d = -\frac{2\lambda P}{\varepsilon_0 t}, \tag{1}$$

(where λ is the effective thickness of the surface-capacitance layer divided by its dielectric constant and t the thickness of the ferroelectric film) and from the calculated average ferroelectric polarization, P, we obtained the quantity λ. We found a value of $\lambda \approx 0.2$ Å for the frozen-phonon data, as opposed to $\lambda \approx 0.1$ Å for the full-relaxation data. Therefore, the lattice softness of $SrRuO_3$ is responsible for a twofold increase in the screening ability of the electrode, which seems to explain the roughly twofold reduction in the critical thickness for ferroelectricity compared to the frozen-phonon case. The correlation between enhanced screening and stability of the ferroelectric phase suggests that the latter is sensitive to the ionic relaxations because of the more favorable electrostatic state of the resulting relaxed structure, rather than because of the purely mechanical or chemical properties of the interface.

We have seen that the ionic polarizability of the nearby-interfacial layers of the electrode are essential in stabilizing the ferroelectric phase in $BaTiO_3$. However, this may not be a universal property of perovskite ferroelectrics. In a recent first-principles work [12], Sai *et al.* have found that $PbTiO_3$, while it retains its ferroelectric character at all thicknesses considered for both Pt and $SrRuO_3$ electrodes, shows polarization enhancement in the case of Pt electrodes and polarization reduction in the case of $SrRuO_3$ electrodes. This suggests that the role of ionic displacements in the electrode is not of primary importance in screening the polarization bound charge for the case of $PbTiO_3$. The case of $SrRuO_3/BaTiO_3/SrRuO_3$ structures was also treated by Sai and co-workers, who report absence of ferroelectricity below a thickness of 2 nm. However, the contradiction with our result is only apparent. The point is that in Ref. [12] the in-plane lattice constant of the stack is

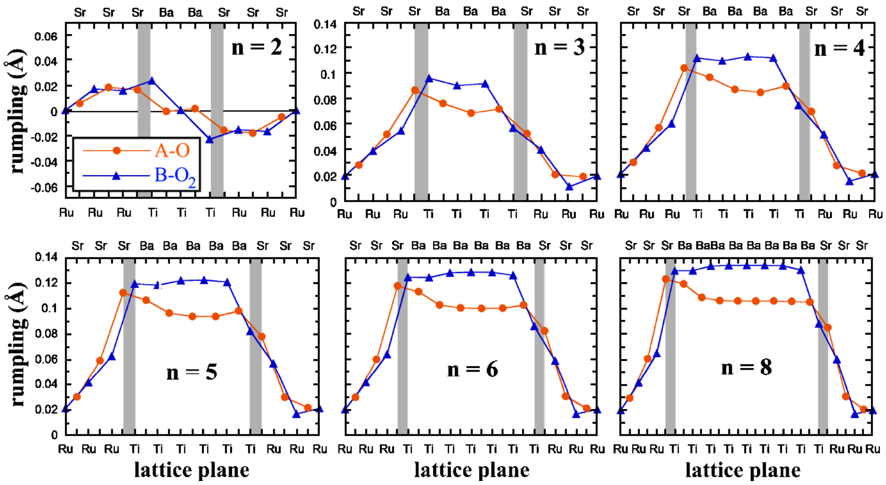

FIG. 3 (color online). The rumpling (i.e., the cation-oxygen relative displacement within each atomic layer) profiles obtained by full minimization of the total energy of the system, for six different thicknesses of the $BaTiO_3$ layer. The rumplings occur along the polar axis only. The *A*-site ions are Sr and Ba, while the *B*-site ions are Ru and Ti.

set equal to that of bulk $BaTiO_3$ at 0 K (3.991 Å). Under such mechanical boundary conditions, $BaTiO_3$ should have a rhombohedral ground state, as opposed to the artificially stabilized tetragonal state chosen in Ref. [5] and in our work. The fact that the atomic relaxation with respect to the out-of-plane coordinates, which was performed in Ref. [12], does not reveal ferroelectric minima along the polar tetragonal axis is therefore not proof of the absence of ferroelectricity.

In conclusion, we have demonstrated that perovskite metal oxides like $SrRuO_3$ can essentially share the ionic displacements that are responsible for the polarization in ferroelectrics. The effect provides a very efficient mechanism of polarization screening, where the bound charges are screened *in situ* within the electrodes. Such a screening mechanism is shown to lead to an essential reduction of the critical thickness for ferroelectricity in $BaTiO_3$ (three unit cells). It also offers an explanation for the beneficial impact of oxide electrodes on the switching and dielectric properties of ferroelectric capacitors, which is extensively documented in experiments. Our calculations suggest that the size effect in a ferroelectric film with oxide electrodes is heavily affected by the lattice softness of the electrode, and thus by no means should the latter feature be neglected when discussing the properties of such systems.

This project was supported by the Swiss National Science Foundation. The NCCR "Nanoscience" program is acknowledged for additional support.

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*Electronic address: guido.gerra@epfl.ch

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