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Dead layer effect and its elimination in ferroelectric thin film with oxide electrodes

Qiong Yang [a], Juexian Cao [b, *], Yichun Zhou [a, **], Lizhong Sun [a], Xiaojie Lou [c]

[a] Key Laboratory of Key Film Materials & Application for Equipment (Hunan Province), School of Materials Science and Engineering, Xiangtan University, Xiangtan, Hunan 411105, China
[b] School of Physics and Optoelectronics, Xiangtan University, Xiangtan, Hunan 411105, China
[c] Frontier Institute of Science and Technology, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT

Interfacial dead layer effect has been widely noticed in the past and was thought to be responsible for the critical thickness of ferroelectric thin film. Despite extensive studies, the origin is still under fierce debate. The dead layer even exists at the perfect interface without defects and impurities. In this paper, we studied the effects of the electrode/ferroelectric interface on the polarization properties of nano-scale $BaTiO_3$ ferroelectric capacitors by first-principle calculation. A thin layer with reversed polarization is found in the TiO_2-teminated $LaNiO_3/BaTiO_3/LaNiO_3$ capacitor. This pinned domain with reversed polarization at the top interface of ferroelectric film acts as a dead layer and reduces the total polarization. Based on our analyses, this reversed polarization is argued to originate from the intrinsic polarization instability near the top interface of TiO_2-teminated ferroelectric thin film and an interfacial electrical field. An interface modification method has been adopted to remove such dead layer effects. Our results show that a $LaXO_3$ (X = Fe, Co) or $YNiO_3$ (Y = Sr, Ba) buffer layer can effectively remove the dead layer effect in $BaTiO_3$ film.

1. Introduction

Due to their switchable macroscopic spontaneous polarization and high permittivity, ferroelectric thin films are promising for many electronic device applications, such as dynamic random access memories, ferroelectric field-effect transistors and ferroelectric tunnel junctions [1–3]. Following the continuing demand for the miniaturization of electronic devices, ferroelectric thin-film capacitors are required to shrink to nanometer scale [4–6]. This procedure allows to achieve a lower operating voltage, but it also entails a size effect which destroys the polarization stability of ferroelectric thin films and limits their practical applications. A depolarizing field, arising from the poor screening of the ferroelectric bound polarization charge due to the polarization discontinuity at the ferroelectric surface, is believed to be the origin of size effect [7,8]. The incomplete screening and depolarization effects are virtually equivalent to adding an interface layer between the ferroelectric and the electrode which forms an extra capacitor in series with the ferroelectric one. Due to the polarization relaxation and the permittivity decrease, this interface layer is also defined as "an effective dead layer" [9]. Apart from its detrimental effects on the polarization and capacitance properties, the so-called dead layer is also believed to contribute to the formation of polydomains [10], electrical fatigue [11,12], imprint [13] and leakage problems [14] in the thin films. Consequently, the existence of dead layer greatly limits the scaling-down of ferroelectric thin films and hinders the miniaturization and integration of ferroelectric-based electronic devices.

Despite having been noticed for decades, the microscopic origin of dead layer is still a contentious issue. It was once believed that growth-introduced defect, strains gradients, grain boundaries, and dislocations [15] could account for the origin of dead layer. However, recent experimental and theoretical results showed that such interfacial dead layers present even in high-quality interfaces, where the defect density is extremely low or even close to zero. By using angle-resolved X-ray photoelectron spectroscopy and X-ray reflectivity technique, Li et al. [16] revealed a transition layer of about 9 Å at the Pt/BTO interface, and there is neither interdiffusion between BTO and Pt nor oxidation of Pt. They also indicated that the interface-induced relaxation might be the origin of the dead layer effect. Zhou and Newns [17] found that there is an intrinsic dead layer on the surface of STO dielectric film which significantly reduces the effective dielectric constant from their Thomas theory study. By using *ab initio* calculations, Stengel and Spaldin [18] also confirmed the existence of a low-permittivity layer in SRO/STO/SRO nanoscale capacitors. Their

* Corresponding author.
** Corresponding author.
E-mail addresses: jxcao@xtu.edu.cn (J. Cao), zhouyc@xtu.edu.cn (Y. Zhou).

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theoretical results suggest that the effect of dead layer is an inherent and unavoidable feature of the dielectric-metal interface. In fact, some experiments indicated that the effect of dead layer does not necessarily exist in the ferroelectric capacitors. For instance, Kim et al. [19] showed that there is no passive layer observed in ultrathin $SrRuO_3/BaTiO_3/SrRuO_3$ ferroelectric capacitors. Plonka et al. [20] also found that the permittivity of single-crystalline $Ba_{0.7}Sr_{0.3}TiO_3$ thin films depends on the types of the top-electrode materials. Chang et al. [21] demonstrated that an inherent dead layer appears in the $SrTiO_3$ single crystal thin film capacitor with Pt electrodes, while it does not exist in an analogous structure involving $BaTiO_3$. Therefore, there seems to be a conflict between the theoretical and experimental work. In specific, the experimental results from different groups sometimes differ from one another even for the capacitor structure with the same electrode/ferroelectric material combination.

By using first principles study, Stengel et al. [9] found that the existence of dead layer effect depends not only on the material combination but also the termination surface of the ferroelectric thin films. By constructing proper interface termination, they found that there could even be a "negative dead layer" in the ferroelectric capacitors. This result may provide an explanation for the aforementioned contradictories in the literature. They also argued that, the local chemical and electrostatic environment at the interface of a ferroelectric thin-film capacitor departs significantly from their parent materials, which makes a full quantum-mechanical treatment proper in describing such interface effects. By using first-principles calculation, Duan et al. [22] found that the polarization near the top interface of the NbO_2-terminated $SrRuO_3/KNbO_3/SrRuO_3$ ferroelectric capacitor was reversed by the oppositely oriented dipole moments, resulting in an interface domain wall (IDW). Wang et al. [23] showed that, under a LaO-layer-induced intrinsic electric field, the electric polarization of $BaTiO_3$ film near the surface will be pinned, pointing to the interior of the $BaTiO_3$ layer. Colla et al. [24] have directly observed the reversely blocked polarization domains at the electrode-ferroelectric interface in $Pt/Pb(Zr_{0.45}Ti_{0.55})O_3/Pt$ structure and pointed out that this may be the origin of electrical fatigue of ferroelectric films. Recently, Han et al. [25] also discovered the nonswitchable domains near the interface of $(Pt/Au)/Pb(Zr_{0.2}Ti_{0.8})O_3/Nb–SrTiO_3$ capacitor, which was attributed to the built-in interfacial electric fields. Polarization pinning caused by the interfacial electric field is further supported by the fact that the asymmetric interfaces often lead to polarization asymmetry of the ferroelectric thin film with the polarization preferring to point to one certain direction [26–28]. Though extensive studies have been conducted on the effect of dead layer, a comprehensive and profound understanding on this issue is still lacking.

The interface effect at the metal-ferroelectric heterojunction plays a key role in determining the depolarizing field and the overall ferroelectric polarization, and has become one of the focal points for ferroelectric material research in the past few years [29]. It is critical to understand the intrinsic relationship between the heterointerface and its resultant ferroelectric behavior at the nanoscale in order to artificially design the interface structure with the aim of improving the performance of ferroelectric devices. To further clarify the origin of dead layer and find the solutions for it, we studied the interface effect on the polarization of BTO ferroelectric thin film with a metal electrode Pt and a typical oxide electrode $LaNiO_3$ (LNO) by using first principles calculation.

2. Calculation details

To construct the electrode/ferroelectric/electrode system, 1×1 supercells are stacked along the BTO [001] pseudocubic direction. BTO layer is set thick enough (11.5 unit cells) to avoid the interreaction between the top and bottom interfaces. In this work, both BaO- and TiO_2-terminations of $BaTiO_3$ (BTO) thin films are investigated. These two types of BTO surface terminations combined with Pt and $LaNiO_3$ (LNO) electrodes forms four types of electrode/ferroelectric interfaces, which can be denoted as (1) BaO/Pt, (2) TiO_2/Pt, (3) BaO/LNO, (4) TiO_2/LNO, respectively. Each structure studied in this work is symmetrical and has two identical film-electrode interfaces, which means that there is no polarization asymmetry induced by the asymmetrical interfaces. The atomic structures for the four types of capacitors can be given by the following general formulas as described in our previous work [30]:

(1) $Pt_4/BaO–(TiO_2–BaO)_{11}/Pt_4$,
(2) $Pt_4/TiO_2–(BaO–TiO_2)_{11}/Pt_4$,
(3) $NiO_2–(LaO–NiO_2)_2/BaO–(TiO_2–BaO)_{11}/(NiO_2–LaO)_2–NiO_2$,
(4) $LaO–(NiO_2–LaO)_2/TiO_2–(BaO–TiO_2)_{11}/(LaO–NiO_2)_2–LaO$.

All the calculations were performed using the Vienna *Ab* Initio Simulation Package (VASP) with the projector-augmented-wave (PAW) method [31]. Exchange and correlation effects were accounted by using the local density approximation (LDA). A 400 eV plane-wave cutoff energy were used for self-consistent calculations. The $12 \times 12 \times 12$ and $6 \times 6 \times 1$ Monkhorst-Pack k-point grids [32] were used in unit cell and supercell calculations, respectively. Atomic relaxations were performed until the Hellmann-Feynman force on each atom was less than 10 meV/Å. With the above-mentioned computational setups, the lattice constant a and axial ratio c/a for the tetragonal BTO were calculated to be 3.946 Å and 1.01, respectively, which are in accurate agreement with the experimental data [33]. In order to study the effect of different interfacial electrostatic environments on the properties of the film, the in-plane lattices are all set to be the theoretical BTO value (i.e, $a = b = 3.946$ Å) in the calculation of interface systems. And open-circuit boundary conditions are imposed with a 15 Å vacuum layer. All the atomic positions are fully relaxed along the direction perpendicular to the interface.

Based on the relaxed structures of ferroelectric capacitors, the local polarization ($\boldsymbol{P}$) of each BTO cell is calculated using the Born effective charge method as defined by the following equation:

$$\boldsymbol{P} = \frac{e}{\Omega_c} \sum_n w_n \boldsymbol{Z}_n^* \cdot \boldsymbol{u}_n, \quad (1)$$

where, Ω_c and e are the unit cell volume and electron charge, respectively. n is the number of atoms in the unit cell. w_n is the weight of the n_{th} atom (1/8, 1/2 and 1 for the corner, face-centred and inner atoms, respectively). $\mathbf{u}_n$ is the ferroelectric displacement of the n_{th} atom, which can be replaced by the atomic coordinates. $\mathbf{Z}_n^*$ is Born effective charge tensor of the n_{th} atom and the value is from Zhong et al.'s calculation [34]. With this method, the spontaneous polarization of the relaxed BTO unit cell was calculated to be 27.0 $\mu C/cm^2$, which is in good agreement with the experimental data [35].

3. The origin of dead layer with reversed polarization

The relaxed structures and the local polarizations of each cell for the four BTO films are shown in Fig. 1. Clearly, one sees that the total polarization magnitude of the TiO_2-terminated film is much smaller than that of the BaO-terminated film. In specific, the polarization near the top interface of the TiO_2-terminated film is largely suppressed. For the film with a TiO_2/LaO interface, a few unit cells with reversed polarization near the top interface could even be found. This phenomenon is in accordance with the interface domain wall (IDW) found by Duan et al. [22] The reversed polarization near the top interface points to the interior of the film and is