Analysis of Multi-domain Ferroelectric Switching in BiFeO₃ 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 BiFeO₃ 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.

Key Words: Phase-field Method, Ferroelectric, Bismuth ferrite, Polarization switching

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^{1-3, 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 temperature¹⁻³. The crystal structure of ferroelectric BFO below Curie temperature is rhombohedral with its spontaneous ferroelectric polarization along the $\langle 111 \rangle_c$ diagonal directions of a pseudocubic cell⁴⁻⁵. 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 Figure 1, are labeled as: $R_1^\pm = \pm[111]_c$, $R_2^\pm = \pm[\bar{1}11]_c$, $R_3^\pm = \pm[\bar{1}\bar{1}1]_c$, and $R_4^\pm = \pm[1\bar{1}\bar{1}]_c$, 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 Figure 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.

Figure 1: Eight possible polarization orientations in rhombohedral BiFeO_3 film.

Figure 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.

In experiments, piezoresponse force microscopy (PFM) and transmission electron microscopy (TEM) are commonly used to investigate the ferroelectric domain structures⁶⁻¹², as well as the electric-field-induced domain switching¹³⁻¹⁷. Statistical analysis of interfacial polarization angles has been done based on PFM domain mapping results, showing that 71° domain wall is the dominant one¹³. By combining out-of-plane and in-plane piezoresponse data, it was observed that 71° rotation is the preferred switching path¹³⁻¹⁶. Theoretically, first-principle methods were used to study the domain wall energies and structures, which are crucial factors for switching dynamics¹⁸⁻²⁰. Phase-field method has also been used to investigate the domain switching behavior of ferroelectric BFO films²¹⁻²⁵. 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 *et. al.*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 $\mathbf{P}=(\mathbf{P}_1, \mathbf{P}_2, \mathbf{P}_3)$, where $\mathbf{P}_i(i=1,2,3)$ 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 method²⁶:

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

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 by²⁵:

$$F = F_{bulk} + F_{grad} + F_{elastic} + F_{elec} \quad (2)$$

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

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

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:

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

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:

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

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 ($\sigma_{ij} = C_{ijkl}(\varepsilon_{kl} - \varepsilon_{kl}^0)$) are obtained by solving the mechanical equilibrium equation

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

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

F_{elec} is the electrostatic energy:

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

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 constant²⁷. The electric potential and electric field are obtained by solving the electrostatic equilibrium equation²⁸.

To study the domain structure, we established a model with a BFO thin film epitaxially grown on a substrate, as shown in Figure 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 reported²¹. In this work we mainly focus on the influence of an external electric field on multi-domain switching.

Figure 3: Schematic illustration of ferroelectric BiFeO_3 thin film model. Short circuit electrical boundary condition was used in the simulation.

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 in the simulation is 32 nm, the temperature is chosen as $T=298$ K. The material parameters used in the simulations for calculating energies of BFO thin film are²⁵: $\alpha_1 = 4.9 \times (T - 1103) \times 10^5 \text{ C}^{-2}\text{m}^2\text{N}$, $\alpha_{11} = 6.5 \times 10^8 \text{ C}^{-4}\text{m}^6\text{N}$, $\alpha_{12} = 1.0 \times 10^8 \text{ C}^{-4}\text{m}^6\text{N}$, $Q_{11} = 0.032 \text{ C}^{-2}\text{m}^4$, $Q_{12} = -0.016 \text{ C}^{-2}\text{m}^4$, $Q_{44} = 0.02 \text{ C}^{-2}\text{m}^4$, $c_{11} = 302\text{GPa}$, $c_{12} = 162\text{GPa}$, $c_{44} = 68\text{GPa}$, in which T is the temperature in Kelvin.

3. Electric-field-induced ferroelectric multi-domain switching

To get a general analysis on electric-field-induced ferroelectric multi-domain switching in BFO thin film, two scenarios are considered including applications of static electric field and time-dependent electric field.

3.1. Static electric field

We discussed the domain switching in BFO from an initial multi-domain state under a downward average electric field of 500 kV/cm, which was realized by applying a static electric potential on the top surface of the film and the value was chosen from experiments¹³. The initial domains for switching were generated by evolving TDGL equation of ferroelectric materials for 2000 time steps from a paraelectric phase. It should be noted that the rhombohedral BFO has eight equivalent polarization directions. However, the fractions of each of the eight domain variants are not equal at final state in this work. This could be attributed to the limited size of the simulation.

Figure 4: (a) Static electric field applied on the film; (b) volume fraction evolution for 8 variants; (c) the switching rate: red line represents 71° switching path; green line represents 109° switching; blue line represents 180° switching. Calculated domain structures of the top layer are inserted to show the evolution process.

As shown in Figure 4(b), once the static electric bias was applied, four field-favorable domains (R_1^- , R_2^- , R_3^- , and R_4^-) grew remarkably in volume fraction while the four field-unfavorable domains (R_1^+ , R_2^+ , R_3^+ , and R_4^+) decreased to almost 0. After 4000 steps, the domain switching slowed down and almost reached steady state.

To describe the dynamics of switching process, we defined the switching rate as the number of grid points that changed their polarization directions within the most recent 100 time steps. This time interval was selected considering both calculation efficiency and evolution stability. The evolution of switching rate for 3 switching paths under a static electric field is shown in Figure 4(c). Once the electric field was applied at 2000 steps, the whole switching process took place in a very short time, as seen in Figure 4(c). Meanwhile, the amount of 71° and 109° switching had a peak, which is especially obvious for 71° rotation. As we can see from Figure 4(c), 71° switching is predominant in multi-domain switching. On the other hand, the 180° switching is hardly seen before and after the electric field was applied.

3.2. Time-dependent electric field

In order to better understand the ferroelectric multi-domain switching process and analyze factors that influence the switching, two separate simulations with linearly changing electric fields along two opposite directions were discussed. Compared with the results of static electric fields, the switching rate of polarization under linear changing fields is much smoother.

Figure 5: Profile of the time-dependent volume fraction (a) downward electric field and (b) upward electric field, the positive sign represents direction of the field along z -axis; volume fraction evolution for the 8 variants under (c) downward field and (d) upward field; the switching rate under (e) downward field and (f) upward field, different color lines represent different switching paths. Calculated domain structures of the top layer are inserted to show the

evolution process.

Multi-domain switching under changing electric fields is shown in Figure 5. Similar to results in static electric field, 71° switching is dominant in the switching process. Comparing Figure 5(c) and Figure 5(d), although electric fields are in opposite directions, the switching behaviors of multi-domain in thin films are alike; for both cases, field-favorable polarizations grown and field-unfavorable polarizations decreased. It is noted that there were differences between the volume fractions of each equivalent variant at the final state. The reason is that the number of the variants in size confined system is limited due to the coarsening process. The orientation of the largest variant depends on the initial state. We obtained different variants distribution by changing the initial random noise in our simulation. Although the variant distribution is different for different initial condition, the probability of the largest variant along each axis is the same. Taking the domain distribution at the step 2000 as the starting point of applying electric field along a symmetry direction to the four easy axes, we finally obtained different domain evolution. However, all the cases have same switching path—mainly 71° switching, and the switching rate vs. applied field is insensitive to the initial conditions.

(a)

(b)

Figure 6: Upward electric fields (red solid line) with different increasing rate were applied on the film. Black dotted lines show the time when electric field reaches its maximum value, i.e. 500kV/cm. Profiles of (a) and (b) are variant fractions and switching rates under the electric field with the changing rate of 0.1kV/(cm •step) respectively. Profiles of (c) and (d) are variant fractions and switching rates under the electric field with the changing rate of 0.2 kV/(cm •step).

Apart from the domain orientation, the influence of the increasing rate of electric field on switching behavior was also studied. Figure 6 shows the temporal evolution for volume fraction of the eight variants and polarization-switching rate for three switching paths. In these cases, electric fields increased to maximum at different increasing rate: as shown in Figures 5(d) (f), it took 10000 steps to get to the maximum value of 500kV/cm; the needed time step is 5000 in Figures 6(a) (c), and 2500 in Figures 6(b) (d). Comparing variants fraction evolutions in Figure 6(a) and Figure 6(c), it can be observed in Figure 6(a) that although the increase of the electric field had stopped, fractions of variants are still changing, and these changes are even obvious in the case in Figure 6(c), the case with a faster increasing electric field. On the other hand, for polarization switching rates in Figure 6(b) and Figure 6(d), 71° switching is the primary switching path for polarization; for a lower increasing rate, shown in Figure 6(b), the switching almost finished when electric field reached its maximum value; while in a high increasing rate, Figure 6(d), switching was still drastic at same condition, which means the polarization switching cannot catch up with the increasing electric field. The lag is proportional to the increasing rate of the electric field. These results show that choosing appropriate electric field increasing rate is an important factor in ferroelectric domain switching

design.

4. Conclusions

Phase-field simulations were employed in this work to investigate the electric-field-induced ferroelectric multi-domain switching process in rhombohedral BFO thin films. The application of a static potential would bring about an abrupt proportion change among all the 8 variants at the very beginning of the field application. Detailed temporal evolution of volume fraction for eight variants and changing rates for three switching types (71° , 109° , and 180°) are presented. The results show that in the presence of a vertical electric field, 71° domain switching is predominant and 180° rotation is hardly observed, which is in good agreement with experimental results¹³⁻¹⁸. Furthermore, results of polarization switching under different changing rate electric field showed that a faster increasing field can cause a flipping lag in the switching process.

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Reference

- 1 Scott, J. F. (2007). Applications of modern ferroelectrics. *Science (New York, N.Y.)*, 315(5814), 954–9. doi:10.1126/science.1129564
- 2 Catalan, G., & Scott, J. F. (2009). Physics and Applications of Bismuth Ferrite. *Advanced Materials*, 21(24), 2463–2485. doi:10.1002/adma.200802849
- 3 Sando, D., Barthélémy, a, & Bibes, M. (2014). BiFeO₃ epitaxial thin films and devices: past, present and future. *Journal of Physics: Condensed Matter*, 26(47), 473201. doi:10.1088/0953-8984/26/47/473201
- 4 Kubel, F., & Schmid, H. (1990). Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite BiFeO₃. *Acta Crystallographica Section B: Structural Science*, 46(6), 698–702.
- 5 Zavaliche, F., Yang, S. Y., Zhao, T., Chu, Y. H., Cruz, M. P., Eom, C. B., & Ramesh, R. (2006). Multiferroic BiFeO₃ films: domain structure and polarization dynamics. *Phase Transitions*, 79(12), 991–1017. doi:10.1080/01411590601067144
- 6 Safi, R., & Shokrollahi, H. (2012). Physics, chemistry and synthesis methods of nanostructured bismuth ferrite (BiFeO₃) as a ferroelectro-magnetic material. *Progress in Solid State Chemistry*, 40(1-2), 6–15. doi:10.1016/j.progsolidstchem.2012.03.001
- 7 Vasudevan, R. K., Jesse, S., Kim, Y., Kumar, a., & Kalinin, S. V. (2012). Spectroscopic imaging in piezoresponse force microscopy: New opportunities for studying polarization dynamics in ferroelectrics and multiferroics. *MRS Communications*, 2(03), 61–73. doi:10.1557/mrc.2012.15
- 8 Andrzejewski, B., Molak, a., Hilczer, B., Budziak, a., & Bujakiewicz-Korońska, R. (2013). Field induced changes in cycloidal spin ordering and coincidence between magnetic and electric anomalies in BiFeO₃ multiferroic. *Journal of Magnetism and Magnetic Materials*, 342, 17–26. doi:10.1016/j.jmmm.2013.04.059
- 9 Ren, W., Yang, Y., Diéguez, O., Íñiguez, J., Choudhury, N., & Bellaiche, L. (2013). Ferroelectric Domains in Multiferroic BiFeO₃ Films under Epitaxial Strains. *Physical Review Letters*, 110(18), 187601. doi:10.1103/PhysRevLett.110.187601
- 10 Jia, C.-L., Jin, L., Wang, D., Mi, S.-B., Alexe, M., Hesse, D., ... Urban, K. W. (2015). Nanodomains and nanometer-scale disorder in multiferroic bismuth ferrite single crystals. *Acta Materialia*, 82, 356–368. doi:10.1016/j.actamat.2014.09.003
- 11 Chen, Z., Zou, X., Ren, W., You, L., Huang, C., Yang, Y., ... Chen, L. (2012). Study of strain effect on in-plane polarization in epitaxial BiFeO₃ thin films using planar electrodes. *Physical Review B*, 86(23), 235125. doi:10.1103/PhysRevB.86.235125
- 12 Huang, Y. T., Fu, X. L., Zhao, X. H., & Tang, W. H. (2013). A Review of the Influential Factors on the Ferroelectric Domain Structure in BiFeO₃ Thin Films. *Key Engineering Materials*, 544, 219–225. doi:10.4028/www.scientific.net/KEM.544.219
- 13 Desmarais, J., Ihlefeld, J. F., Heeg, T., Schubert, J., Schlom, D. G., & Huey, B. D. (2011). Mapping and statistics of ferroelectric domain boundary angles and types. *Applied Physics Letters*, 99(16), 162902. doi:10.1063/1.3643155

- 14 Pantel, D., Chu, Y.-H., Martin, L. W., Ramesh, R., Hesse, D., & Alexe, M. (2010). Switching kinetics in epitaxial BiFeO₃ thin films. *Journal of Applied Physics*, 107(8), 084111. doi:10.1063/1.3392884
- 15 Zavaliche, F., Shafer, P., Ramesh, R., Cruz, M. P., Das, R. R., Kim, D. M., & Eom, C. B. (2005). Polarization switching in epitaxial BiFeO₃ films. *Applied Physics Letters*, 87(25), 252902. doi:10.1063/1.2149180
- 16 Nelson, C. T., Gao, P., Jokisaari, J. R., Heikes, C., Adamo, C., Melville, A., ... Pan, X. (2011). Domain dynamics during ferroelectric switching. *Science (New York, N.Y.)*, 334(6058), 968–71. doi:10.1126/science.1206980
- 17 Vasudevan, R. K., Matsumoto, Y., Cheng, X., Imai, a, Maruyama, S., Xin, H. L., ... Nagarajan, V. (2014). Deterministic arbitrary switching of polarization in a ferroelectric thin film. *Nature Communications*, 5, 4971. doi:10.1038/ncomms5971
- 18 Lubk, A., Gemming, S., & Spaldin, N. (2009). First-principles study of ferroelectric domain walls in multiferroic bismuth ferrite. *Physical Review B*, 80(10), 104110. doi:10.1103/PhysRevB.80.104110
- 19 Diéguez, O., Aguado-Puente, P., Junquera, J., & Íñiguez, J. (2013). Domain walls in a perovskite oxide with two primary structural order parameters: First-principles study of BiFeO₃. *Physical Review B*, 87(2), 024102. doi:10.1103/PhysRevB.87.024102
- 20 Wang, Y., Nelson, C., Melville, A., Winchester, B., Shang, S., Liu, Z.-K., ... Chen, L.-Q. (2013). BiFeO₃ Domain Wall Energies and Structures: A Combined Experimental and Density Functional Theory+U Study. *Physical Review Letters*, 110(26), 267601. doi:10.1103/PhysRevLett.110.267601
- 21 Winchester, B., Wu, P., & Chen, L. Q. (2011). Phase-field simulation of domain structures in epitaxial BiFeO₃ films on vicinal substrates. *Applied Physics Letters*, 99(5), 052903. doi:10.1063/1.3605674
- 22 Wang, J., Shi, S.-Q., Chen, L.-Q., Li, Y., & Zhang, T.-Y. (2004). Phase-field simulations of ferroelectric/ferroelastic polarization switching. *Acta Materialia*, 52(3), 749–764. doi:10.1016/j.actamat.2003.10.011
- 23 Ashraf, K., & Salahuddin, S. (2012). Phase field model of domain dynamics in micron scale, ultrathin ferroelectric films: Application for multiferroic bismuth ferrite. *Journal of Applied Physics*, 112(7), 074102. doi:10.1063/1.4754800
- 24 Li, Y. L., Hu, S. Y., Liu, Z. K., & Chen, L. Q. (2001). Phase-field model of domain structures in ferroelectric thin films. *Applied Physics Letters*, 78(24), 3878. doi:10.1063/1.1377855
- 25 Zhang, J. X., Li, Y. L., Choudhury, S., Chen, L. Q., Chu, Y. H., Zavaliche, F., ... Jia, Q. X. (2008). Computer simulation of ferroelectric domain structures in epitaxial BiFeO₃ thin films. *Journal of Applied Physics*, 103(9), 094111. doi:10.1063/1.2927385
- 26 Chen, L. Q., & Shen, J. (1998). Applications of semi-implicit Fourier-spectral method to phase field equations. *Computer Physics Communications*, 108(2), 147-158.

- 27 Woo, C. H., and Yue Zheng. "Depolarization in modeling nano-scale ferroelectrics using the Landau free energy functional." *Applied Physics A* 91.1 (2008): 59-63.
- 28 Li, Y. L., S. Y. Hu, Z. K. Liu, and L. Q. Chen. "Effect of electrical boundary conditions on ferroelectric domain structures in thin films." *Applied Physics Letters* 81, No. 3 (2002): 427-429.