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Analysis of multi-domain ferroelectric switching in $BiFeO_3$ thin film using phase-field method

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ABSTRACT

A phase-field model is developed to elucidate the process of polarization switching in $BiFeO_3$ thin film. The results demonstrated an energy-favorable mechanism for domain switching path and revealed possible ferroelectric domain switching modes. It is shown that 71° switching is dominant among the three possible switching paths, namely 71°, 109° and 180° switching. This might provide significant references for the application of ferroelectric materials under electric fields.

1. Introduction

During the past decades, ferroelectric oxides have attracted growing attention in materials research. They exhibit many interesting properties that could be utilized in memories, actuators, sensors, and multiferroic devices. There are usually two or more easy polarization directions coexisting in one crystal. The switching of the polarization occurs between different easy directions under an applied electric field [1–5]. The switching process is complex and depends on the interrelationship between the external electric field and polarizations, the interaction and competition among different electric domains, etc. The orientations of domains and switching of polarizations have crucial impacts on the physical properties of ferroelectrics. Therefore, studying the switching process of multi easy-axis materials is important for their applications.

$BiFeO_3$ (BFO), one of the most studied ferroelectric materials, exhibits both ferroelectric and antiferromagnetic characteristics at room temperature [1–3]. The crystal structure of ferroelectric BFO below Curie temperature is rhombohedral with its spontaneous ferroelectric polarization along the $\langle 1\,1\,1\rangle_c$ diagonal directions of a pseudocubic cell [4,5]. Geometrically, each cell has four diagonals. For each diagonal, the polarization has two possible directions that are opposite to each other. Therefore, there are eight possible polarization orientations altogether for a rhombohedral structure BFO. These possible variants, shown in Fig. 1, are labeled as: $R_1^{\pm} = \pm[1\,1\,1]_c$, $R_2^{\pm} = \pm[\bar{1}\,1\,1]_c$, $R_3^{\pm} = \pm[\bar{1}\,\bar{1}\,1]_c$, and $R_4^{\pm} = \pm[1\,\bar{1}\,1]_c$, with the signs indicating upward or downward polarizations. When an external electric field is applied, ferroelectric variants will change their orientations toward the electric-field-favorable directions, and accordingly giving rise to a multi-domain switching process. For the domain switching in a rhombohedral crystal or thin films, there are three possible paths, which are usually named on the basis of the angle between the polarization vectors before and after switching. These three paths are shown in Fig. 2. If one component of the diagonal polarization is reversed, the angle between the polarization vectors before and after switching is about 71° and the switching path is named as 71° switching. When two components are reversed, the angle is 109°; and when all three components of the polarization are reversed, it is a 180° switching. In ferroelectric materials, 71° switching and 109° switching will change the lattice structure of the material, as a result, change the direction of closely interlinked magnetic moments. This coupling consequently leads to the modulation of ferromagnetic/antiferromagnetic ordering via ferroelectric polarization switching.

In experiments, piezoresponse force microcopy (PFM) and transmission electron microscopy (TEM) are commonly used to investigate the ferroelectric domain structures [6–12], as well as the electric-field-induced domain switching [13–17]. Statistical analysis of interfacial polarization angles has been done based on PFM domain mapping results, showing that 71° domain wall is the dominant one [13]. By combining out-of-plane and in-plane piezoresponse data, it was observed that 71° rotation is the

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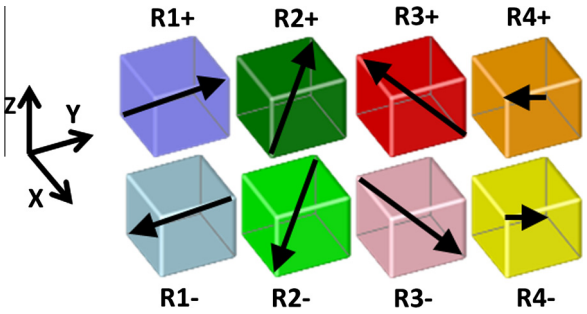

Fig. 1. Eight possible polarization orientations in rhombohedral $BiFeO_3$ film.

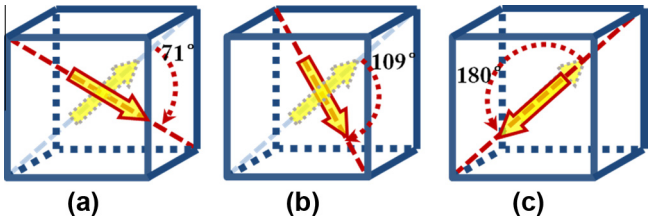

Fig. 2. Summary of the three polarization switching paths for rhombohedral $BiFeO_3$ thin films: (a) 71° switching, with only one polarization component changing its direction; (b) 109° switching, with two polarization components changing their directions; (c) 180° switching, with a flip of the polarization direction. The grey dashed hollow arrows in each unit cell show the original polarization direction, while the red solid hollow arrows represent the polarization after switching. Dashed curve arrows serve as the aid of eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

preferred switching path [13–16]. Theoretically, first-principle methods were used to study the domain wall energies and structures, which are crucial factors for switching dynamics [18–20]. Phase-field method has also been used to investigate the domain switching behavior of ferroelectric BFO films, [21–25]. Wang et al. [22] systematically studied the polarization switching as a function of electric field or a stress field during the cubic to tetragonal transition. Ashraf and Salahuddin [23] developed an extended micro scale phase-field model to study ferroelectric domain switching in multiferroic BFO with the electrical and mechanical boundary conditions.

Although many experimental and computational studies have been performed on domain morphology and switching behavior in ferroelectric thin films, there is still a lack of knowledge on the fundamental physics of multi-domain switching dynamics. This article reports a phase-field study of multi-domain switching processes and switching paths under out-of-plane external electric fields in a ferroelectric BFO epitaxial thin film. The rest of the paper is organized as follows: Section 2 describes the phase-field model system and main parameters of ferroelectric BFO; Section 3 discusses the features of electric-field-induced domain switching and corresponding temporal evolution of variant volume fraction, as well as the influences of different kinds of external electric fields, including static and time-dependent electric fields; Section 4 summarizes the paper and draws the conclusions.

2. Phase-field modeling

In the present phase-field model, the ferroelectric domain structure is described by the spatial distribution of local ferroelectric polarization vectors $\boldsymbol{P} = (P_1, P_2, P_3)$, where P_i ($i = 1, 2, 3$) represents the component on each axis respectively. The temporal evolution of the domain structure is obtained by solving the following Time-Dependent Ginzburg–Landau (TDGL) equations [21,24,25] using semi-implicit Fourier spectral method [26]:

$$\frac{\partial P_i(t)}{\partial t} = -L\frac{\delta F}{\delta P_i} \tag{1}$$

where L is the kinetic coefficient related to the domain evolution; F denotes the total free energy of a multi-domain ferroelectric thin film and is given by [25]:

$$F = F_{bulk} + F_{grad} + F_{elastic} + F_{elec} \tag{2}$$

where F_{bulk} is the bulk free energy, which is written as a 4th order polynomial expansion of the polarization components P_i:

$$F_{bulk} = \int [\alpha_1(P_1^2 + P_2^2 + P_3^2) + \alpha_{11}(P_1^4 + P_2^4 + P_3^4) + \alpha_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2)]dV \tag{3}$$

where α_1, α_{11}, and α_{12} are Landau coefficients and α_1 is related to the transition temperature and susceptibility based on Curie–Weiss law.

F_{grad} is the gradient energy, which represents the energy arising from the polarization gradient across domain walls and is written as:

$$F_{grad} = \int \frac{1}{2}G_{11}[(P_{1,1})^2 + (P_{1,2})^2 + (P_{1,3})^2 + (P_{2,1})^2 + (P_{2,2})^2 + (P_{2,3})^2 + (P_{3,1})^2 + (P_{3,2})^2 + (P_{3,3})^2]dV \tag{4}$$

Here G_{11} is the gradient energy coefficient, $P_{i,j} = \frac{\partial P_i}{\partial x_j}$, $(i,j = 1,2,3)$.

$F_{elastic}$ is the elastic energy:

$$F_{elastic} = \frac{1}{2}\int c_{ijkl}e_{ij}e_{kl}dV \tag{5}$$

Here c_{ijkl} is the elastic stiffness tensor, e_{ij} is the elastic strain which is calculated from $e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0$, ε_{ij} is the total strain of the bulk compared to the parent paraelectric phase, and ε_{ij}^0 is the stress-free strain, induced by the spontaneous polarization. The total strain ε_{ij} and elastic stress ($\sigma_{ij} = C_{ijkl}(\varepsilon_{ij} - \varepsilon_{ij}^0)$) are obtained by solving the mechanical equilibrium equation

$$\sigma_{ij,j} = 0 \quad (i,j = 1 \sim 3) \tag{6}$$

Detailed calculation of strain is described in Ref. [25].

F_{elec} is the electrostatic energy:

$$F_{elec} = -\int \left(E \cdot P + \frac{1}{2}\varepsilon_b E^2\right)dV \tag{7}$$

where E is the electric field that is related to the electric potential through $E_i = -\phi_{,i}$ ($i = 1 \sim 3$) and ε_b is the background dielectric constant [27]. The electric potential and electric field are obtained by solving the electrostatic equilibrium equation [28].

To study the domain structure, we established a model with a BFO thin film epitaxially grown on a substrate, as shown in Fig. 3. A homogeneous electric field was applied perpendicular to the film along the z-axis. In the film-substrate model shown in Fig. 3, periodic boundary conditions are applied along X_1 and X_2 axes. The top surface of the film is assumed to be stress-free, and the bottom surface is constrained by the substrate. Effect of strain on domain structures and spontaneous polarization of BFO thin film has previously been reported [21]. In this work we mainly focus on the influence of an external electric field on multi-domain switching.

In the simulation, a discretized size of $128\Delta \times 128\Delta \times 32\Delta$ was used, where Δ is the grid size. The grid size is related to real size via the information on the domain wall energy. In the present work, Δ is set as 1 nm, hence the thickness of the film