Interfacial effects on the polarization of $BiFeO_3$ films

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Abstract

By considering an interfacial layer between the electrode and the $BiFeO_3$ (BFO) layer, the polarization and the hysteresis behavior of BFO film are simulated. It is found that the non-ferroelectric interface will increase the coercive field, and remarkably suppress the polarization of the ultrathin film under low applied fields. Due to the competition between the interfacial effect and the internal compressive stress, the maximum polarization on the P-E loop of a BFO film can be independent on the film thickness under an adequate applied field.

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I. INTRODUCTION

Recently, the perovskite-type oxides, which display ferroelectric and magnetic properties, have attracted considerable interest for their potential applications in multifunctional magnetoelectric devices\[1\]. It has been shown that \( BFO \) is a good candidate which exhibits the coexistence of ferroelectric and antiferromagnetic orders with high Curie temperature\[2\] and Néel temperature\[3\]. Numerous studies have been performed on \( BFO \) samples and especially, more recently, on thin films. Generally, bottom and top electrodes are fabricated to form a capacitor configuration for ferroelectric measurements. The physical origin of the interfacial layer has been proposed to be process-induced domain evolution or the effect of lattice misfit between the electrode and surface of the film. The interfaces in \( BFO \) film capacitors have already been verified by using X-ray diffraction and scanning transmission electron microscope high-angle annular dark-field imaging\[4\], and the effect of the interface on the dielectric behavior of \( BFO \) film capacitor was also investigated in experiment\[5\]. For epitaxial system, the substrate-induced strains have been proven to have great influence on the ferroelectric properties of ferroelectric material\[6\]. The previous studies show that substrate-induced strains can lead to a substantial increase in spontaneous polarization for BFO films\[7, 8, 9\]. The mechanical substrate effects and thickness dependence of ferroelectric properties in epitaxial BFO films are investigated within the framework of Landau-Devonshire theory. Although the interface between the electrode and the BFO layer has been reported in experiment\[4, 10\], there is no theoretical investigation of the interfacial effect on the polarization of BFO film. In this paper, the interfaces between electrode and \( BFO \) layer are considered with different film thickness. It is found that the interface will have great influence on the polarization and the hysteresis behavior of ultrathin \( BFO \) films. Due to the interfacial effect, the maximum polarization on the P-E loop of thin film can be lower(or higher) than that of thickness film, and the maximum polarization can also be thickness-independent through the competition between the interfacial effect and the compressive stress under an adequate applied field.
II. MODEL AND THEORY

Here, we consider a BFO film grown on SrTiO$_3$ substrate with a bottom SrRuO$_3$ electrode and a top Pt electrode\cite{11,12}. It is known that there is a clear and sharp interface between BFO layer and the bottom SrRuO$_3$ electrode, and a rough, inter-diffused interface between BFO layer and the top Pt electrode, which can be confirmed by the cross-section HR-TEM image\cite{4,10}. It is reasonable that the interface between BFO and the bottom electrode can be neglected for simplicity. Therefore, we simulate the BFO film by a ferroelectric layer with a top non-switching interface, and investigate the effects of the interface on the P-E loop with different film thickness. The electric displacement across BFO layer is given by

$$D_f = \varepsilon_f E_f + P_f,$$

where $\varepsilon_f$, $E_f$ and $P_f$ denote the permittivity, the local electric field and the spontaneous polarization of BFO layer, respectively. The electric displacement across the interface is $D_{in} = \varepsilon_{in} E_{in}$, where $\varepsilon_{in}$ and $E_{in}$ stand for the permittivity and the local electric field of interface. The applied field $E_{ex}$ can be written as

$$E_{ex} = (1 - v_{in})E_f + v_{in}E_{in}, \quad (1)$$

where $v_{in}$ is the thickness ratio of interface. The continuity of the total current density across the film can be expressed as

$$J = \sigma_{in}E_{in} + \varepsilon_{in}\dot{E}_{in} = \sigma_fE_f + (\varepsilon_f + \frac{\partial P_f}{\partial E_f})\dot{E}_f. \quad (2)$$

Combining Eq. (1) with Eq. (2), we obtain

$$\sigma_{in}E_{ex} + \varepsilon_{in}\dot{E}_{ex} = [(1 - v)\sigma_{in} + v\sigma_f]E_f$$

$$+ [v(\varepsilon_f + \chi_f) + \varepsilon_{in}(1 - v)]\dot{E}_f, \quad (3)$$

where $\sigma_{in}$ and $\sigma_f$ are the conductivities of top interface and BFO layer, respectively, $\chi_f$ is the electric susceptibility of BFO layer, which equals $\partial P_f/\partial E_f$\cite{13}

$$\chi_f = P_f\{2\delta cosh^2[(E_f - E_c)/2\delta]\}^{-1},$$

$$\delta = E_c[\log(1 + P_{fs}/P_{fr})/P_{fs}]^{-1}, \quad (4)$$

where $P_{fr}$, $P_{fs}$ and $E_c$ denote the remanent polarization, saturate polarization and coercive field of BFO layer, respectively, which can be determined through Landau-Devonshire theory\cite{8}. 

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The BFO films with different thickness are supposed to grow on (001)-oriented SrTiO$_3$ substrate. A tetragonal structure of BFO thin film based on cubic perovskite structure with symmetry lowered to P4mm (neglect the small monoclinic distortion of about 0.5° of c axis) is suggested with an elongated c axis [14]. The polarization for such a single phase is along with c axis. The thermodynamic potential of pseudo cubic BFO film is expressed as the function of magnetization $M_f$, polarization $P_f$, temperature $T$ and misfit strain $u_m = (a_s - a_0)/a_s$, where $a_s$ is the in-plane lattice parameter for substrate and $a_0$ is the equivalent cubic lattice constant of free standing film. We do not include the magnetic effect and the coupling between magnetic order and ferroelectric order, owing to a relative weak magnetic order compared to the stronger ferroelectric one. The thermodynamic potential of BFO layer can be written as following,

$$\tilde{F}(P_f, T) = \alpha_1^* P_f^2 + \alpha_{11}^* P_f^4 + \alpha_{111}^* P_f^6 - E_f P_f + \frac{u_m^2}{S_{11} + S_{12}},$$

(5)

where $\alpha_1^* = \alpha_1 + u_m \frac{Q_{12}^E}{S_{11} + S_{12}}$, $\alpha_{11}^* = \alpha_{11} + \frac{(Q_{12}^E)^2}{S_{11} + S_{12}}$, $Q_{ij}^E$ is the electrostrictive coefficient, $S_{ij}$ is the elastic compliances, and the dielectric stiffness coefficient $\alpha_1 = (T - T_c)/2\varepsilon_0 C$. The equilibrium state polarization $P_f$ under a local field $E_f$, $P_{fr}$ and $P_{fs}$ in Eq. (4) can be numerically resolved from Eq. (5) by $\partial \tilde{F}/\partial P_f = 0$,

$$2\alpha_1^* P_f + 4\alpha_{11}^* P_f^3 + 6\alpha_{111} P_f^5 - E_f = 0.$$  

(6)

In order to introduce the misfit strain into the epitaxial BFO film, an effective substrate lattice parameter $\tilde{a}_s$ is defined as $\tilde{a}_s = \frac{a_s(T)}{\rho a_s(T) + 1}$, which is used to calculate the misfit strain $u_m$ instead of actual substrate lattice parameter $a_s$, and $u_m = \frac{\tilde{a}_s(T) - a_0(T)}{\tilde{a}_s(T)}$. $\rho$ is the equilibrium linear misfit dislocation density at the deposition temperature $T_G$. $\rho = \frac{u_m(T_G)}{a_0(T_G)(1 - h_p)},$ where $h_p$ is the critical film thickness corresponding to the generation of misfit dislocation. All the coefficients in Landau expansion used in this letter are given in Ref. [15].

### III. NUMERICAL RESULTS AND DISCUSSIONS

From Eq. (6), we calculate the spontaneous polarization $P_f$ without considering the interface. The hysteresis behavior of the single BFO layer is shown in Fig. 1, where solid line stands for the hysteresis loop of the 77-nm-thick film, and dotted line for the 960-nm-thick film. The remanent polarization of the 960nm BFO film is $64\mu C/cm^2$, which is close to the...
polarization of single crystal\[16\]. We can see that the spontaneous polarization increases as the thickness decreases, and our results are qualitatively consistent with previous theoretical works\[7, 8\]. It is obviously that the compressive stress between $\text{BFO}$ layer and substrate $\text{SrTiO}_3$ will remarkable increase the polarization, and the spontaneous polarization $P_f$ will increase with the decrease of thickness. However, as observed by AFM\[4\] and simulated by the capacitor configuration\[5\], there really exists an interface between top electrode and $\text{BFO}$ layer. So, the measured polarization is not the polarization of a single ferroelectric layer. In the following, an interface between the top $\text{Pt}$ electrode and $\text{BFO}$ layer is introduced, and two $\text{BFO}$ film samples of thickness 77nm and 960nm are selected in our simulation\[7\]. The dielectric constant and the conductivity of the $\text{BFO}$ layer are selected as 100\[17\] and $1 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$\[11\], respectively. Due to the interface is formed between the metal material and $\text{BFO}$ layer, we assume its conductivity and dielectric constant take the values of $1 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$\[5\] and 20. The thickness of interface is introduced by taking into account the thickness ratio of interface to $\text{BFO}$ layer. The ratio $v$ will increase as the decrease of film thickness, and the ratios $v$ are taken as 0.02 and 0.002 for the two samples.

For a given sinusoidal field $E_{ex}$, the effective field $E_f$ can be calculated from Eq. (3) as a function of time $t$. Then the polarization $P_f$ at the $m$th increment in time is calculated by using $P_{fm} = P_{fm-1} + (E_{fm} - E_{fm-1}) \frac{\partial P_f}{\partial E_f}|_{m-1}$. The simulated hysteresis loops corresponding to different applied fields are shown in Fig. 2, the frequency of the applied field in our simulation is 2kHz. The solid lines in Fig. 2 denote the loops of 77-nm-thick film, and the dotted lines stand for the loops of 960-nm-thick film. From Fig. 2(a) to (d), the maximum field are selected as 1.0 MV/cm, 1.25 MV/cm, 1.6 MV/cm and 2.5 MV/cm, respectively. By taking into account the interface, the local field $E_f$ will decrease as the decrease of thickness.
under the same applied field. For the 960-nm-thick film, due to the small proportion of the interface component, the local field $E_f$ is close to the applied field, and the P-E loop is already saturated in Fig. 2(a), whereas the P-E loop for 77-nm-thick film does not saturated, and the maximum polarization on the P-E loop is smaller than the saturated polarization of 960-nm-thick film. One can see, from Fig. 1 and Fig. 2(a), that the interface will great suppress the polarization of the ultrathin film, and the interfacial effect of an ultrathin film is more important than the internal stress effect under a low applied field. For a selected applied field $E_{max}=1.25$ MV/cm in Fig. 2(b), the maximum polarization on the P-E loop is independent on the thickness of the film, which is the consequence of the competition between the interfacial effect and the internal compressive stress effect. In Fig. 2(c), the maximum polarization of the ultrathin film is larger than that of the thick film, which had also been observed in experiment(See Fig. 4(d) in Ref. [18]), and it shows that the interfacial effect is less dominant for the ultrathin film under a high applied field. As further increasing the maximum field, the polarizations for the two samples are both saturated, and the saturated polarization of the 77-nm-thick film is larger than that of the 960-nm-thick film. In addition, the P-E loops for materials such as $BFO$ film are often dominated by leakage current, and the saturated P-E curve in Fig. 2(d) for an ultrathin film can only be observed for samples with high resistivity and high breakdown field.

In summary, the epitaxial $Pt/BFO/SrRuO_3/SrTiO_3$ film is simulated by a multilayer model which takes the effect of interface. It is found that the existence of interfacial layer will increase the coercive field, and change the shape of the P-E loop, especially for an
ultrathin film. The P-E loop will become more slant for the ultrathin film, which is resulted from the decreasing of the effective field in $BFO$ layer. For different maximum fields, the maximum polarization of the ultrathin film can be smaller (or larger) than that of the thick film. For an adequate applied field, the maximum polarization on the P-E loop could be thickness-independent, and the origin is caused by the competition between the interfacial effect and the internal compressive stress. It is concluded that the effect of interface between the electrode and $BFO$ layer has great influence on the polarization of $BFO$ film. When measuring the saturated P-E loops for multiferroic ultrathin films with metal contacts, one should apply a field large enough to saturate the polarization.

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[15] List of parameters in the calculation of spontaneous polarization in Eq. (6) are selected as[8].

\[
T_C = 830^\circ C, \ C = 2.45525 \times 10^7 \circ C, \ \alpha_{11} = 6.4 \times 10^6 m^5/C^2 F, \ \alpha_{111} = 6 \times 10^5 m^9/C^4 F, \\
S_{11} = 4.35 \times 10^{-12} m^2/N, \ S_{12} = -4 \times 10^{-12} m^2/N, \ a_s(T) = 3.905, \ a_0(T) = 3.962, \ TEC = 10.0 \times 10^{-6} K^{-1} \ and \ h_p = 10nm \ for \ BFO \ thin \ film, \ and \ TEC = 11.7 \times 10^{-6} K^{-1} \ for \ SrTiO_3 \ substrate.
\]

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Figure Captions

FIG1: Polarization of BFO layer as a function of the applied field without considering the interface.

FIG2: P-E loop of BFO film with interface for different applied fields. Solid lines correspond to the 77-nm-thick film, and the dotted lines correspond to the 960-nm-thick film.