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Citation: Journal of Applied Physics 114, 034109 (2013); doi: 10.1063/1.4816350
View online: http://dx.doi.org/10.1063/1.4816350
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Interface effect on the magnitude and stability of ferroelectric polarization in ultrathin PbTiO$_3$ films from first-principles study

Q. Yang, J. X. Cao, Y. Ma, Y. C. Zhou, X. J. Lou, and J. Yang

1Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Xiangtan University, Xiangtan, Hunan 411105, China
2Frontier Institute of Science and Technology, Xi’an Jiaotong University, Xi’an 710054, China

(Received 5 May 2013; accepted 8 July 2013; published online 19 July 2013)

The interface effects on the ferroelectric polarization and stability of PbTiO$_3$ (PTO) films with metallic (Pt) or oxide (LaNiO$_3$, SrRuO$_3$) electrodes were studied using density functional theory calculation. It was found that the PTO film with oxide electrodes has stronger electrode/ferroelectric interface adhesion, lower polarization magnitude, and worse polarization stability, than that with Pt electrode. The PbO-terminated PTO films show weaker adhesion with the electrodes, but have higher polarization magnitude and better polarization stability than the TiO$_2$-terminated ones. The strain effects induced by misfit interface were also studied. Results show that the ferroelectric polarization and its stability can be enhanced by applying compressive strain, while depressed by applying tensile strain. © 2013 AIP Publishing LLC.

I. INTRODUCTION

In the last few decades, we have witnessed the extensive growth in research interest all over the world on ferroelectric materials for numerous electronic device applications, such as sensors and actuators, nonvolatile ferroelectric memories, integrated capacitors, and ferroelectric tunnel junctions, etc. For all these applications, a stable and significant remanent polarization is one of the necessary conditions for ferroelectric materials of any practical use. On the other hand, different from its ferromagnetic counterpart, ferroelectricity is a measured overall property, which reflects the whole system of the device, including the ferroelectric part, two interfaces, two electrodes, and the supporting substrate. From the device application point of view, a freestanding ferroelectric film is meaningless. Recently, many studies have demonstrated that the polarization strength, coercive field, as well as the fatigue and retention properties of a ferroelectric film are strongly dependent on the type of substrate and electrode used. The structural and electrical properties of the interface between the ferroelectric film and different electrode materials are believed to play important roles on the properties of the whole ferroelectric system. Driven by the continuing miniaturization of electronic devices, the thickness of ferroelectric films will fall into nanoscale, which makes the interface effect more critical than before regarding the ferroelectric polarization stability. The interface affect on the properties of ferroelectric devices has long been a complex, but attractive, question for scientists in the ferroelectric community.

With the continuous development of sophisticated experimental and theoretical approaches, numerous studies have been focused on the interfacial microstructure and its effect on the ferroelectricity. Using first principles calculations, Duan et al. have demonstrated an intrinsic 180° domain wall induced by the electrode/ferroelectric interface in ultrathin KNbO$_3$ ferroelectric films. Moreover, the stability of the polarization states would be destroyed by the interfaces which have been indicated by Lu et al. in the SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ heterostructures. By means of high-resolution transmission electron microscopy, Jia et al. found that the ferroelectricity and tetragonality near the interface and surface in epitaxial ultrathin PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film are greatly suppressed. Stengel et al. suggested that the atomic structure and chemical bonding at the interface of a ferroelectric device may significantly impact its ferroelectric state. However, a systematic study on the effect of the interface between the ferroelectric thin film and various types of electrodes is still lacking in the literature. In this paper, the ferroelectricity and stability of an ultrathin PbTiO$_3$ (PTO) film sandwiched between metallic or conductive oxide electrodes were systematically studied using the density functional theory (DFT) calculation. The atomic and electron structures were analyzed with the aim of further understanding the interface affects on the ferroelectricity. And we also studied the ferroelectricity in strained systems to reveal the affects of misfit strain induced by the substrate.

II. COMPUTATIONAL DETAILS

First-principles DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) with the projector-augmented-wave (PAW) method. Exchange and correlation effects were accounted for using the local density approximation (LDA). A 500 eV plane-wave cutoff energy and a 6 × 6 × 1 Monkhorst-Pack k-point grid were used for self-consistent calculations. Atomic relaxations were performed until the Hellmann-Feynman force on each atom was less than 5 meV/Å. With the above-mentioned computational setups, the lattice constant $a$ and axial ratio $c/a$ for the tetragonal PTO were calculated to be 3.854 Å and 1.05.
respectively, which are in accurate agreement with former LDA calculation\(^{19}\) and in reasonable agreement with the experimental data.\(^{20}\) For the electrode/ferroelectric/electrode (EFE) system, a \(1 \times 1\) supercell is stacked along the PTO [001] pseudocubic direction. This supercell implies a film which is infinite in the \(x\) and \(y\) directions due to the periodic boundary condition. \(\text{Pt, SrRuO}_3, \text{or LaNiO}_3\) electrodes, which contact with either the \(\text{PbO}-\text{or TiO}_2\)-terminated PTO,\(^{21}\) are taken into consideration during studying the interface affect. Herein, the supercells for the six types of interface systems can therefore be described by the following general formulas:

1. \(\text{Pt}_8/\text{TiO}_2-(\text{PbO-TiO}_2)_8/\text{Pt}_4\)
2. \(\text{Pt}_8/\text{PbO}-(\text{TiO}_2-\text{PbO})_8/\text{Pt}_4\)
3. \(\text{LaO}-(\text{NiO}_2-\text{LaO})_2/\text{TiO}_2-(\text{PbO-TiO}_2)_8/(\text{LaO-NiO}_2)_2-\text{LaO}\)
4. \(\text{NiO}_2-(\text{LaO-NiO}_2)_2/\text{TiO}_2-(\text{PbO-}\text{TiO}_2)_8/(\text{NiO}_2-\text{LaO})_2-\text{NiO}_2\)
5. \(\text{SrO}-(\text{RuO}_2-\text{SrO})_2/\text{TiO}_2-(\text{PbO-TiO}_2)_8/(\text{SrO-RuO}_2)_2-\text{SrO}\)
6. \(\text{RuO}_2-(\text{SrO-RuO}_2)_2/\text{PbO}-(\text{TiO}_2-\text{PbO})_8/(\text{RuO}_2-\text{SrO})_2-\text{SrO}\)

Note that each structure studied in this work is symmetrical and has two identical film-electrode interfaces. This means that there is no polarization asymmetry induced by the asymmetrical interface structures as in Ref. 4. And open-circuit boundary conditions are imposed with a 15 Å vacuum layer. In order to compare the effect of different interfaces, the in-plane lattices are all set to be the theoretical PTO layer. In order to compare the effect of different interfaces, the in-plane lattices are all set to be the theoretical PTO layer. In order to compare the effect of different interfaces, the in-plane lattices are all set to be the theoretical PTO layer. In order to compare the effect of different interfaces, the in-plane lattices are all set to be the theoretical PTO layer.

### III. RESULTS AND DISCUSSION

#### A. Interface bonding strength

The bonding strengths of each interface were estimated by calculating the work of separation (\(W_{\text{sep}}\)) according to the following equation:

\[
W_{\text{sep}} = \left( E_{\text{electrodes}} + E_{\text{PbTiO}_3} - E_{\text{electrode}/\text{PbTiO}_3/electrode} \right) / 2.23
\]

where \(E_{\text{electrodes}}, E_{\text{PbTiO}_3},\) and \(E_{\text{electrode}/\text{PbTiO}_3/electrode}\) are the total energies of the two free-standing electrodes, a freestanding PTO film and the capacitor (i.e., the whole system), respectively. \(W_{\text{sep}}\) for the six types of heterostructures is given in Table I. It can be concluded that \(W_{\text{sep}}\) for the oxide electrodes is greater than that for metallic electrodes, which is in accordance with the situation in ultrathin ferroelectric KNbO\(_3\) films.\(^{14}\) And \(W_{\text{sep}}\) for the TiO\(_2\)-terminated interfaces is about 0.5 J/m\(^2\) greater than that for the PbO-terminated ones. Some research studies indicated that the interface adhesion of the electrode to the ferroelectric ceramic film is the key factor determining the fatigue endurance of the sample.\(^{24–26}\) Thus, higher \(W_{\text{sep}}\) may be one of the reasons for better thermodynamically stability and deterioration resistance for the oxide electrode/ferroelectric device system.\(^{5,6,27}\)

The present results also imply a better fatigue resistance for the PTO films with TiO\(_2\)-terminated interfaces, compared with those with the PbO-terminated ones.

#### B. Ferroelectric polarization and its stability

We also investigated the layer-by-layer lattice tetragonality for the ultrathin PTO film with different electrodes. Fig. 2 shows the \(c/a\) ratio of each PTO cell layer in the ferroelectric capacitors (note that the in-plane lattice constants are the same). It can be seen that the PTO capacitor with Pt electrodes shows larger lattice parameter \(c\) than that with oxide electrodes. And the tetragonality for the PTO with PbO-terminated interfaces is larger than that with the TiO\(_2\)-terminated interfaces. Interestingly, the tetragonality for the Pt\(/\text{PbO}-(\text{TiO}_2-\text{PbO})_8/\text{Pt}_4\) system is even larger than the bulk value, corresponding to a very large spontaneous polarization value. And the SrO-(RuO\(_2\)-SrO\(_2\))\(_2\)/TiO\(_2\)-(PbO-TiO\(_2\))\(_8\)/(SrO-RuO\(_2\))\(_2\)-SrO system exhibits the minimum tetragonality, corresponding to the smallest polarization value.

The polarization magnitude and polarization stability of ultrathin PTO films were investigated in order to study the interface affect on their ferroelectricity. Due to the linear relationship between ferroelectric polarization and the cation displacements relative to oxygen ions,\(^{15}\) the ion rumplings of each layer in the PTO film are given [Figs. 3(a)–3(c)] instead of the accurate polarization value. The ferroelectric displacements for PTO are in strict accordance with the aforementioned lattice tetragonality. The PTO film sandwiched between two Pt electrodes shows the largest ferroelectric polarization. The PbO-terminated PTO film with Pt electrodes exhibits the same ferroelectric displacement as the calculated value for bulk PTO. It can be seen that at the bottom interface of this system, the Pt atom below the O ion shows

![Fig. 1. The atomic structures for the six types of electrode/PTO/electrode systems. All the polarization orientations are set upward.](image-url)

**TABLE I. Work of separation (\(W_{\text{sep}}\), in J/m\(^2\)) for the six types of heterostructures.**

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Pt-electrode</th>
<th>LNO-electrode</th>
<th>SRO-electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)-terminated</td>
<td>3.10</td>
<td>4.04</td>
<td>3.46</td>
</tr>
<tr>
<td>PbO-terminated</td>
<td>2.73</td>
<td>3.54</td>
<td>3.00</td>
</tr>
</tbody>
</table>
an enormously large displacement in comparison with the coplanar Pt atom below the Pb ion [see Fig. 3(a)]. This type of atomic arrangement can lead to a strong interaction between the Pt atom and the O ion at the interface, which may offer a complete screening of the depolarization field. In the oxide electrode system, however, the ferroelectric displacement can penetrate into the electrode, which is in accordance with many theoretical and experimental results obtained previously.28,29 The rumpling of interface atomic layer for LNO electrodes (the Ni-O displacement at PbO-terminated bottom interface and the La-O displacement at TiO-terminated top interface) is even larger than that in the adjacent PTO layer. The ionic polarization in SRO electrode is rather small compared with that in LNO electrode. Due to atomic-scale compensation,29 PTO sandwiched between two LNO electrodes naturally show a larger polarization than that sandwiched between SRO electrodes. For all the three types of electrodes, the PTO film with PbO-terminated interface shows a larger ferroelectric displacement than that with TiO-terminated interfaces. The Sr0.5RuO3.5/SrTiO3/PbTiO3/Sr0.5RuO3.5/ (SrO-RuO2-SrO)2/SrO system shows the lowest polarization magnitude.

Furthermore, the polarization stability for these electrode/ferroelectric/electrode capacitors is also examined. To study the polarization stability in each system, a switching path is fabricated by constructing a series of intermediate atomic configurations between negative and positive polarization states [negative polarization state (P<sup>-</sup>) is the inversely symmetrical structure of the positive polarization state (P<sup>+</sup>)] using a linear interpolation method mentioned in Ref. 30. The coordinate of atom m is described by the following formula:

\[
z_m(\lambda) = \lambda z^+_m + (1 - \lambda)z^-_m
\]

where \(z^+_m\) and \(z^-_m\) are the \(z\) coordinate of atom \(m\) in positive and negative polarized states. And the dimensionless constant \(\lambda\) equal to 0 or 1 represents the negative and positive polarization states, respectively. The total energies for the intermediate structures are calculated by fully self-consistent calculations in order to obtain the energy barriers for switching for each ferroelectric capacitor [Figs. 3(d)–3(f)]. A higher barrier for switching suggests the ferroelectric film has a better polarization stability and therefore a larger coercive field. For comparison, the ferroelectric displacements at different types of interfaces are normalized with respect to the bulk PTO ferroelectric displacement (bulk soft-mode distortion). It can be seen that the Pt, LNO, and SRO electrodes-sandwiched PTO films show energy barriers for switching with successively decreasing magnitude. And the PbO-terminated PTO films show better polarization stability.
than the TiO$_2$-terminated ones. Corresponding to its small ferroelectric polarization, SrO-(RuO$_2$-SrO)$_2$/TiO$_2$-(PbO-TiO$_2$)$_8$/(SrO-RuO$_2$)$_2$-SrO system exhibits a very low energy barrier for polarization reversal (only about 3 meV/unit cell), which is about 57 times smaller than the highest barrier in the Pt$_4$/PbO-(TiO$_2$-PbO)$_8$/Pt$_4$ system (172 meV/unit cell). This result is in accordance with the experimental observations, showing that the ferroelectric film with metallic electrodes shows a larger remanent polarization and coercive field than that with oxide electrodes$^{6,7}$ and so does the ferroelectric film with LNO electrodes than that with SRO electrodes.$^{31}$

C. Charge structures at the interface

To further reveal the interface interaction, the charge transformation between the electrodes and the PTO film is studied. The charge transformation is obtained by calculating the charge difference defined by $\rho_{\text{diff}} = \rho(\text{Capacitor}) - \rho(\text{Electrodes}) - \rho(\text{PTO})$, in which $\rho(\text{Capacitor})$, $\rho(\text{Electrodes})$, $\rho(\text{PTO})$ are the charge density of the capacitor, two freestanding electrodes, and a freestanding PTO film, respectively. Figs. 4(a) and 4(b) show the charge difference in the Pt$_4$/PbO-(TiO$_2$-PbO)$_8$/Pt$_4$ capacitor. On the bottom interface [Fig. 4(a)], the Pt and O atoms lose charge, which is redistributed between the Pt and Ti atoms, leading to the formation of a Pt-Ti alloy. On the top interface [Fig. 4(b)], however, Pt and Ti atoms lose charge, giving rise to a similar Pt-Ti charge sharing. This result is in agreement with the theoretical calculation published previously.$^{21}$ However, in the Pt$_4$/PbO-(TiO$_2$-PbO)$_8$/Pt$_4$ capacitor, there is abundant charge transfer from the Pt to O at the bottom interface [Fig. 4(c)]. This interaction leads to a strong bond between Pt and O (notice that Pt-O bond length is 1.989 Å, comparable with the Ti-O short bond). And the charge transformation at the top interface is inconspicuous [Fig. 4(d)]. The compensation effect caused by the Pt-O short bond in the PbO-terminated system is more intensive than that in the TiO$_2$-terminated one. Now, we examine the charge transformation in the oxide electrode and PTO interface. In the LaO-(NiO$_2$-LaO)$_2$/TiO$_2$-(PbO-TiO$_2$)$_8$/ (LaO-NiO$_2$)$_2$-LaO capacitor, the interfacial Ti provides charge for the O atom in the electrode at both top and bottom interfaces [Figs. 4(e) and 4(f)]. While in the NiO$_2$-(LaO-NiO$_2$)$_2$/PbO-(TiO$_2$-PbO)$_8$/(NiO$_2$-LaO)$_2$-NiO$_2$ capacitor, the Ni atom in the electrode offers abundant charge to O at both interfaces [Figs. 4(g) and 4(h)]. The amount of transformation charge from Ni to O in the PbO-terminated interface is much greater than that from Ti to O at the TiO$_2$-terminated interface. The charge transformation in the SRO-PTO interface [Figs. 4(i) and 4(j)] is similar with, but less than that in the LNO-PTO interface. This may be the reason for the smaller polarization in the SRO-sandwiched PTO.

D. Strain effect on the polarization magnitude and stability

Misfit strain induced by the single-crystalline substrate is believed to be one of the most important interface effects that significantly influence the physical properties of the epitaxial ferroelectric film.$^{32,33}$ The misfit strain from the underlying substrate is often imposed on the ferroelectric film through an epitaxial bottom electrode. In this paper, the strain-induced changes in polarization magnitude and stability for the unanimously strained electrode/PTO/electrode ferroelectric capacitors are also studied. Considering the computational cost, only the PbO-terminated capacitors are chosen to study the strain effect. $ab$-biaxial strains of $-1.5\%$ and $1.5\%$ are applied on each type of electrode/PTO/electrode ferroelectric capacitors. The misfit strain from the PbO-terminated capacitors is often imposed on the ferroelectric film through an epitaxial bottom electrode. In this paper, the strain-induced changes in polarization magnitude and stability for the unanimously strained electrode/PTO/electrode ferroelectric capacitors are also studied. Considering the computational cost, only the PbO-terminated capacitors are chosen to study the strain effect. $ab$-biaxial strains of $-1.5\%$ and $1.5\%$ are applied on each type of electrode/PTO/electrode ferroelectric capacitors, respectively. The atomic positions along the $c$ axis are relaxed in order to calculate the stable ferroelectric polarization under different strains. Fig. 5 shows the ferroelectric displacements and the energy barriers for switching in the strained films. The corresponding values for bulk PTO are
FIG. 5. The relative ferroelectric displacements (a) and energy barriers for switching (b) of the PbO-terminated capacitors under different strains. The lattice constants \(a\) (in angstrom) of a few electrodes and substrates are given by green and orange arrows, respectively. The experimental lattice constants \(a\) (in angstrom) of these three types of electrodes are marked in Fig. 5, along with a few other perovskite-oxide substrates with the aim of giving the reader an impression about the magnitude of the misfit strain on the epitaxial thin film induced by the substrate. The electrodes shown here include Pt, LNO, and SRO calculated previously. The perovskite-oxide substrates include (LaAlO\(_3\))\(_{0.29}\) (LSAT), (LaGaO\(_3\)) (LGO), (SrTiO\(_3\)) (STO), (DyScO\(_3\)) (DSO), and (GdScO\(_3\)) (GSO). The misfit strain between the lattice constants of these substrates and PTO comes from the experimental data and the simulation results using phase-field approaches. These results are in good accordance with the experimental data and the simulation results using phase-field approaches, which focus on the change in the remanent polarization and the coercive field of the perovskite ferroelectric with misfit strain.

The experimental lattice constants \(a\) (in angstrom) of a few electrodes and substrates are given by green and orange arrows, respectively. It can be seen that the ferroelectric polarizations and the energy barriers for switching for three types of capacitors are all enhanced under a compressive strain and decreased under a tensile strain. These results are in good accordance with the experimental data and the simulation results using phase-field approaches, which focus on the change in the remanent polarization and the coercive field of the perovskite ferroelectric with misfit strain.

The experimental lattice constants \(a\) (in angstrom) of three types of electrodes are marked in Fig. 5, along with a few other perovskite-oxide substrates with the aim of giving the reader an impression about the magnitude of the misfit strain on the epitaxial thin film induced by the substrate. The electrodes shown here include Pt, LNO, and SRO calculated previously. The perovskite-oxide substrates include (LaAlO\(_3\))\(_{0.29}\) × (SrAl\(_{0.5}\)Ta\(_{0.5}\)O\(_3\))\(_{0.71}\) (LSAT), (LaGaO\(_3\)) (LGO), (SrTiO\(_3\)) (STO), (DyScO\(_3\)) (DSO), and (GdScO\(_3\)) (GSO). The misfit strain between the lattice constants of these substrates and PTO comes from the experimental values.

IV. CONCLUSIONS

The effect of the electrode/ferroelectric interface on the ferroelectricity and polarization stability in ultrathin PTO films is systematically studied using DFT calculation. Six interface types between TiO\(_2\)-terminated or PbO-terminated PTO and metallic (Pt) or oxide (LaNiO\(_3\), SrRuO\(_3\)) electrodes are studied. It is found that oxide electrodes possess stronger interface adhesion with the PTO film, which is believed to be one of the origins for the better fatigue resistance in ferroelectric thin films sandwiched between two conductive oxide electrodes. However, the PTO film in contact with oxide electrodes exhibits a lower tetragonality, lower polarization magnitude, and lower energy barrier for switching than that in contact with Pt electrodes. Furthermore, the termination surface of the PTO film also significantly influences the properties of ferroelectric capacitors. The PbO-terminated PTO films show weaker interface adhesion with the electrodes, larger ferroelectric polarization and better polarization stability, than the TiO\(_2\)-terminated films. The misfit strain effects on the PTO film induced by the substrate are also studied using the PbO-terminated capacitors as the model systems. Our results show that a compressive strain can improve the ferroelectric polarization and its stability, while a tensile strain does the opposite.

ACKNOWLEDGMENTS

This work was financially supported by National Natural Science Foundation of China (Grant Nos. 11032010 and 11172257). Calculations are performed at the Research Center of Supercomputing Application, National University of Defense Technology. X. J. Lou would like to thank the “One Thousand Youth Talents” program and the Ministry of Science and Technology of China through a 973-Project under Grant No. 2012CB619401 for support.

Pt is above the oxygen atoms on the TiO$_2$-terminated surface, and above Pb and O atoms on the PbO-terminated surface as the energy stability consideration.

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