Ferroelectricity in ultra-thin perovskite films

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(Dated: March 23, 2022)

We report studies of ferroelectricity in ultra-thin perovskite films with realistic electrodes. The results reveal stable ferroelectric states in thin films less than 10 Å thick with polarization normal to the surface. Under short-circuit boundary conditions, the screening effect of realistic electrodes and the influence of real metal/oxide interfaces on thin film polarization are investigated. Our studies indicate that realistic electrodes on ultrathin films, nor how monodomain thin film ferroelectricity is affected by the interactions at the metal/oxide interfaces. We demonstrate this effect in ferroelectric PbTiO$_3$ and BaTiO$_3$ films.

The effect of size on thin-film ferroelectricity has been known for a long time, but has not been completely understood. Initial experiments and mean field calculations based on the Landau theory suggested that below a critical correlation volume of electrical dipoles between 10-100 nm$^3$, ferroelectricity vanishes due to intrinsic size effects. For thin films with the polar axis perpendicular to the surface, incomplete compensation of surface charges creates a depolarizing field that has been shown to further reduce the polarization.

Recently, however, monodomain ferroelectric phases have been observed in very thin films, below ten unit-cells thick. Furthermore, Fong et al. showed that ferroelectric phases can be stable down to ~12 Å (three unit cells) in PbTiO$_3$ films by forming 180° stripe domains, suggesting that no fundamental thickness limit is imposed by the intrinsic size effect in thin films. This idea has been corroborated by ab initio calculations carried out on perovskite films, which tell that no critical thickness exists for polarization parallel to the surface and that polarization perpendicular to the surface can exist in films three unit-cells thick if the depolarization field is artificially removed.

On the other hand, it has been found that the depolarization field plays a dominant role in reducing polarization normal to the surface and depressing ferroelectric transition temperatures in thin films. In a continuum model by Batra et al. which includes the depolarization effect, a critical thickness of 100 Å for perovskite films was analytically derived, assuming a Thomas-Fermi screening length of 1 Å for the metal electrodes. Also, a recent first-principles calculation revealed that BaTiO$_3$ films with SrRuO$_3$ electrodes lose ferroelectricity below ~24 Å (6 unit cells) thus suggesting that a minimum thickness limit exists for useful ferroelectric films. While indeed a minimum film thickness must be influenced by the polarization of the ferroelectrics and the screening length of the electrodes, it is not yet clear whether the depolarizing field can ever be completely removed by realistic electrodes on ultrathin films, nor how monodomain thin film ferroelectricity is affected by the choice of electrodes and by the interactions at the metal/oxide interface.

In this paper, we provide answers to these questions. In particular, we investigate how the critical thickness varies in different systems with realistic electrodes. We find that even though ferroelectricity is lost in BaTiO$_3$ thin films, polarization close to the bulk value can be stabilized in PbTiO$_3$ thin films with thickness less than 10 Å; the behavior in BaTiO$_3$ is therefore not universal to all ferroelectric thin films. Furthermore, we show that inequivalent ferroelectric/electrode interfaces can assist in stabilizing ferroelectricity in thin films.

We apply density functional theory (DFT) calculations to ultrathin ferroelectric capacitors that are constructed of PbTiO$_3$ and BaTiO$_3$ films sandwiched between two conducting electrodes. Two electrodes commonly used in ferroelectric devices are studied: platinum (Pt) and the metallic oxide SrRuO$_3$. Short-circuit boundary conditions are imposed by the periodic boundary conditions and electrodes of sufficient thickness.

We consider AO (PbO or BaO) and TiO$_2$ ferroelectric terminations, and we examine different ferroelectric-electrode interfaces, focusing on the lowest energy for each termination. Pt is most stable with the first layer situated above the oxygen atoms on the TiO$_2$ terminated surface, and above A and O atoms on the AO-terminated surface. The periodically repeated supercells can thus be described by the general formula $\text{Pt}_4/\text{AO}-(\text{TiO}_2-\text{AO})_m/\text{Pt}_5$ and $\text{Pt}_4/\text{TiO}_2-(\text{AO}-\text{TiO}_2)_m/\text{Pt}_5$ with Pt electrodes and $(\text{SrO-RuO}_2)_2/\text{AO}-(\text{TiO}_2-\text{AO})_m/(\text{RuO}_2-\text{SrO})_2-\text{RuO}_2$ and $(\text{RuO}_2-\text{SrO})_2/\text{TiO}_2-(\text{AO}-\text{TiO}_2)_m/(\text{SrO-RuO}_2)_2$ SrO with SrRuO$_3$ electrodes (periodic boundary conditions means that the ferroelectric slabs are separated by nine layers of electrode). Figure 1 shows the structures for two representative systems at $m=2$. Although ferroelectric instabilities can be present in the directions parallel and perpendicular to the film, here we focus only on the latter situation, as our primary interest is the depolarization effect. Therefore, for all the capacitors considered, the in-plane atomic positions are kept fixed at the ideal perovskite positions and the in-plane lattice constants are set equal to the experimental value for the corresponding bulk ferroelectric perovskite, i.e. $a=3.935$ Å for PbTiO$_3$, and $a=3.991$ Å for BaTiO$_3$.

We start by determining the fully relaxed structures...
FIG. 1: (a) TiO$_2$-terminated Pt/PbTiO$_3$/Pt structure. (b) PbO-terminated SrRuO$_3$/PbTiO$_3$/SrRuO$_3$ structure. The ferroelectric displacement patterns are shown by arrows. The rumpling of each layer (displacement of cations relative to anions) is marked, in Å.

TABLE I: Polarization ($P$) and tetragonality ratio $c/a$ for PbTiO$_3$ films with Pt and SrRuO$_3$ electrodes. The bulk values are given in the last line.

| termination electrode | $m$ | $P$ (C/m$^2$) | $c/a$ |
|-----------------------|-----|---------------|-------|
| PbO                  | 1   | 0.89          | 1.109 |
| PbO                  | 2   | 1.00          | 1.140 |
| PbO                  | 4   | 0.88          | 1.058 |
| TiO$_2$              | 2   | 0.86          | 1.110 |
| TiO$_2$              | 4   | 0.85          | 1.055 |
| PbO                  | 2   | 0.36          | 1.049 |
| TiO$_2$              | 2   | 0.32          | 1.040 |
| bulk                 |     | 0.75          | 1.060 |

of the supercells. The atomic positions and strains are fully relaxed along the surface normal direction. Figure 1(a) shows the relaxed supercell structure of the TiO$_2$-terminated PbTiO$_3$ film with Pt electrodes and $m=2$. The displacements from the centrosymmetric structures are calculated. The relative displacement between the cations and anions for each PbTiO$_3$ layer (see Figure 1(a)) clearly demonstrates that the structure is in a ferroelectric state. As Table I shows, PbTiO$_3$ films with Pt electrodes are ferroelectric for all thicknesses down to $m=1$. For both terminations, the polarization values in these systems are slightly larger than the corresponding bulk value.\(^19\)

These results suggest that bulk ferroelectric polarization can be stabilized in thin films below 10 Å with realistic electrodes. As Figure 1 illustrates, an upward pointing polarization leads to an enhancement of the displacements at the bottom interface, and a reduction at the top interface, relative to the interior layers. This observation is in agreement with previous DFT calculations with external fields.\(^12\) In going from $m=2$ to $m=4$, both $P$ and $c/a$ decrease towards the bulk values as the surface-to-volume ratio decreases and the surface effect is averaged over more layers. To further check whether there exists a thickness limit below which ferroelectricity disappears in this system, we examine the structure at $m=1$. We find that a single unit-cell has a stable polarization of 0.89C/m$^2$, despite the stoichiometrically different environment as compared to bulk PbTiO$_3$.\(^9\) We therefore find strong evidence for an absence of a critical thickness for ferroelectricity in PbTiO$_3$ films with Pt electrodes. In contrast to the PbTiO$_3$ films, none of the BaTiO$_3$ structures were found to be ferroelectric for $m=2$ or $m=4$, in agreement with the results in Ref. 13.

To make contact with earlier analytic theory,\(^4\,14\) we examine the electric field in the Pt/PbTiO$_3$/Pt capacitor by plotting the macroscopic-averaged electrostatic potential, as shown in Figure 2. Also shown in Figure 2 is the potential in the free-standing PbTiO$_3$ film in which a bulk ferroelectric displacement perpendicular to the surface is imposed.\(^21\) The potential in the PbTiO$_3$ slab, which is the depolarizing field, is significantly smaller in the capacitor (0.009 V/Å), than in the free-standing slab (0.324 V/Å). Our calculations show that in the absence of electrodes, the latter field brings the system back to the paraelectric structure. The cancellation of a substantial fraction (97%) of the depolarizing field is due to metallic screening from the grounded electrodes that compensates the polarization charge.

FIG. 2: Macroscopic-averaged electrostatic potential along the film normal direction of the TiO$_2$-terminated Pt/PbTiO$_3$/Pt capacitor (solid curve) and a free-standing PbTiO$_3$ slab with a fixed bulk ferroelectric displacement (dashed curve). The potential is constant inside the Pt electrodes.

In addition, the screening is accompanied by the formation of unequal local dipoles at the two interfaces due to different chemical bonding, as shown in Figure 3. On the top interface, the Pt and Ti atoms lose charge, which
is redistributed between the atoms, forming a Pt-Ti alloy. On the bottom interface, where the Pt-O distance is the shortest, the Pt and O atoms lose charge, the Pt from the \( d_{x^2-y^2} \) orbitals, and the O from the \( p_z \) orbitals, while the Pt \( d_{xy} \) and \( d_{yz} \) orbitals gain charge. Similar behavior is observed at the ferroelectric/electrode interfaces of the AO-terminated capacitors. This inequivalent charge arrangement at the two ferroelectric/metal interfaces is consistent with the different interface polarizations we noted earlier.

![Image](image.png)

**FIG. 3:** Contour plot of the induced charge density for the TiO\(_2\)-terminated Pt/PbTiO\(_3\)/Pt capacitor structure at the (a) top interface (b) bottom interface. (The Pt layers farther from the interfaces are not shown.) Electron loss is given by solid lines and electron gain by dotted lines. The induced charge density is found by subtracting the charge densities of free-standing Pt and PbTiO\(_3\) slabs from the total charge density in the capacitor.

With SrRuO\(_3\) electrodes, the heterostructures also adopt a ferroelectric state, as shown in Figure 3(b). However, unlike with Pt electrodes, the polarization with SrRuO\(_3\) electrodes is only half the bulk value, indicating that the surface charges are only partially compensated. The \( c/a \) ratio for the SrRuO\(_3\)/PbTiO\(_3\)/SrRuO\(_3\) capacitor falls to 1.045 as the film thickness decreases to two unit cells. The corresponding electrostatic potential shows a depolarizing field of 0.07 V/Å across the PbTiO\(_3\) slab, which is much smaller than in the free-standing PbTiO\(_3\) film and explains why the polarization is stabilized at a significant level. Nevertheless, the stronger field compared to that in the Pt/PbTiO\(_3\)/Pt structures also confirms the weaker screening effect of SrRuO\(_3\) compared to Pt and other transition metals.

We note further that allowing the internal coordinates of the SrRuO\(_3\) electrodes, especially those in the boundary layers, to relax together with the PbTiO\(_3\) ions is crucial. When the SrRuO\(_3\) ions are fixed in their ideal positions, we find only paraelectric structures for either of the PbTiO\(_3\) terminations. This result indicates that the interaction between the PbTiO\(_3\) and the SrRuO\(_3\) electrodes plays a crucial role in stabilizing ferroelectricity: the screening effect alone cannot account for the significant reduction of the depolarizing field.

The results presented so far have suggested that ferroelectric polarization normal to the surfaces can be stabilized in thin films less than 10 Å thick. However they do not explain why the ferroelectric instability can be retained in PbTiO\(_3\) but not in BaTiO\(_3\) films when the same electrodes are applied. To address this question, we turn now to look at the depolarizing field and screening effects in these systems. The depolarizing field was previously addressed in phenomenological studies, and is shown to scale with the spontaneous polarization of the ferroelectrics, the screening length of the electrodes and the inverse ferroelectric film thickness. Hence the depolarizing field would be expected to be negligible only in very thick films.

In our calculations, inspection of the electrostatic potential in the free-standing film with a fixed bulk ferroelectric displacement shows that the potential drop across the ferroelectric slab (\( \Delta_1 \)) is different from the potential difference between the two asymptotic vacuum potentials (\( \Delta_2 \)), as illustrated in Figure 4. This difference arises because the two surfaces have different work functions, as a result of the polarization orientation, parallel to the top surface normal and anti-parallel to the bottom one. Because Pauli repulsion keeps metal electrons out of the ferroelectric, the potential drop that is “seen” and screened by the electrodes is \( \Delta_2 \), not \( \Delta_1 \). An electrostatic analysis of the potential and the electric field in the slabs shows that this difference must be taken into account when modeling the screening in all realistic systems.

![Image](image.png)

**FIG. 4:** The electrostatic potential of a free-standing film with a fixed bulk ferroelectric displacement (lower curve); the self-consistent potential from solving the Poisson equation for Thomas-Fermi screening charges (upper curve). Panel (a) is PbTiO\(_3\) film and panel (b) is BaTiO\(_3\) film.

We use a simple Thomas-Fermi model to highlight the effect of metallic screening on a ferroelectric slab, without the complex structural and electronic relaxations of DFT calculations. We treat the DFT macroaveraged electrostatic potential of the free-standing film as an ini-
tial potential and find the metallic screening charge using Thomas-Fermi theory. We then find the total self-consistent potential by solving the Poisson equation. Figure 4 shows that in a PbTiO$_3$ slab of two unit cells, where $\Delta_2/\Delta_1 \sim 1.1$, metallic screening from the electrodes results in a potential that is close to constant in the PbTiO$_3$ slab. On the other hand, in a BaTiO$_3$ slab where $\Delta_2/\Delta_1 \sim 0.9$, a similar calculation yields a screening potential with a significantly larger depolarizing field. These Thomas-Fermi results can be explained as follows. Suppose that the metal screens a fraction $f$ of the potential drop $\Delta_2$. For $\Delta_2 > \Delta_1$, this translates into screening a larger fraction $f\Delta_2/\Delta_1$ of the ferroelectric potential drop $\Delta_1$. However, if $\Delta_2 < \Delta_1$, then the fraction of the ferroelectric potential drop, $f\Delta_2/\Delta_1$, is less than $f$. The difference in the polarization stability of ultrathin PbTiO$_3$ and BaTiO$_3$ films is therefore directly related to the relation of $\Delta_2$ and $\Delta_1$ for the two materials. We therefore emphasize the importance of the inequivalence of the work functions in determining the ferroelectric behavior of ultra-thin films at this range of thickness.

In this paper, we have presented the first ab initio demonstration of realistic electrodes stabilizing polarization normal to the surface in ultra-thin films of <10 Å thick. We have shown that proper electrical and chemical boundary conditions are essential in stabilizing ferroelectricity. Using various electrodes, we find that monodomain ferroelectricity can persist down to one unit cell, suggesting that thin film ferroelectrics are not specific to a single system. The ferroelectric polarization results in a difference in the work functions at oxide surfaces that must be considered in modeling the metallic screening. We demonstrate this difference in PbTiO$_3$ and BaTiO$_3$ films in which we find significantly different screening behaviors with the same electrodes.

The authors would like to thank I-Wei Chen and E. J. Mele for insightful discussions. This work was supported by the Office of Naval Research, under Grants N00014-00-1-0372 and N00014-01-1-0365, and by the NSF MRSEC Program, Grant DMRL-79909. Computational support was provided by the HPCMO and by the DURIP program, as well as by the NSF CRIF Program, Grant CHE-0121132. AMK is supported by an Arkema Inc. fellowship.

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17. The slabs all have access to a paraelectric state with perfect inversion symmetry; this ensures that ferroelectricity is due only to spontaneous symmetry breaking.
18. When slightly smaller in-plane lattice constants of substrate materials such as SrTiO$_3$ are used instead, all c/a ratios are increased slightly compared to the values shown in Table II.
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21. This system can be realized by imposing the atomic displacement of the bulk ferroelectric state in the center of a slab, and relaxing the surface layers structure. The slope of the potential is determined by the band gap and thickness of the ferroelectric.
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