Electrical control of ferromagnetism in multiferroic bismuth ferrite-based heterostructures

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NANYANG
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**ELECTRICAL CONTROL OF FERROMAGNETISM IN
MULTIFERROIC BISMUTH FERRITE-BASED
HETEROSTRUCTURES**

YOU LU

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2011

**ELECTRICAL CONTROL OF FERROMAGNETISM IN
MULTIFERROIC BISMUTH FERRITE-BASED
HETEROSTRUCTURES**

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ABSTRACT

Recent renaissance of magnetoelectric multiferroics pivots on the coupling mechanisms between electrical and magnetic order parameters, as the magnetoelectric coupling might lead to the electrical manipulation of the ferromagnetic spins which is essential to the next generation of spin-based non-volatile memories with low power consumption. BiFeO_3 (BFO), as the only known room temperature multiferroic with vigorous magnetoelectric coupling, inspires a potential route to accomplish the functionality of electrically-controllable ferromagnetism through the interface exchange coupling with another ferromagnetic thin layer, which forms the backbone of this dissertation.

In the course towards this ultimate goal, the growth kinetics of BFO thin film was firstly investigated to map out the proper growth window. A thorough study of the oxygen pressure dependence reveals a great impact of composition stoichiometry on the relevant ferroelectric properties, which can be elucidated by the interactions between polar order and defect chemistry. Subsequently, the optimization and engineering of the BFO domain structures can be achieved by a number of approaches including compositional yields, film growth rate, vicinal substrates and anisotropic substrates. The domain structures of the as-grown films can be delicately controlled by electric field using quasi-planar electrodes. Quantitative study and domain dynamics of polarization switching under planar geometry create the basis of device architecture for further study. Finally, ferromagnetic $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) epilayer was introduced on top of BFO films to pursue the control of ferromagnetic moments by electric field. The growth and characterization of LSMO deposited on BFO with different domain patterns indicate that the magnetic properties of LSMO are greatly influenced by the epitaxial strain via Jahn-Teller distortion. Most intriguingly, a uniaxial magnetic anisotropy was observed in LSMO grown on BFO with regular 71° stripe domain arrays. Moreover, there is

strong correlation between the ferroelectric domains of BFO and ferromagnetic domains of LSMO. A microscopic model building upon the magnetoelectric coupling in BFO and the exchange coupling between LSMO and BFO was established to fully explain these fascinating phenomena. Last but not least, preliminary results of ferromagnetic domain manipulation by switching ferroelectric domains of BFO provides the directly evidence of electrical control of local ferromagnetism in LSMO/BFO epitaxial heterostructure at room temperature.

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TABLE OF CONTENTS

ABSTRACT1

ACKNOWLEDGEMENTS	3
------------------------	---

TABLE OF CONTENTS	5
-------------------------	---

LIST OF FIGURES	8
-----------------------	---

LIST OF TABLES	13
----------------------	----

Chapter 1 Introduction.....	14
-----------------------------	----

1.1 Magnetoelectrics and Multiferroics	14
--	----

1.2 Previous work on BiFeO ₃	20
---	----

1.2.1 Physical Properties of Multiferroic BiFeO ₃	20
--	----

1.2.2 Intrinsic Magnetoelectric Coupling in BiFeO ₃	25
--	----

1.2.3 Extrinsic Exchange Coupling in Ferromagnet/BiFeO ₃ Heterostructures ..	27
---	----

1.3 Purpose of Research.....	32
------------------------------	----

Chapter 2 Growth and Characterizations of BiFeO ₃ Thin Films.....	36
--	----

2.1 Introduction to Pulsed Laser Deposition.....	36
--	----

2.2 Experimental Procedure.....	38
---------------------------------	----

2.3 Optimization of Thin Film Growth Conditions	40
---	----

2.4 Influence of Oxygen Partial Pressure on the Ferroelectric Properties	43
--	----

2.5 Conclusions.....	51
----------------------	----

Chapter 3 Domain Engineering and Domain Switching in BiFeO ₃ Thin Films..	53
--	----

3.1 Ferroelectric Domain Engineering in BiFeO ₃ Epitaxial Thin Films.....	54
--	----

3.1.1 Introduction.....	54
-------------------------	----

3.1.1.1 Ferroelectric Domain Structures in Epitaxial BiFeO ₃ Thin Films.....	54
---	----

3.1.1.2 Domain Characterization in BiFeO ₃ by Piezoresponse Force Microscopy..	57
---	----

3.1.2	<i>Experimental Procedure</i>	61
3.1.3	<i>Ferroelectric Domain Engineering during BiFeO₃ Growth</i>	63
3.1.3.1	<i>Domain Control through Target Composition</i>	64
3.1.3.2	<i>Domain Control through Film Growth Rate</i>	67
3.1.3.3	<i>Domain Control through Substrate Vicinality</i>	69
3.1.3.4	<i>71° and 109° Domain Patterns on Orthorhombic Substrate</i>	73
3.2	<i>In-plane Ferroelectric Domain Switching in BiFeO₃ thin films</i>	75
3.2.1	<i>Introduction to Polarization Switching Mechanisms in BiFeO₃ thin films</i>	75
3.2.2	<i>Experimental Procedure</i>	77
3.2.3	<i>Ferroelectric Properties of Quasi-planar Capacitors</i>	78
3.2.4	<i>Domain Switching Dynamics in Quasi-planar Capacitors</i>	82
3.3	<i>Conclusions</i>	88
Chapter 4 Electrical Control of Ferromagnetism in La_{0.7}Sr_{0.3}MnO₃/BiFeO₃		
Heterostructures		91
4.1	<i>Introduction</i>	91
4.2	<i>Experimental Procedure</i>	93
4.3	<i>Growth and Characterizations of La_{0.7}Sr_{0.3}MnO₃/BiFeO₃ Heterostructures</i>	94
4.3.1	<i>Orientation-Dependent Magnetic Properties of La_{0.7}Sr_{0.3}MnO₃/BiFeO₃ Heterostructures</i>	94
4.3.2	<i>Effect of Structural Relaxation in BiFeO₃ Films on the Magnetization of La_{0.7}Sr_{0.3}MnO₃/BiFeO₃ Heterostructures</i>	96
4.4	<i>Exchange Coupling between La_{0.7}Sr_{0.3}MnO₃ and Stripe domain BiFeO₃</i>	101
4.4.1	<i>Uniaxial Magnetic Anisotropy in La_{0.7}Sr_{0.3}MnO₃ Induced by Ferroelectric Stripe Domain of BiFeO₃</i>	102

4.4.2	<i>Local Correlation between Ferroelectric Domains of BiFeO₃ and Ferromagnetic Domains of La_{0.7}Sr_{0.3}MnO₃</i>	110
4.5	Preliminary Results of Electrical Switching of Local Ferromagnetism in La _{0.7} Sr _{0.3} MnO ₃ /BiFeO ₃ Heterostructures	113
4.6	Conclusions.....	116
Chapter 5	Summary and Future Work	118
5.1	Summary	118
5.2	Future Work.....	121
REFERENCES		123

LIST OF FIGURES

Figure 1.1 (a) Schematic showing the relationship between magnetoelectric and multiferroic materials. (Figure adapted from Eerenstein, <i>et al.</i> [14]) (b) Ternary diagram illustrating the possible coupling effects between primary ferroic orders in multiferroics. (Figure adapted from Spaldin, <i>et al.</i> [3])	16
Figure 1.2 (a)-(c) Crystal structure of BFO viewed from different directions. (Figure adapted from Zavaliche <i>et al.</i> [30]) Ferroelectric hysteresis loops obtained from (d) thin-film sample and (e) single-crystal sample. (Figures adapted from Wang, <i>et al.</i> [10] and Lebeugle, <i>et al.</i> [31], respectively).....	21
Figure 1.3 Schematic illustrating the eight possible polarization variants and corresponding three possible domain walls in BFO. (Figure adapted from Catalan, <i>et al.</i> [39])	23
Figure 1.4 G-type antiferromagnetic order with weak canting moments in BFO, superimposed by an incommensurate cycloidal modulation. (Figure adapted from Martin, <i>et al.</i> [49] and Lebeugle, <i>et al.</i> [27]).....	24
Figure 1.5 Magnetic easy axis of BFO under (a) compressive and (b) tensile strain. (Figures adapted from Holcomb, <i>et al.</i> [51]) (c) Schematic showing the effect of 71°, 109° and 180° polarization switchings on the easy magnetization plane of BFO. (Figure adapted from Zhao, <i>et al.</i> [26]).....	26
Figure 1.6 Schematic illustration of the spin configuration in an exchange biased ferromagnetic–antiferromagnetic bilayer. (a) Field cooling from above T_N . (b)-(e) Different stages of magnetic hysteresis loop. (Figure adapted from Martin, <i>et al.</i> [58])	28
Figure 1.7 In-plane ferroelectric domain structures of BFO imaged by PFM and corresponding ferromagnetic domain structures of $\text{Co}_{0.9}\text{Fe}_{0.1}$ probed by XMCD–PEEM in a coplanar-electrode $\text{Co}_{0.9}\text{Fe}_{0.1}$ /BFO device (a) in the as-grown state, (b) after first electrical switching and (c) after second electrical switching. (Figure adapted from Chu <i>et al.</i> [54]) ..	30
Figure 1.8 Proposed model for orbital reconstruction induced ferromagnetism state in BFO at the interface with LSMO. (a) Electronic orbital reconstruction between Fe and Mn ions. (b) Proposed coupling mechanism and spin configuration at the interface. (c) Ferromagnetism due to enhanced canting angle of antiferromagnetic spins in BFO via interfacial coupling. (Figure adapted from Yu <i>et al.</i> [73])	31
Figure 1.9 (a) Sketch of a possible MRAM element incorporated with a multiferroic ferroelectric-antiferromagnetic layer, which is coupled to the bottom ferromagnetic layer. The antiferromagnetic spins can be switched using electric field via magnetoelectric coupling, which subsequently causes the ferromagnetic spins to switch through interface exchange coupling. In this way, the device can be toggled between high and low resistance states electrically. (Figure adapted from Bibes, <i>et al.</i> [76]) (b) Schematic showing the indirect path to control the ferromagnetism using electric field through magnetoelectricity and exchange coupling. (Figure adapted from Martin, <i>et al.</i> [49]).....	33
Figure 2.1 Sketch of the structure layout of a standard pulsed laser deposition system.....	37

Figure 2.2 (a) SrTiO ₃ substrate with atomic flat surface. (b) SrRuO ₃ deposited on SrTiO ₃ in step-flow growth mode. (c) XRD pattern of SrRuO ₃ /SrTiO ₃ with Kiessig fringes and rocking curve of small FWHM indicate small roughness and high crystallinity. The height scale in (a) and (b) is 2 nm.	40
Figure 2.3 Temperature–oxygen pressure phase diagram of BFO thin film grown by PLD. (Red symbols are data obtained in this study, black ones are data adapted from Béa, <i>et al.</i> [87])	41
Figure 2.4 Ferroelectric polarization hysteresis loops of (001), (110) and (111)-oriented BFO films. The inset shows the normalized values after projecting the polarization of three different orientation samples onto <111> directions.	43
Figure 2.5 XRD patterns of BFO thin films deposited under various oxygen pressures ranging from 1 mTorr to 40 mTorr.	44
Figure 2.6 Ferroelectric properties of BFO films grown under different oxygen pressures. (a) Ferroelectric polarization hysteresis loops, P – E . (b) Leakage current versus electric field. (c) Dielectric hysteresis loops, ϵ_r – E . (d) Piezoelectric hysteresis loops, d_{33} – E	45
Figure 2.7 (a) Relationship between Bi/Fe ratio and the oxygen pressure during film growth. (b) Magnetic hysteresis loops of BFO films grown at different oxygen pressures. (c) Bi/Fe ratio dependence of remanent polarization P_r , dielectric constant ϵ_r and film resistivity at 100 kV/cm. (d) Bi/Fe ratio dependent remanent d_{33} and electrostrictive coefficient Q_{eff} . The linear fit in (a) is to guide the eyes.	47
Figure 2.8 (a) & (b) Topography, (c) & (d) Out-of-plane domain structures and (e) & (f) Local d_{33} hysteresis loops of BFO films deposited under oxygen pressures of 5 and 20 mTorr, respectively. Yellow or purple tone in (c) & (d) represents upward-pointing or downward-pointing domains. The local d_{33} hysteresis loop in each domain was plotted in the corresponding color.	49
Figure 2.9 Ferroelectric domain configuration at different stages of the dielectric hysteresis cycle. The clear double-loop feature is due to the internal field (light blue) induced by defect-dipole pairs. Upward and downward domains are displayed in yellow and purple tones, respectively.	50
Figure 3.1 (a) Schematic of all four possible structural variants, corresponding to eight possible polarization variants in (001)-oriented BFO films. (Polarization vectors are indicated in colors consistent with those in PFM images.) (b) & (c) Domain configurations of the prototypical 71° and 109° patterns in rhombohedral epitaxial thin films.	55
Figure 3.2 (a) & (b) Topography and in-plane PFM images of BFO film with mosaic domain pattern. (c) & (d) Topography and in-plane PFM images of BFO film with stripe domain pattern.	57
Figure 3.3 (a) Schematic illustration of a typical PFM setup, where topography, in-plane and out-of-plane domain structures can be simultaneously recorded. (b) Out-of-plane signal originates from vertical deflection of the cantilever induced by out-of-plane polarization	

component. (c) In-plane signal originates from lateral torsion of the cantilever induced by in-plane polarization component..... 59

Figure 3.4 Interpretation of the domain contrasts in (a) out-of-plane and (b) in-plane PFM images in (001)-oriented BFO thin films with eight possible polarization variants. The color of each polarization variant represents the tone of corresponding domain in the PFM images. 71° , 109° and 180° domain walls can be determined depending on the angles between the polarization variants..... 60

Figure 3.5 Influence of the target composition on the domain structures of BFO thin films. (a)-(d) in-plane domain patterns of (001)-oriented BFO thin films deposited by targets with different Bi/Fe ratios. The insets are the corresponding out-of-plane PFM images with uniform yellow tone, indicating all the polarizations are pointing upwards. 65

Figure 3.6 Influence of the film growth rate on the domain structures of BFO thin films. (a)-(c) Topography and (d)-(f) corresponding in-plane domain structures of BFO (001) films with decreasing growth rate. (g) XRD θ - 2θ patterns and (h) rocking curves of (001) peak of BFO films with different growth rate. (i) Correlations among surface roughness, out-of-plane lattice constant and FWHM of (001) peak in (001)-oriented BFO thin films. 67

Figure 3.7 Influence of the substrate vicinality on the domain structures of BFO thin films. (a)-(d) Topography and (e)-(h) corresponding in-plane domain structures of BFO (001) films grown on STO substrates with various miscut angles. 70

Figure 3.8 Schematic illustration of the energetically favorable and unfavorable domain configurations of (001)-oriented BFO films grown on STO substrates with miscut along [100] and [010] directions, respectively..... 71

Figure 3.9 (a) & (d) Topography, (b) & (e) In-plane domain patterns and (c) & (f) Out-of-plane domain patterns of BFO films grown on DSO substrates with 71° and 109° stripe domains, respectively. 74

Figure 3.10 (a) Sketch of the device layout of a quasi-planar BFO capacitor. (b) Cross-sectional view of in-plane electric field distribution of a $1.4\text{-}\mu\text{m}$ -wide capacitor under 1 V bias, simulated using finite element analysis. The relative permittivities of BFO and STO used in the simulation are 80 and 300, respectively. 79

Figure 3.11 (a) Dual-pass voltage waveforms in remanent hysteresis measurement. The remanent hysteresis loop is obtained by subtracting the non-remanent component from the total switched polarization. (b) The deduction of remanent hysteresis loop of a $5.3\text{-}\mu\text{m}$ -wide capacitor using the method described in (a). (c) Remanent hysteresis loops of a $5.3\text{-}\mu\text{m}$ -wide capacitor measured using different voltages. (d) PUND measurements of quasi-planar BFO capacitors with different channel widths using 0.1 ms voltage pulse..... 80

Figure 3.12 (a) Plots of capacitor's channel width versus remanent polarization P_r and nominal coercive field E_{cn} . (b) Amended effective coercive field E_{ce} of quasi-planar BFO capacitors with varying thicknesses (channel widths). Solid line shows the Kay-Dunn scaling fit of data in this study (red symbols) and from literature (black symbols). 82

Figure 3.13 In-plane and out-of-plane (inset) ferroelectric domain structures of a quasi-planar BFO capacitor (a) in as-grown state, (c) & (d) after electrical poling with opposite bias and (b) at the intermediate stage during poling. The inset also schematically illustrates the corresponding in-plane domain configuration. The AFM cantilever is scanning along [110] direction in all PFM images. The marking in the red circle serves as an aid for the reader; domain merging region is denoted by blue circle.	83
Figure 3.14 Voltage dependent switching dynamics of ferroelectric domains in a quasi-planar BFO capacitor. (a) Starting state. (b) After applying 25 V pulse. (c) After applying 28 V pulse. (d) After applying 30 V pulse. The voltage pulse width is fixed at 1 ms. Corresponding domain configurations are depicted in the insets of (a) & (d).	86
Figure 3.15 Dynamic switching of quasi-planar BFO capacitors with varying angles between electrode edge and [100] direction. (a), (d), (g) As-grown state; (b), (e), (h) after electric poling to one direction; (c), (f), (i) after reverse electric poling for capacitors with angles of 0°, 20° and 45°, respectively. Relevant in-plane domain configurations are schematically illustrated in (j).	87
Figure 4.1 Schematic showing the spin configurations on (001), (110) and (111) surfaces of BFO, respectively. Both (001) and (110) surfaces possess fully compensated spins, whereas the (111) surface is fully uncompensated.	92
Figure 4.2 Temperature dependent magnetization hysteresis loops of (a) (001), (b) (110) and (c) (111) oriented BFO/LSMO bilayer samples. (d) The relationship between film coercivity and temperature for all three orientation samples.	95
Figure 4.3 (a), (b) and (d) In-plane ferroelectric domain structures of BFO films in LSMO/BFO heterostructures. The inset shows the corresponding topography after LSMO growth. (c) Corresponding magnetization hysteresis loops of LSMO/BFO heterostructures with various BFO domain structures.	96
Figure 4.4 (a) & (b) XRD θ -2 θ patterns of LSMO/BFO heterostructures shown in Figure 4.3 (d) & (b) before and after LSMO growth. (c) XRD θ -2 θ patterns of LSMO/BFO heterostructures with different strain relaxations. (d) Correlation between BFO and LSMO c lattice constant and the magnetization of LSMO layers. The saturated magnetization of single layer of LSMO grown on bare STO is indicated by red dash line.	97
Figure 4.5 (a)-(d) Topographies of STO substrate, LSMO/STO, BFO/STO and LSMO/BFO/STO samples, respectively. The height scales are 2 nm in (a) and 5 nm in (b)-(d). (e) & (f) In-plane and out-of-plane domain structures of BFO layer in the LSMO/BFO heterobilayer, respectively. The phase scale is 180° in the PFM images.	103
Figure 4.6 (a) M-T curves of LSMO single layer and LSMO/BFO bilayer samples measured under field cooling condition. The cooling and measuring fields are both 100 Oe. The inset shows the zoom-in dM/dT -T curves around Curie temperature. (b) Temperature dependence of coercive field of LSMO single layer and LSMO/BFO bilayer samples. The inset is the magnetization hysteresis loop of both samples at 10 K. (c) Comparison of XRD θ -2 θ patterns of LSMO/BFO heterostructure before and after LSMO growth. No obvious BFO relaxation is observed.	104

Figure 4.7 (a) Magnetization hysteresis loops of LSMO single layer and LSMO/BFO bilayer samples measured along [100] and [010] directions at 10 K respectively. Magnetic anisotropy is visible in both samples. (b) Angular dependent M_r/M_s and H_c curves of both samples measured at 300 K. Solid lines are theoretical fits. (c) Schematic drawing of the in-plane ferroelectric domain configuration of BFO layer and the angular measurement geometry. (d) Large scan (8 μm * 8 μm) of the in-plane domain structure of the underlying BFO film used in the study. Imperfect region of stripe domains and extra domain variants (purple tone) are enclosed in blue lines. The phase scale is 180° 106

Figure 4.8 Schematic illustration of the microscopic coupling mechanism at the LSMO/BFO interface. Local polarization and spin configurations are indicated by arrows. The top right corner shows a zoom-in picture of spin coupling in a single domain region. 108

Figure 4.9 (a) In-plane ferroelectric domain pattern of BFO with equal amount of two sets of stripe domains. (b) The corresponding angular dependent M_r/M_s and H_c curves of LSMO layer grown on top of BFO film shown in (a). 110

Figure 4.10 (a) & (c) Topographies of BFO film and after growing LSMO on top scanned at the same location. (b) & (d) Corresponding in-plane ferroelectric domain pattern of BFO and magnetic domain pattern of LSMO, respectively. (e) Large scan of the magnetic domain pattern of LSMO at a different location. (f) A zoom-in scan of (e). The height scale is 5 nm in (a) & (c). The PFM phase scale is 180° in (b). The MFM phase scale is 3° in (d), (e) and (f). Polarization vectors are denoted by blue arrows, while possible spin configurations are indicated by red arrows. 111

Figure 4.11 (a) Sketch of the device layout and experimental setup for electrical switching of ferromagnetism in a LSMO/BFO heterostructure. (b) Cross-sectional view of the device structure and the corresponding electric field distribution within the BFO layer. 113

Figure 4.12 Dynamic switching of the ferromagnetic domains of LSMO using electric field in LSMO/BFO heterostructure. Corresponding topography, in-plane ferroelectric domain structure of BFO and ferromagnetic domain structure of LSMO (a) in as-grown state, (b) after first electrical switching and (c) after second electrical switching back. The height scale, PFM phase scale and MFM phase scale are 80 nm, 180° and 3° respectively. Red circles indicate domain areas that can be reversibly switched by electric field, whereas blue circle denote the domain area with no significant change upon electric poling. 114

LIST OF TABLES

Table 1.1 A list of multiferroics. Notation: FE - ferroelectric, FM - ferromagnetic, AF - antiferromagnetic and CO - charge-ordered. (Table adapted from Wang, <i>et al.</i> [20])	19
Table 2.1 List of the deposition parameters used for the optimization of BFO thin films growth.	39
Table 2.2 Melting point, boiling point and vapor pressure of bismuth and iron elements. (Adapt from [88]).....	42
Table 3.1 List of the deposition parameters used for tuning the domain structures of BFO thin films.	63
Table 4.1 List of the deposition parameters used for BFO and LSMO growth by PLD.	93
Table 4.2 List of lattice parameters of BFO, LSMO and STO adapted from literature [28,34,133-134].....	99

Chapter 1 Introduction

Electricity and magnetism in the universe are inherently coupled. As unified in the Maxwell's equations, moving charges create a magnetic field whereas a changing magnetic field generates current. However, such interaction exists in a dynamic fashion. On the other hand, in the realm of condensed matter physics, electric and magnetic orders can coexist in the same material termed multiferroic, which raises the question of whether they are intimately coupled in such materials. Motivated by increasing demand for energy conservation and multifunctional applications, electric-field control of magnetism using magnetoelectric and multiferroic materials has emerged as a central focus of scientific research, which is also the purpose of our study. In this chapter, I will briefly introduce the basic concepts of magnetoelectrics and multiferroics, followed by a detailed review of previous work on a prototype multiferroic, BiFeO_3 (BFO). Finally, a novel device paradigm based on the multiferroism of BFO is proposed to achieve electric-field control of magnetism, forming the main thread of this dissertation.

1.1 Magnetoelectrics and Multiferroics

Research work on magnetoelectrics and multiferroics can be traced back to the 1950s and 1960s [1], although the development of this field was relatively slow due to the scarcity of materials. Recent years have seen a great resurgence of interest in this group of materials [2-5]. The revival of this area was initiated by a series of single-phase multiferroics found both experimentally and theoretically. Developments in material synthesis techniques have paved the way for discovery of new types of multiferroics [6-9]

and reexamination of the old ones [10] both in bulk and thin film forms. Additionally, advanced first-principle calculations have served as a guide for designing novel materials and played an important role in understanding the coupling effect between electric and magnetic order parameters in magnetoelectrics and multiferroics [11-13].

Before looking into the field, unambiguous definitions of ‘magnetoelectric’ and ‘multiferroic’ must be established first. Unfortunately, the corresponding taxonomy had been quite equivocal for a long time until a detailed classification in a recent report [14]. As depicted in Figure 1.1 (a), the relationship between ‘magnetoelectric’ and ‘multiferroic’ is neither equivalent nor irrelevant. There is an incomplete overlap between them. The term ‘multiferroics’ coined by H. Schmid, originally referred to single-phase materials with the coexistence of two or more primary ferroic orders, namely ferroelectricity, ferromagnetism, ferroelasticity and ferrotorodicity (under debate) [15]. Customarily, non-primary ferroic orders such as antiferroelectricity, antiferromagnetism or ferrimagnetism have also been included in the scope of multiferroism. In addition to the coexistence of the spontaneous ferroic orders, the close interactions between them are also considered as a prerequisite for multiferroics. Compared to multiferroics, the definition of magnetoelectric materials is much less restrictive. Any materials which are both electrically and magnetically polarizable can be regarded as magnetoelectrics as long as these two parameters are intercoupled directly or indirectly, such as strain-mediated magnetoelectric composites that are not even a single-phase material. In short, multiferroic emphasizes the coexistence of spontaneous ferroic orders and the coupling between them, whereas magnetoelectric only describes an intimate coupling phenomenon in materials irrespective of the nature of the electric and magnetic order parameters.

Figure 1.1 (a) Schematic showing the relationship between magnetoelectric and multiferroic materials. (Figure adapted from Eerenstein, *et al.* [14]) (b) Ternary diagram illustrating the possible coupling effects between primary ferroic orders in multiferroics. (Figure adapted from Spaldin, *et al.* [3])

As mentioned above, multiferroics possess more than one spontaneous long-range order. From the application point of view, the significance of incorporating electronic and magnetic properties into one material is self-evident for device miniaturization. More importantly, these order parameters usually exhibit intricate cross-coupling with each other, which greatly extends the device functionalities. The ternary diagram in Figure 1.1 (b) illustrates all of the possible coupling effects among ferroelectricity, ferromagnetism and ferroelasticity induced by the corresponding external stimulus, namely electric, magnetic and stress field. For instance, most ferroelectrics are accompanied by a spontaneous distortion in the unit cell, giving rise to ferroelasticity. They interact with each other through piezoelectric effect, which is described by the conversion between electrical and mechanical energies. Such functionality makes ferroelectrics indispensable to the sensing and actuation industry.

Among all the coupling effects, magnetoelectric coupling is gaining more and more attention in scientific research owing to its potential for a wide variety of applications. In general, magnetoelectric coupling can be divided into two major categories. The first one specifically refers to magnetoelectric effect, or usually linear magnetoelectric effect,

which describes the induction of magnetization by an electric field or polarization by a magnetic field. In Landau theory, the induced electric polarization P and magnetization M can be described by the following expressions [2]:

$$P_i = \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_i E_j - \dots \quad (1)$$

$$M_i = \alpha_{ij} E_j + \beta_{ijk} E_i H_j + \frac{1}{2} \gamma_{ijk} E_j E_k - \dots \quad (2)$$

where E and H denote the electric and magnetic fields, respectively and α represents the linear magnetoelectric coefficient, whereas higher-order terms are designated as β and γ . Suffixes i, j, k refer to the Cartesian axes. This effect can occur in any single-phase magnetoelectric or multiferroic material, provided that the magnetic and electric order parameters are coupled to each other. However, the linear magnetoelectric effect in most single-phase materials is very small. Other than the direct magnetoelectric coupling in single-phase systems, in composite materials, the ferroelectricity and ferromagnetism from separate phases can be coupled through strain-mediated piezoelectric (electrostriction) and piezomagnetic (magnetostriction) effects, which could give rise to orders-of-magnitude enhancement of the coupling coefficient. Such linear magnetoelectric effect may find applications in transducers, magnetic field sensors and tunable microwave devices.

The other type of magnetoelectric coupling exists only in multiferroics, where the electric and magnetic long-range orders are strongly correlated. The coupling may lead to magnetization reversal by electric field or vice versa. Therefore, this phenomenon is termed as magnetoelectric switching [14]. Unlike linear magnetoelectric effect which describes collective properties, magnetoelectric switching takes effect on a microscopic scale. Ferromagnetic materials have been widely used for data storage for decades.

Alternatively, ferroelectrics can also perform in a similar way as a memory medium, leading to the so-called ferroelectric random access memory (FeRAM). Magnetoelectric switching in multiferroics thus provides us the possibility to control magnetization electrically, so that the problems associated with destructive reading in FeRAM and large power consumption during magnetic writing can be avoided. Besides, multiferroics can be incorporated into the emerging spintronics industry by taking advantage of the magnetoelectric switching effect, through which the spin states in giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) devices can be controlled by an electric field instead of magnetic field generated by large current density.

However, theoretical studies have revealed that the underlying driving forces for ferroelectricity and ferromagnetism are mutually exclusive [11-12]. In most perovskite (ABO_3) ferroelectrics, the cation off-centering displacement that leads to polarization is stabilized by empty transition metal d orbitals, while on the other hand, magnetism requires partially filled d shells. This explains the scarcity of single-phase multiferroic materials. Hence, alternative mechanisms for magnetism and/or ferroelectricity must be pursued to produce new multiferroic materials. There are mainly four types of multiferroics: (1) materials with A-site cation driven ferroelectricity and B-site induced magnetic property such as BiMnO_3 [16], and BFO [10]; (2) geometric frustration induced multiferroic materials such as YMnO_3 [17]; (3) rare-earth manganites such as TbMnO_3 [7], and TbMn_2O_5 [8] where ferroelectricity is induced by magnetoelastically driven lattice modulation; and (4) LuFe_2O_4 [9], Fe_3O_4 [18] and $(\text{Pr,Ca})\text{MnO}_3$ [19] where non-centrosymmetric charge-ordering induces ferroelectricity. Some of the commonly-studied multiferroic materials are listed in Table 1.1, adapted from reference

[20]. The readers are referred to the original paper for a complete list.

Table 1.1 A list of multiferroics. Notation: FE - ferroelectric, FM - ferromagnetic, AF - antiferromagnetic and CO - charge-ordered. (Table adapted from Wang, *et al.* [20])

Compound	Type of electric order	Type of magnetic order	Ferroelectric transition temperature (K)	Magnetic transition temperature (K)
$\text{Pb}(\text{B}_{1/2}\text{B}'_{1/2})\text{O}_3$ (B=Fe,Mn,Ni,Co; B'=Nb,W,Ta)	FE	AF	~385	~143
BiFeO_3	FE	AF	~1103	~643
BiMnO_3	FE	FM	~800	~100
$(\text{Y}, \text{Yb})\text{MnO}_3$	FE	AF	~950	~77
RMn_2O_5 (R=Y, Tb, Dy, etc.)	FE	AF	~38	$T_N = 43 \text{ K}$ $T_{CM} = 33 \text{ K}$ $T_{ICM} = 24 \text{ K}$
LuFe_2O_4	FE	CO	~330	~330
RMnO_3 (R = Tb, Dy)	FE	AF	~28	~28
HoMnO_3	FE	AF	~875	76K for Mn^{3+} 5K for Ho^{3+}
...	...	...	...	...

As expected, very few multiferroics exhibit simultaneous coexistence of ferroelectricity and ferromagnetism. Moreover, in most known multiferroics, at least one of the transition

temperatures of the order parameters is well below room temperature, preventing them from practical applications. One exception is BFO, whose magnetic and electric orders persist up to very high temperatures. This makes BFO a promising candidate for magnetoelectric devices that operate at room temperature.

1.2 Previous work on BiFeO₃

Ever since the day its intrinsic large polarization was revealed in epitaxial thin films [10], BFO has become the focus of research in multiferroics, comparable to yttrium barium copper oxide (YBCO) in superconductors [21] or manganese-based perovskite oxides in colossal magnetoresistance (CMR) materials [22-23]. To date, BFO is still the only known single-phase material with both robust ferroelectric (Curie temperature $\sim 820^\circ\text{C}$) [24] and magnetic (Neél temperature $\sim 370^\circ\text{C}$) [25] ordering coexisting at room temperature. Furthermore, the direct coupling between these order parameters has been confirmed in both thin film and single-crystal samples [26-27], which makes electrical control of magnetism possible, paving the way for applications in memories and spintronics. In the following sections, previous work on BFO will be reviewed in details, including studies on the fundamental properties of BFO and attempts towards functional devices.

1.2.1 Physical Properties of Multiferroic BiFeO₃

The crystal structure of bulk BFO is characterized by a perovskite unit cell with rhombohedral distortion along its body diagonal, denoted as pseudocubic $\langle 111 \rangle$ directions [28] (Miller indices based on the pseudocubic lattice are used in this

dissertation for simplification), as shown in Figure 1.2 (a)-(c). It has a lattice constant $a_{rh} = 3.96 \text{ \AA}$ and a rhombohedral angle of $89.3\text{-}89.4^\circ$. The large relative displacement between Bi and FeO_6 octahedron is believed to originate from the high stereochemical activity of Bi 6s lone pair, giving rise to a large spontaneous polarization along $\langle 111 \rangle$ directions [29]. The FeO_6 octahedra in two adjacent unit cells rotate around the polar axes in opposite directions, leading to the so-called antiferrodistortive order (Figure 1.2 (b)) [28]. The rotation angle is around $11\text{-}14^\circ$. It is closely related to the Fe–O–Fe angle which is critical in determining the antiferromagnetic superexchange coupling between Fe^{3+} ions.

Figure 1.2 (a)-(c) Crystal structure of BFO viewed from different directions. (Figure adapted from Zavaliche *et al.* [30]) Ferroelectric hysteresis loops obtained from (d) thin-film sample and (e) single-crystal sample. (Figures adapted from Wang, *et al.* [10] and Lebeugle, *et al.* [31], respectively)

For epitaxial BFO thin films, if deposited on (001) SrTiO_3 (STO) substrates, it is widely accepted that there will be a symmetry reduction from rhombohedral to monoclinic (or lower symmetry) due to the in-plane compressive epitaxial strain [32-35].

Some reports on ultrathin BFO films even suggest a tetragonal structure [36-37], which seems to contradict the finite in-plane component of the polarization observed using piezoresponse force microscopy (PFM) [38]. However, as pointed out by Catalan and Scott [39], both claims can be compatible with each other. While the external lattice could appear to be tetragonal, the internal degrees of freedom that determine the polarization may belong to a monoclinic symmetry.

The first quantitative measurement of the polarization of BFO was carried out at 77K in 1970, revealing a polarization value $\sim 6.1 \mu\text{C}/\text{cm}^2$ along $\langle 111 \rangle$ directions [24]. Thirty years later, in 2003, Wang *et al.* reported about one order of magnitude enhancement of polarization in (001) epitaxial thin film on STO substrate (Figure 1.2 (d)), corresponding to $\sim 100 \mu\text{C}/\text{cm}^2$ along $\langle 111 \rangle$ directions, which was initially assumed to be induced by epitaxial strain [10]. This important discovery has spurred a flurry of research work focusing on BFO in various forms. Subsequent strain dependent study indicates that the intrinsic polarization of the BFO epitaxial films is actually insensitive to the strain [34], consistent with theoretical calculation [40]. This was further verified by the large intrinsic polarization measured in BFO single crystals (Figure (e)) [31,41]. Instead of changing the magnitude of the intrinsic polarization, the strain can cause the polarization vector to rotate in-plane or out-of-plane depending on the nature of the strain (tensile or compressive) [42].

As described previously, the spontaneous polarization in BFO lies along the $\langle 111 \rangle$ body diagonals. Consequently, there are totally eight possible polarization directions corresponding to four structural variants, as shown in Figure 1.3. Three different types of domain walls thus can be formed depending on the angle between the polarization vectors

in the neighboring domains, namely 71° , 109° and 180° domain walls. In a similar manner, three possible switching paths can be identified. A more detailed discussion on the domain structures and domain switching scenarios will be covered in Chapter 3.

Figure 1.3 Schematic illustrating the eight possible polarization variants and corresponding three possible domain walls in BFO. (Figure adapted from Catalan, *et al.* [39])

Research work on the magnetic configurations of bulk BFO was pioneered by Sosnowska *et al.* in 1980s [43]. Based on their neutron diffraction studies, they proposed an antiferromagnetic G-type spin configuration, with each Fe^{3+} spin surrounded by six antiparallel nearest neighbors. In another word, the spins are coupled ferromagnetically within the (111) planes, and antiferromagnetically between adjacent planes (Figure 1.4). Additionally, a small canting of the antiferromagnetic spins is also permitted by the system symmetry through Dzyaloshinskii-Moriya interaction [44-45], leading to a small net magnetic moment. Superimposed on the G-type antiferromagnetic ordering is a cycloidal spiral modulation with a period of 620 ± 20 Å. This model agrees well with recent neutron scattering result of high quality single crystal samples [27]. However, the

magnetic property of BFO thin films is controversial. Wang *et al.*'s original work reported a significant enhancement of the magnetization ($\sim 0.5 \mu_B/\text{Fe}$) due to the suppression of spiral spin structure by the epitaxial strain.[10] Later work by Bai *et al.* [46] and Béa *et al.* [37] indicated that strain did destroy the cycloidal spin modulation, but only unleashed very weak ferromagnetism ($\sim 0.02 \mu_B/\text{Fe}$). The enhanced magnetic response is thus suggested to be associated with the valence change of Fe ions or magnetic second phases [47-48]. A general consensus is gradually reached that the intrinsic magnetization of BFO thin films due to the small canting is essentially very weak. Enhanced ferromagnetism can be induced by chemical doping, size effect or different types of domain walls, which might be related to the local frustration of the antiferromagnetic spins.

Figure 1.4 G-type antiferromagnetic order with weak canting moments in BFO, superimposed by an incommensurate cycloidal modulation. (Figure adapted from Martin, *et al.* [49] and Lebeugle, *et al.* [27])

1.2.2 Intrinsic Magnetoelectric Coupling in BiFeO₃

The importance of multiferroic BFO lies in the interaction between the electric and magnetic order parameters rather than a simple sum-up of the individual properties. The first demonstration of magnetoelectric switching of the antiferromagnetism by electric field in BFO epitaxial thin films was reported by Zhao *et al.* [26] using a combination of PFM and photoemission electron microscopy (PEEM) techniques. Given that the long-range cycloidal modulation is absent in epitaxial films, the antiferromagnetic spins are confined in an easy magnetization plane perpendicular to the polarization axis, as illustrated in Figure 1.5. Upon application of an electric field, three types of ferroelectric switching events may take place. 180° switching is purely ferroelectric without changing the lattice distortion. Thus, from symmetry consideration, the easy magnetization plane doesn't have to change. However, in 71° and 109° ferroelastic switching events, the polarization rotation is also accompanied by a coherent rotation of the magnetization plane containing the spins. In this manner, the orientation of the antiferromagnetic spins can be switched using an electric field. In addition to the coupling between the polar distortion and easy magnetization plane, another prerequisite for deterministic electrical control of the antiferromagnetic spins is to establish a one-to-one correlation between the polar direction and antiferromagnetic axis. However, in rhombohedral BFO the crystal symmetry results in sixfold-degenerate magnetic easy axes within the magnetization plane [50]. Fortunately, epitaxial strain here plays a key role in lifting the degeneracy through symmetry breaking, leading to an energetically favorable antiferromagnetic axis. According to a recent report [51] shown in Figure 1.5 (a) & (b), compressive strain forces the magnetic easy axis to point as far out of plane as possible along the $\langle 112 \rangle$ axes, while

tensile strain tends to drag the spins to align in the plane, thus along the $\langle 110 \rangle$ axes. The different preferred axes can be intuitively understood based on the magnetostrictive effect. At this point, an unambiguous correlation between the ferroelectric polar direction and the antiferromagnetic spin alignment can be established, leading to a decisive magnetoelectric switching of the spins upon polarization rotation.

Figure 1.5 Magnetic easy axis of BFO under (a) compressive and (b) tensile strain. (Figures adapted from Holcomb, *et al.* [51]) (c) Schematic showing the effect of 71° , 109° and 180° polarization switchings on the easy magnetization plane of BFO. (Figure adapted from Zhao, *et al.* [26])

The strong magnetoelectric coupling effect is further confirmed by similar work on single-crystalline BFO, where the spin rotation plane can be toggled by polarization switching because it is defined by the polarization vector and the cycloid propagation vector [27]. However, due to the degeneracy of the cycloid propagation vectors, the magnetoelectric switching in single-crystal BFO is less deterministic than in thin films. Nevertheless, this intimate magnetoelectric coupling marks an essential step forward towards the realization of electrical control of ferromagnetism.

1.2.3 Extrinsic Exchange Coupling in Ferromagnet/BiFeO₃ Heterostructures

Owing to the antiferromagnetic cancelling of all magnetic moments, BFO thin films only exhibit weak magnetism macroscopically, thus preventing it from direct device applications. In 2005, Binek and Doudin [52] proposed a number of novel device designs based on magnetoelectrics, where electrically generated net magnetic moment in the magnetoelectric film can effectively change the magnetic state of an adjacent ferromagnetic layer via exchange coupling. This idea was soon employed in the applications of antiferromagnetic multiferroics such as YMnO₃ [53] and BFO [54]. Here, another coupling effect at the ferromagnet-antiferromagnet interface, namely exchange coupling, is introduced in addition to the intrinsic magnetoelectric coupling in multiferroics. Generally, exchange coupling can manifest itself in two different manners. The first one, termed exchange bias, is a clear shift of the magnetization hysteresis loop due to the unidirectional pinning of the ferromagnetic moments by uncompensated antiferromagnetic spins. The second one, called exchange enhancement, is an enhancement of the coercive field resulted from the interaction of the ferromagnetic spins and the fully compensated or unpinned antiferromagnetic surface spins. Whereas the exchange bias has been extensively studied for decades [55-57], the exchange enhancement attracts much less attention.

The underlying mechanism of exchange coupling is schematically shown in Figure 1.6. When the ferromagnetic–antiferromagnetic bilayer system is cooled through the Néel temperature (T_N) of the antiferromagnetic layer (providing that the Curie temperature, T_C , of the ferromagnetic layer higher than T_N) under a magnetic field, the highly-aligned ferromagnetic spins will drive the interfacial antiferromagnetic spins to align in the

parallel (or antiparallel in some cases) direction. Due to the large antiferromagnetic anisotropy energy, the magnetic field has little impact on the antiferromagnetic spin configurations. Thus, the interfacial antiferromagnetic spins can serve as an effective pinning layer, giving rise to an internal field acting on the ferromagnetic spins. Consequently, an obvious loop shift can be detected when measuring the magnetization hysteresis. The exchange biased hysteresis loop is usually accompanied by an increase in the coercive field, which can be understood by the antiferromagnetic spin drag during ferromagnetic spin rotation. This dragging effect is more pronounced when the antiferromagnetic anisotropy is small, leading to an increased coercivity.

Figure 1.6 Schematic illustration of the spin configuration in an exchange biased ferromagnetic–antiferromagnetic bilayer. (a) Field cooling from above T_N . (b)–(e) Different stages of magnetic hysteresis loop. (Figure adapted from Martin, *et al.* [58])

Throughout the years, a number of theoretical models have been proposed to explain the fundamentals behind the exchange bias. Originally, the phenomenon is interpreted based on an intuitive picture with a collinear coupling between the ferromagnetic spins and the uncompensated antiferromagnetic spins [59]. However, this simple

one-dimensional model fails to explain the actual magnitude of the experimentally observed exchange bias. Later on, Malozemoff [60-62] brought in a random-field theory, suggesting that the uncompensated surface spins can arise from surface roughness, defects or other disordered factors. The random exchange interaction between the uncompensated spins and the ferromagnetic layer acts as a random field on the antiferromagnet, leading to the formation of antiferromagnetic domains during field cooling and pinned uncompensated spins required for exchange bias. This model has been widely cited as it gives a reasonable estimation of the amplitude of the exchange bias. A few years ago, a spin-flop model was introduced by Koon and expanded by Schulthess and Bulter [63-65], claiming a perpendicular coupling between the ferromagnetic and antiferromagnetic spins. The model is successful in explaining the large exchange bias generated by fully compensated surface and the so-called positive exchange bias effect. Recently, Dong *et al.* has proposed that the exchange bias can be induced by Dzyaloshinskii-Moriya interaction and ferroelectric polarization in multiferroics with a G-type antiferromagnetic order [66]. However, owing to the diversity of the exchange-biased systems, a universal picture of the exchange coupling between interfacial spins remains elusive so far.

When it comes to the ferromagnet/BFO heterostructures, most of previous research work have been focusing on the high T_C transition metal alloys, e.g. NiFe [67], CoFeB [68] and CoFe [69], coupled with epitaxial BFO thin films, where robust room temperature exchange bias has been observed. Quantitative measurements revealed that the exchange bias strength is inversely proportional to the antiferromagnetic domain size

of BFO [70] (equivalent to ferroelectric domains, since they are intimately coupled) or the length of 109° domain walls [71], in agreement with the random-field theory.

Figure 1.7 In-plane ferroelectric domain structures of BFO imaged by PFM and corresponding ferromagnetic domain structures of $\text{Co}_{0.9}\text{Fe}_{0.1}$ probed by XMCD–PEEM in a coplanar-electrode $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{BFO}$ device (a) in the as-grown state, (b) after first electrical switching and (c) after second electrical switching. (Figure adapted from Chu *et al.* [54])

Armed with the strong exchange interactions between the ferromagnetic layer and multiferroic BFO, the first attempt on dynamic electrical switching of the ferromagnetic domains at room temperature has been demonstrated by Chu *et al.* [54] in 2008. He used a combination of PFM and X-ray magnetic circular dichroism (XMCD)–photoemission electron microscopy (PEEM) techniques to study a planar-electrode $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{BFO}$ device. As depicted in Figure 1.7, the ferromagnetic domains are changed upon ferroelectric domain switching in the underlying BFO, and can be recovered by applying a reverse bias. This marks another step forward towards electrically controllable magnetic devices at room temperature. Following this breakthrough, a similar work on single-crystal BFO was also carried out, where the magnetic anisotropy axis of a permalloy layer can be rotated by 90° upon electrical switching [72]. It is necessary to point out that exchange bias is not a prerequisite for the magnetoelectric switching of the

ferromagnetism. In fact, the exchange enhancement interaction plays a more essential role.

Figure 1.8 Proposed model for orbital reconstruction induced ferromagnetism state in BFO at the interface with LSMO. (a) Electronic orbital reconstruction between Fe and Mn ions. (b) Proposed coupling mechanism and spin configuration at the interface. (c) Ferromagnetism due to enhanced canting angle of antiferromagnetic spins in BFO via interfacial coupling. (Figure adapted from Yu *et al.* [73])

The ferromagnetic layers used previously are all polycrystalline or amorphous metal alloys which are essentially incompatible with oxide multiferroics. Structurally coherent heteroepitaxial structures are believed to exhibit higher coupling strength and reliability. An ideal candidate material that naturally comes into mind is ferromagnetic half-metal $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), which possesses a perovskite lattice that is compatible with BFO. According to a very recent report, ultrathin LSMO layer on BFO thin film displays an exchange bias after field cooling from above its Curie temperature [73]. By probing the magnetic state of Fe ions at the interface, it is found that a larger canting angle of the antiferromagnetic spins are induced by the adjacent Mn spins through orbital

reconstruction, leading to enhanced magnetic moment at the BFO surface, which is closely related to the observed exchange bias. Moreover, the electrical control of the exchange bias has also been realized recently [74], laying the cornerstone for spin-based functional devices. The underlying mechanism for the electrically-controllable exchange bias still remains unclear, though the Dzyaloshinskii-Moriya interaction and ferroelectric polarization induced exchange bias may provide a possible explanation to this [66].

1.3 Purpose of Research

Driven by the increasing demand for low power consumption and better performance, different types of non-volatile memories have been studied intensively as the next generation primary storage device. Among them, magnetoresistive random access memory (MRAM) is the most competitive candidate because it possesses all the advantages of other types of non-volatile memories, such as good scalability, infinite retention, high reading/writing speed and low cost [75]. However, one major issue that prevents the MRAM from large-scale commercialization is the relatively high power requirement during the writing process. The typical configuration of a MRAM device is similar to a spin valve, which consists of a magnetic tunnel junction (MTJ) with two ferromagnetic layers (blue) separating by an insulating layer (red). According to magnetoresistive effect, the MTJ can be switched between high and low resistance states depending on whether the spins in the two ferromagnetic layers are parallel or antiparallel to each other. To switch the spins in the ferromagnetic layers, writing by both conventional magnetic field and the latest spin transfer switching require a substantial current, which consumes a large amount of energy.

Figure 1.9 (a) Sketch of a possible MRAM element incorporated with a multiferroic ferroelectric-antiferromagnetic layer, which is coupled to the bottom ferromagnetic layer. The antiferromagnetic spins can be switched using electric field via magnetoelectric coupling, which subsequently causes the ferromagnetic spins to switch through interface exchange coupling. In this way, the device can be toggled between high and low resistance states electrically. (Figure adapted from Bibes, *et al.* [76]) **(b)** Schematic showing the indirect path to control the ferromagnetism using electric field through magnetoelectricity and exchange coupling. (Figure adapted from Martin, *et al.* [49])

So can we use other approaches to control the spins instead of a large current? An alternative scheme was proposed to integrate a ferroelectric-antiferromagnetic layer (green) into the MRAM element (Figure 1.9 (a)). Through the magnetoelectric coupling in the multiferroic, the topmost spins in the antiferromagnetic multiferroic can be reversed by an electric field. Subsequently, the ferromagnetic spins adjacent to the antiferromagnetic layer will also switch due to the interface exchange coupling. By combining these two coupling scenarios, the electrical control of ferromagnetic spins can be realized indirectly (Figure 1.9 (b)). Using electric field to write is much more economic in power consumption, especially when the device size is scaled down to nanometers. Besides MRAM, we can expect a wide range of integrations of multiferroic materials into spintronic devices as proposed by Binek and Doudin [52], leading to a great variety of electrically controllable spin-based functional applications. Moreover, from a

fundamental point of view, the physics behind either the magnetoelectric coupling or the exchange coupling is rich, and worth further exploration.

In this work, we choose the LSMO/BFO heterostructure as the candidate system to explore the possibility of manipulating ferromagnetism by electric field. BFO is used as the multiferroic pinning layer simply because of its robust spontaneous electric and magnetic orders with high transition temperatures, which makes it unique from other multiferroic materials. Besides, the robust coupling between the ferroelectric and antiferromagnetic orders has been clearly established [26-27,77-78]. Given that room temperature ferroelectric ferromagnet still remains absent, BFO thus provides an alternative to achieve the goal of electrical control of magnetism.

The reason to choose LSMO as the ferromagnetic layer lies in its room temperature ferromagnetism and good structural compatibility with BFO. In a strongly correlated electron system like LSMO, the charge, spin, orbital and lattice degrees of freedom are intimately interacting with each other. Small perturbation of one order parameter may provoke significant variations in other order parameters, thus modulating the related physical properties. Once the multiferroic orders from BFO are also brought into play, the interplay within this heteroepitaxial system will become even more complex. New physics and novel properties may emerge due to the frustration of the order parameters at the interface. Furthermore, the CMR effect of LSMO may add on to the functionalities of the potential device, assuming that the spin states in LSMO can be manipulated via the BFO layer.

The study on BFO-based ferromagnetic-multiferroic systems is still at the primitive stage. Through the investigation of LSMO/BFO heterostructure, we aim to gain more

insight into the mechanisms that underpin the exchange interactions. Although we notice a few very recent reports [73-74] on the exchange bias of the LSMO/BFO system during writing this dissertation, a microscopic picture of the exchange coupling and its relationship with the ferroelectric domains of BFO remains obscure, which will be discussed in detail later in the dissertation. Our ultimate goal is to manipulate the ferromagnetic domains of LSMO by electric field. The roadmap of the study can be summarized in the following steps:

- (i) Grow high quality epitaxial BFO thin films on STO substrates using pulsed laser deposition by optimizing the growth parameters and characterize the relevant ferroelectric properties.
- (ii) Control the ferroelectric domains of BFO, thus the antiferromagnetic domains, since the two are intimately coupled. This can be done through domain engineering during growth or ex-situ domain manipulation via external electric field.
- (iii) Investigate the exchange coupling effect between BFO and LSMO thin films. Construct a prototype device to attempt the electrical manipulation of the local ferromagnetism in LSMO.

Chapter 2 Growth and Characterizations of BiFeO₃ Thin Films

Although early studies on BFO can be dated back to 1970s, poor sample quality prevented the discovery of the outstanding ferroelectric properties of BFO [24]. With the significant progress in thin film deposition techniques, the intrinsic properties of BFO were finally unraveled a few years ago in thin-film form, leading to the renaissance of the field [39]. Therefore, sample quality is critical to the subsequent study of the functionalities of BFO. In this chapter, we aim to grow high quality epitaxial BFO thin film on single crystal STO substrate using pulsed laser deposition (PLD) technique. To achieve this goal, the film growth parameters are optimized by varying the substrate temperature and oxygen partial pressure. The phase purity and related ferroelectric properties of the BFO thin films grown under different oxygen pressures are examined systematically to reveal the influence of the oxygen pressure, which serves as a guide in epitaxial BFO thin film growth.

2.1 Introduction to Pulsed Laser Deposition

The successful growth of cuprate superconductor thin films via PLD in late 1980s [79] triggered the rapid development of PLD in laboratories for thin film deposition, especially for functional oxides (i.e. high T_C superconductor, colossal magnetoresistive oxides, etc.) [58]. Throughout the past two decades, PLD has become one of the most popular thin film growth techniques for scientific research [80-84].

Conceptually and experimentally, PLD seems to be a rather simple technique. Absorption of the laser radiation leads to the rapid heating and vaporization of the target

material, forming a dense plasma which contains energetic molecules, neutral atoms, ions and electrons. The remainder of the laser pulse keeps heating and accelerating the plasma, which propagates perpendicular to the target surface and moves towards the substrate. This is followed by the film growth process on the heated substrate.

Figure 2.1 Sketch of the structure layout of a standard pulsed laser deposition system.

A typical PLD system is schematically shown in Figure 2.1. The central part is a deposition chamber equipped with vacuum pumps, target holder, substrate heater and rotators. Various pressure gauges are used to control the chemical environment during deposition. For oxide growth, oxygen or ozone is widely used. Another important component is the optical system which consists of the excimer laser and the optics including apertures, mirrors and lens. After focusing, the energy density can reach 1 to 5 J/cm² at the target surface, which is more than enough to ablate almost all materials. Due to the high energy output, the induced plasma contains energetic species which will cause the deposition process to be far from equilibrium. However, it is just the advantage of PLD over other deposition techniques. Such nonequilibrium ablation is favored in

preserving the complex stoichiometry, namely, the congruent transfer of material. Therefore, PLD is successful in growth of materials with very complex compositions. Moreover, by switching between multiple targets, artificially layered structures such as superlattices and composites can be fabricated with ease. The low-cost and versatility of PLD makes it an excellent tool for exploring a wide range of novel materials in research laboratories.

However, like other growth techniques, PLD also suffers from some drawbacks. The biggest issue that limits PLD to mostly research level is the uniformity of the thin film. Due to the highly forward directional nature of the plume, a uniform thickness can only be obtained within a very limited area (typically 1 to 2 cm in diameter in our case), preventing it from scale-up to larger wafers. Another inevitable problem is the ejection of micron-sized particulates which will be detrimental to the film properties. Such effect is called “splashing”, mainly resulting from overheated molten droplets being expelled from the target. Last but not least, due to the many factors involved, the deposition of novel materials usually requires laborious work on the optimization of deposition parameters, including temperature, oxygen pressure, laser energy density, target-to-substrate distance and so on.

2.2 Experimental Procedure

BFO epitaxial thin films were grown on SRO-coated STO substrates with (001), (110) and (111) orientations by ablating a stoichiometric target using PLD. After substrate ultrasonic cleaning and target preparation, they were both placed in the deposition chamber, which would then be pumped to a base pressure of $<10^{-5}$ Torr. Subsequently,

the oxygen flow would be controlled to reach a desired partial pressure for deposition while heating the substrate. During thin film growth, a KrF excimer laser with 248 nm wavelength was executed at frequencies between 1-20 Hz with a laser energy density of around 1 J/cm². Once the deposition was finished, the sample would be slowly cooled under 760 Torr oxygen at a rate of 5 °C/min. The detailed deposition parameters are listed in Table 2.1. The thicknesses of the BFO films were controlled to be around 200 nm to enable ferroelectric measurements.

The structure and phase purity of the films were examined using a high-resolution X-ray diffractometer (Panalytical X-pert Pro). 40-μm square Pt top electrodes were patterned via a standard photolithography process for electrical measurements using Presicion LC ferroelectric testing system (Radiant Technologies). Chemical analyses were performed by energy dispersive X-ray spectroscopy (EDS) equipped on a scanning electron microscope (SEM) (JSM-6360). Surface morphology and PFM were imaged on an atomic force microscope (AFM) (Asylum Research MFP-3D) using Pt/Ir coated tips. Magnetic properties are characterized by a vibrating sample magnetometer (VSM) (LakeShore 7400) under ambient condition.

Table 2.1 List of the deposition parameters used for the optimization of BFO thin films growth.

Deposition Parameters	Substrate Temperature	Oxygen Pressure	Laser Frequency	Laser Fluence	Target-to-substrate Distance
SRO	700 °C	100 mTorr	3 Hz	~1 J/cm ²	6 cm
BFO	600-750 °C	1-100 mTorr	1-20 Hz	~1 J/cm ²	5 cm

2.3 Optimization of Thin Film Growth Conditions

In this work, epitaxial BFO thin films were mainly deposited on STO single crystal substrates using PLD. Due to the small lattice mismatch between BFO (bulk lattice constant ~ 3.96 Å) and STO (bulk lattice constant ~ 3.905 Å), epitaxy is facilitated during film growth.

Figure 2.2 (a) SrTiO₃ substrate with atomic flat surface. (b) SrRuO₃ deposited on SrTiO₃ in step-flow growth mode. (c) XRD pattern of SrRuO₃/SrTiO₃ with Kiessig fringes and rocking curve of small FWHM indicate small roughness and high crystallinity. The height scale in (a) and (b) is 2 nm.

The quality of the substrate is critical for the thin film growth. Quasi-ideal STO surface can be obtained through buffered HF treatment (Figure 2.2 (a)) [85-86]. The purpose of substrate treatment is to obtain atomic flat surface with one-unit-cell steps, whose width is determined by the miscut angle of the substrate. Such nanoscale-engineered structure can serve as a template to control the growth mode, the crystal structure and the domain structure of the films deposited on it. Prior to BFO growth, metallic SrRuO₃ (SRO) (bulk lattice constant ~ 3.93 Å) layer was deposited first as the bottom electrode to facilitate the electrical measurements. Under appropriate conditions (Table 2.1), SRO can be grown in step-flow mode to preserve the atomic-flat morphology of the substrate (Figure 2.2 (b)). The Kiessig fringe in the XRD pattern is a manifestation of the smooth surface and sharp interface. Full Width at Half Maximum (FWHM) of the SRO (002) peak exhibits a value close to the substrate, implying high crystallinity and coherent lattice (Figure 2.2 (c)).

Figure 2.3 Temperature–oxygen pressure phase diagram of BFO thin film grown by PLD. (Red symbols are data obtained in this study, black ones are data adapted from Béa, *et al.* [87])

The deposition process is affected by a number of parameters. Among them, substrate temperature and oxygen partial pressure are believed to be the two most important ones, as they, to a great extent, determine the thermodynamic environment for the phase formation and stabilization. Therefore, the optimization of the BFO growth conditions was mainly focused on these two parameters. By varying the temperature between 600 °C and 750 °C and oxygen pressure between 1 mTorr and 100 mTorr, we were able to map out the growth window, within which phase-pure BFO can be grown. As depicted in Figure 2.3, lower temperature and higher oxygen pressure leads to the formation of bismuth oxides, while iron oxides start to appear under the opposite conditions. Such behavior can be explained by the volatility of Bi element, which will be more prominent under high temperature and low oxygen pressure. Our result is qualitatively consistent with the report by Béa *et al.* [87], except for a shift in the temperature axis, which might be due to the temperature variation from chamber to chamber.

It seems to be commonsense to use Bi-excess target to compensate for the Bi loss during deposition [34,47,87]. However, in this work, excessive Bi oxides were usually found in the film rather than Fe oxides if stoichiometric BFO target was used. By analyzing the composition using EDS, it is found that the ablated target area is highly Bi-deficient with Bi/Fe ratio as low as 0.5, which means that more Bi are sputtered out by the laser compared to Fe during deposition. This finding is in agreement with the volatile nature of the Bi, which has much lower melting point, boiling point and vapor pressure than Fe (Table 2.1). Therefore, following the vaporization process of the target material, more Bi will reach the substrate. By selecting proper temperature and oxygen pressure, extra Bi will reevaporate from the substrate surface, leaving stoichiometric BFO. However, when temperature is low and/or oxygen pressure is high, not all excessive Bi will evaporate, resulting in Bi oxide impurities. On the contrary, excessive Bi element will reevaporate more intensively under the opposite conditions, leading to Bi-deficient BFO films. At even higher temperatures or lower oxygen pressures, BFO may become thermodynamically unstable, and Fe oxides start to form.

Table 2.2 Melting point, boiling point and vapor pressure of bismuth and iron elements. (Adapt from [88])

Element	Melting point (°C)	Boiling point (°C)	Vapor pressure at 760 °C (mmHg)
Bismuth (Bi)	271	1450	1420
Iron (Fe)	1535	3000	2735

The ferroelectric properties of the films grown under optimized condition were first studied with respect to different crystal orientations. Hysteresis loops of (001), (110) and (111) oriented films are shown in Figure 2.4, with $P_r \sim 60 \mu\text{C}/\text{cm}^2$ for (001) films, ~ 80

$\mu\text{C}/\text{cm}^2$ for (110) films and $\sim 100 \mu\text{C}/\text{cm}^2$ for (111) films. After projecting the polarizations onto the same [111] direction, the values coincide with each other. This result confirms that the intrinsic polarization direction of BFO thin film is close to $\langle 111 \rangle$ directions, in good agreement with previous report [32].

Figure 2.4 Ferroelectric polarization hysteresis loops of (001), (110) and (111)-oriented BFO films. The inset shows the normalized values after projecting the polarization of three different orientation samples onto $\langle 111 \rangle$ directions.

2.4 Influence of Oxygen Partial Pressure on the Ferroelectric Properties

Within the growth window where phase-pure BFO can be obtained, an oxygen pressure dependence study is conducted to investigate its effect on the film properties [89]. 200 nm BFO thin films were deposited on SRO coated STO (100) substrates at oxygen pressures ranging from 1 to 100 mTorr, while fixing other growth parameters. The XRD patterns of BFO thin films are shown in Figure 2.5. Only (00L) peaks of BFO are present, indicating epitaxial growth of the films. The upper limit for single phase BFO formation is 20 mTorr, above which excessive Bi oxides begin to appear. On the other hand, even at the lowest

oxygen pressure of 1 mTorr, no trace of Fe oxides is observed within the detection limit of the XRD machine. However, the intensities of the BFO peaks indeed decrease with the reduced oxygen pressure, indicating poorer crystallinity.

Figure 2.5 XRD patterns of BFO thin films deposited under various oxygen pressures ranging from 1 mTorr to 40 mTorr.

Ferroelectric properties including polarization, leakage current, permittivity and piezoelectric coefficient were thoroughly investigated for BFO films grown under different oxygen pressure. The results are summarized and plotted in Figure 2.6. As the oxygen pressure decreases, the remanent polarization, dielectric constant and piezoelectric coefficient all continue to drop, accompanied by a minor loop shift towards the negative side of electric field axis, corresponding to a preferred polarization direction pointing “up”. The shape of the polarization hysteresis loops change from square at high oxygen pressure to slim/canting at low oxygen pressure, with no obvious difference in the coercive field. The leakage current is the only one that doesn’t decrease monotonically with the oxygen pressure. The films grown under 20 mTorr or above show leakage

current 2-3 orders of magnitude larger than those grown under low oxygen pressures. As a result, ϵ_r and d_{33} data could not be obtained for samples grown under high oxygen pressure as they tend to break down under dc bias stress. It is also worth noting that there are clear double-loop features in the dielectric hysteresis curves with two peaks locating at the coercive field and around zero bias, respectively.

Figure 2.6 Ferroelectric properties of BFO films grown under different oxygen pressures. (a) Ferroelectric polarization hysteresis loops, $P-E$. (b) Leakage current versus electric field. (c) Dielectric hysteresis loops, ϵ_r-E . (d) Piezoelectric hysteresis loops, $d_{33}-E$.

To understand the different electrical properties of BFO films grown under different oxygen pressures, the film compositions were investigated using EDS, since the oxygen pressure greatly affects the Bi/Fe ratio during growth. Since EDS is a semiquantitative technique, a stoichiometric BFO target was used as a reference. As plotted in Figure 2.7 (a), the Bi/Fe ratio in the films decreases monotonically with the reducing oxygen pressure. It is quite unexpected that for BFO film grown under the lowest oxygen pressure

the Bi deficiency can reach ~ 0.6 without forming considerable Fe oxides that is detectable in XRD as shown in Figure 2.5 (1 mTorr sample). Contrarily, tiny Bi excess at high oxygen pressure results in Bi oxide impurities (Figure 2.5, 40 mTorr sample). This finding suggests that the BFO lattice in the perovskite phase has a large tolerance for Bi vacancies, which is consistent with the previous report on molecular-beam epitaxy derived BFO films [90], and is similar to the PbTiO_3 system [91]. In order to detect the possible presence of minor Fe oxides in the films, the magnetic properties of the films were measured using VSM (Figure 2.7 (b)). Although all the samples exhibit very weak magnetic response, the saturated magnetization indeed increases as the oxygen pressure goes down, in good agreement with previous study [48]. Therefore, we cannot rule out the presence of a tiny amount of $\gamma\text{-Fe}_2\text{O}_3$ impurity or the valence change of Fe ions from 3+ to 2+.

The relationships between the Bi/Fe ratios and the ferroelectric properties are plotted in Figure 2.7 (c). It is widely accepted that the stereochemically active Bi^{3+} electron lone pair is the main driving force for the large spontaneous polarization in BFO [29]. Hence, introducing more Bi vacancies (V_{Bi}'') inevitably would deteriorate the ferroelectric property in the film. In addition to the intrinsic decrease of polarization, domain pinning by charged defects can also contribute to the reduced ferroelectric properties. The canted ferroelectric hysteresis loops at low Bi/Fe ratios resemble that observed in fatigued samples, which is related to the frozen domains due to defect rearrangement [92]. Other than V_{Bi}'' , oxygen vacancies ($V_{\text{O}}^\bullet$) are thermodynamically unavoidable in the film to maintain the charge neutrality. These two oppositely-charged point defects usually combine to form $V_{\text{Bi}}'' - V_{\text{O}}^\bullet$ defect-dipole pairs, generating an effective internal field to

pin the ferroelectric domains [93-95], giving rise to the reduction of switchable polarization. When the Bi/Fe ratio increases to the stoichiometric region, the polarization gradually saturates to the intrinsic value of $60 \mu\text{C}/\text{cm}^2$ along (001) direction.

Figure 2.7 (a) Relationship between Bi/Fe ratio and the oxygen pressure during film growth. (b) Magnetic hysteresis loops of BFO films grown at different oxygen pressures. (c) Bi/Fe ratio dependence of remanent polarization P_r , dielectric constant ϵ_r and film resistivity at 100 kV/cm. (d) Bi/Fe ratio dependent remanent d_{33} and electrostrictive coefficient Q_{eff} . The linear fit in (a) is to guide the eyes.

There is less dependence on the Bi concentration in the relative dielectric constants, which typically range from 60 to 80. All the samples show little frequency dependence up to 2 MHz, excluding extrinsic contributions such as space charge or domain wall motion. The piezoelectric coefficient, d_{33} , in a single crystal can be expressed by the following semiempirical phenomenological equation [96]:

$$d_{33} = 2\epsilon_0\epsilon_{\text{int}}Q_{\text{eff}}P \quad (1)$$

where ϵ_0 is the vacuum permittivity, ϵ_{int} is intrinsic relative permittivity, P is the polarization, Q_{eff} is effective electrostrictive coefficient along [001] direction. Based on

the measured d_{33} , ϵ_{int} and P data, Q_{eff} values for different Bi/Fe ratio can be calculated, as shown in Figure 2.7 (d). The larger Q_{eff} at Bi-deficient region indicates that the BFO lattice is easily distorted.

On the contrary, the resistivity exhibits a totally different trend with respect to the Bi/Fe ratio. There are two main sources for the commonly observed large leakage current in BFO thin films. One is the highly conductive Bi oxide phase [97]; the other is related to oxygen vacancies [98-99]. The deficiency of Bi content will undoubtedly suppress the formation of Bi oxides. Moreover, as described previously, Bi vacancies will to some extent compensate the n-type doping effect of oxygen vacancies. Consequently, compared with the stoichiometric or Bi-rich samples, the Bi-poor samples are much more resistive. From this point of view, Bi vacancies can be considered as a self doping, leading to leakage current reduction similar to that induced by the widely reported aliovalent/aliovalent cations doping [100-103].

To better understand the correlation between composition and ferroelectric properties at the microscopic level, PFM was used to probe the local domain structures and piezoelectric response. The ferroelectric domain images were recorded in contact scan mode together with the topographies of the films. The AFM tip serves as a movable electrode to measure the piezoelectric hysteresis loops at different locations. The surfaces of the samples grown under low oxygen pressure (5 mTorr) are typically characterized by island-growth features. The corresponding ferroelectric domains are mosaic with an average domain size of ~50 nm. Local d_{33} hysteresis loops measured at random points all exhibit a slight shift towards negative bias, in agreement with the dominantly preferred

polarization direction of pointing “up”, which is also consistent with the macroscopic polarization hysteresis loops.

Figure 2.8 (a) & (b) Topography, (c) & (d) Out-of-plane domain structures and (e) & (f) Local d_{33} hysteresis loops of BFO films deposited under oxygen pressures of 5 and 20 mTorr, respectively. Yellow or purple tone in (c) & (d) represents upward-pointing or downward-pointing domains. The local d_{33} hysteresis loop in each domain was plotted in the corresponding color.

In contrast, the topographies of samples grown at high oxygen pressure are dramatically different with crack-like features, leading to large ferroelectric domains at micron meter scale. Considering the deposition temperature of BFO thin films is much lower than its Curie temperature, the film growth is accompanied by significant ferroelastic strain. The

formation of distinct boundaries separating domains is a signature of strain relaxation for large ferroelastic distortion. However, such cracks could be another reason for the high leakage currents of Bi-rich samples [104].

Based on the macroscopic ferroelectric properties and microscopic domain structures, a defect-dipole model can be proposed to explain the different properties of samples grown under different oxygen pressures. During the film growth at low oxygen pressure, randomly distributed Bi vacancies combined with the oxygen vacancies to form $V_{\text{Bi}}'' - V_{\text{O}}^{\bullet\bullet}$ defect-dipole pairs, generating an internal electric field which orients the ferroelectric domain in random “up” and “down” directions, leading to the mosaic-like domain pattern. Once the oxygen pressure increases, the Bi vacancies will be greatly reduced, giving rise to less defect-dipole pairs in the film, where larger domains with uniform polarization directions can be grown. Macroscopically, the double peaks observed in the dielectric hysteresis loops are the consequence of the internal bias induced by the defect dipoles.

Figure 2.9 Ferroelectric domain configuration at different stages of the dielectric hysteresis cycle. The clear double-loop feature is due to the internal field (light blue) induced by defect-dipole pairs. Upward and downward domains are displayed in yellow and purple tones, respectively.

As illustrated in Figure 2.8, when the external electric field is large enough, the internal bias can be overwhelmed, resulting in a fully poled polarization state. However, owing to the immobility of the point defects, it is almost impossible to reorient or eliminate the defect dipoles. Thus, upon removing the external electric field or applying a small opposite field, part of the ferroelectric domains can be easily switched back to the original state. The backswitching of the polarization manifests itself as a peak close to the zero bias. Once the electric field exceeds the coercive field of the film, the second peak will show up. The amplitudes of the peaks also reflect the amounts of switched polarization, which is in good agreement with the percentage of “up” and “down” domains in the as-grown films (Figure 2.8 (c)).

2.5 Conclusions

Fabrication of high quality epitaxial BFO thin films forms the critical basis for the exploration of its multiferroic properties. To achieve this goal, in this chapter, I mainly focus on two growth parameters, namely, temperature and oxygen pressure to sketch out the appropriate growth window for epitaxial BFO thin films by PLD. A systematic study on the oxygen pressure dependence of ferroelectric properties was then carried out to give more insight into the interplay between film composition and the related properties. The results and findings are summarized as follows:

- (i) By depositing BFO films under various temperatures and oxygen pressures, the deposition phase diagram can be mapped out. According to the diagram, high temperature and low oxygen pressure lead to Bi deficiency (or Fe excess), while low temperature and high oxygen pressure result in Bi excess (or Fe deficiency).

- (ii) Through compositional analysis, it is confirmed that the Bi/Fe ratio in the film decreases when the oxygen pressure goes down. Consequently, BFO epitaxial thin films with low Bi content give rise to inferior ferroelectric properties. For the microstructure and ferroelectric domain structure, films grown at low oxygen pressure are characterized by island-growth morphology and mosaic-like domain pattern. Large irregular ferroelectric domains are observed in films grown at high oxygen pressure, however, with cracks on the topography which lead to high leakage current. A defect-dipole model was proposed to explain the correlation between the Bi/Fe ratios and related ferroelectric properties.

To sum up, single-phase epitaxial BFO thin films are successfully fabricated via PLD on SRO-coated single crystal STO substrates. Excellent ferroelectric properties are obtained in films grown at high oxygen pressure (20 mTorr) with film composition close to stoichiometry. However, the microstructure of the films grown at high oxygen pressure shows crack-like features and irregular-shape domain patterns. These findings pave the way for the subsequent ferroelectric domain control and engineering of BFO epitaxial thin films.

Chapter 3 Domain Engineering and Domain Switching in BiFeO₃ Thin Films

The functionalities of multiferroic BFO are not limited to the magnetoelectric coupling between ferroelectricity and antiferromagnetism. Recent discoveries of fascinating properties related to the domain walls in BFO have led to a new surge of research work to explore their potential applications [71,105-106]. To investigate either the magnetoelectric coupling or the domain wall functionalities, BFO thin films with well controlled domain structures are highly desirable. In Chapter 2, we have demonstrated that phase-pure epitaxial BFO thin films can be obtained under appropriate growth window and their ferroelectric properties can be tailored via tuning the oxygen pressure. However, the corresponding domain structure of BFO films with mosaic patterns for low pressure samples and crack-like features for high pressure samples will undermine our subsequent research into its magnetoelectric applications. Thus, the goal of this chapter is to further control the ferroelectric domain structures of epitaxial BFO thin films both in-situ during film growth and ex-situ via electrical switching. To realize domain engineering during growth, a series of variables including target composition, film growth rate, substrate vicinality and substrate anisotropy will be investigated separately to reveal their influence on the domain structures. Moreover, the response of ferroelectric domains of BFO films to the external electric field will be studied, which is a critical step in the pursuing electrically manipulable magnetism in BFO-based devices.

3.1 Ferroelectric Domain Engineering in BiFeO₃ Epitaxial Thin Films

3.1.1 Introduction

3.1.1.1 Ferroelectric Domain Structures in Epitaxial BiFeO₃ Thin Films

The systematic study on the ferroelectric domain structures of BFO began in recent years when high quality epitaxial film can be grown via advanced thin film deposition techniques [30]. Bulk BFO has a rhombohedral unit cell with polarization along one of the body diagonals. In thin film form, it is suggested that the rhombohedral symmetry is reduced due to the epitaxial strain, resulting in a monoclinic lattice with the distortion along $\langle 111 \rangle$ directions. Thus, there are totally four ferroelastic structural variants, corresponding to eight ferroelectric polarization variants in BFO (Figure 3.1 (a)). Depending on the angle between the neighboring polarization variants, 71°, 109° and 180° domain walls can be formed. The domain structures of BFO films on (110) and (111) oriented STO substrates are relatively simple. For (110) films, the compressive strain will drive the polarization towards the out-of-plane direction. Thus, only two structural variants out of four will be favorable. In (111) films, the domain variants will be further reduced. Only one structural variant with the polarization perpendicular to the film surface is energetically stable, giving rise to a single domain state [107].

Now let us focus on the (001) oriented films. In this case, the four structural variants are energetically degenerate, meaning that all of them can exist in the films. Thus, complicated domain patterns can be formed through the combination of different polarization variants. Although the epitaxial BFO thin films adopt a lower crystal symmetry than the bulk, their domain patterns can still be predicted based on the domain patterns in epitaxial rhombohedral ferroelectric films proposed by Streiffer *et al.* [108] By

considering the mechanical and electrical compatibility at the domain boundaries, two types of coherent twin boundaries are permitted in (001) BFO films: $\{101\}$ -type domain walls corresponding to 71° domain patterns; and $\{100\}$ -type domain walls corresponding to 109° domain patterns. As for the 180° domain walls, since it is ferroelectric rather than ferroelastic, there is no elastic constraint on it. Thus, it doesn't need to follow any specific crystallographic planes.

Figure 3.1 (a) Schematic of all four possible structural variants, corresponding to eight possible polarization variants in (001)-oriented BFO films. (Polarization vectors are indicated in colors consistent with those in PFM images.) (b) & (c) Domain configurations of the prototypical 71° and 109° patterns in rhombohedral epitaxial thin films.

Figure 3.1 (b) & (c) illustrates the formation of 71° and 109° domain structures, respectively. On the (001) surface, both domain structures lead to stripe patterns parallel to the $[100]$ or $[010]$ axis. To satisfy the lattice coherence requirement at the domain wall,

109° domain structures show a puckered fashion on the topography compared with the flat surface of 71° domain structures. In order to maintain the charge neutrality at the domain boundaries, the polarization vectors follow a head-to-tail arrangement in both 71° and 109° domain structures. However, if we consider the total net polarization of the film, 71° domain structures have a finite component in the substrate normal direction, corresponding to a fully-poled state, whereas the normal components of polarizations in 109° domain structures cancel out with each other, given that each domain has the same width. As a consequence, 109° domain structures should be more effective in reducing the depolarization field in BFO films, especially when grown on an insulating substrate such as STO. Surprisingly, BFO films deposited on bare (001) STO normally exhibit fully-poled state with all the polarizations pointing “up”. Thus, only 71° domain patterns are observed in the films. Accordingly, our discussion of BFO domain control on STO will be limited to the four upward-pointing polarization variants. The underlying mechanism of this self-poling effect is still unclear at this point, though some reports suggest that it is closely related to oxygen vacancies [109-110]. Detailed investigations are underway to unravel the factors that control the polarization directions of the as-grown films. Since it is beyond the scope of this dissertation, it will not be discussed here.

The 71° and 109° domain structures described above are ideal cases under the presumption that the ferroelectric film undergoes an equilibrium phase transition upon cooling through its Curie temperature (T_C) [108]. Practically, the deposition temperature is usually lower than the T_C of BFO. Furthermore, the growth conditions in PLD or other techniques are generally far from thermodynamic equilibrium. That is why mosaic

domain patterns with multiple polarization variants are usually observed for (001) BFO films grown on STO substrate [111-112]. The complexity of mosaic domain structures will hinder the in-depth exploration of the novel functionalities of BFO thin films and usually leads to inferior ferroelectric properties [104,113]. Therefore, domain engineering to reduce the polarization variants and simplify the domain structures is highly desirable. Figure 3.2 illustrates two typical domain structures in (001)-oriented BFO epitaxial thin films: disordered mosaic domains and ordered stripe domains.

Figure 3.2 (a) & (b) Topography and in-plane PFM images of BFO film with mosaic domain pattern. (c) & (d) Topography and in-plane PFM images of BFO film with stripe domain pattern.

3.1.1.2 Domain Characterization in BiFeO_3 by Piezoresponse Force Microscopy

In this study, the domain structures of BFO thin films are mainly characterized using PFM. After almost two decades' development since first introduced in 1990s [114], PFM

has become the most popular technique in probing the electromechanical interactions and imaging ferroelectric domains at the nanometer scale [115-116].

The system setup of a typical PFM is schematically shown in Figure 3.3 (a). PFM detects the piezoelectric deformation of the sample surface induced by an external electric field. It is performed under contact scan mode, where the cantilever of the AFM probe is pressed against the surface under a constant force. The bending of the cantilever results in a constant vertical deflection of the reflected laser beam on the photodetector. During scan, through the feedback system, the piezo unit attached to the probe will drive the cantilever up or down according to the topography underneath in order to maintain the constant deflection. In this way, the three-dimensional surface morphology can be constructed based on the displacements of the piezo unit. In the meantime, a small-signal AC voltage is applied between the tip and the sample. Due to the piezoelectric effect, the surface of ferroelectric material will elongate and shrink accordingly. Since the tip is kept in mechanical contact with the sample surface, the cantilever and thus the laser beam on the photodetector will oscillate at the same frequency as the input AC bias. Subsequently, this oscillation signal can be picked up using a lock-in amplifier. The amplitude of the signal corresponds to the magnitude of the piezoelectric coefficient, while the phase provides information about the direction of the polarization vector. Although the PFM signal is superimposed on the topographic signal, there is little convolution between them due to the large difference in signal frequency. In this way, the ferroelectric domain images can be acquired together with the topography images.

Conventional PFM at the early stage only measures the vertical deformation of the sample, which is defined by the effective piezoelectric coefficient d_{33} related to the

out-of-plane polarization component (Figure 3.3 (b)). To obtain the three-dimensional domain structures, vector PFM has been developed, which also monitors the angular torsion of the cantilever induced by the lateral movement of the sample surface [117-118]. This process involves the piezoelectric coefficient d_{15} associated with the in-plane polarization component (Figure 3.3 (c)). By combining both the vertical and lateral PFM images, three-dimensional polarization vectors can be reconstructed to elucidate the full picture of the domain configurations.

Figure 3.3 (a) Schematic illustration of a typical PFM setup, where topography, in-plane and out-of-plane domain structures can be simultaneously recorded. (b) Out-of-plane signal originates from vertical deflection of the cantilever induced by out-of-plane polarization component. (c) In-plane signal originates from lateral torsion of the cantilever induced by in-plane polarization component.

As depicted in Figure 3.3 (a), the photodetector is divided into four quadrants. The out-of-plane signal is obtained from the difference between the top and bottom halves of the photodetectors, namely $(a + b) - (c + d)$, while the in-plane one is the difference between the left and right halves, $(a + c) - (b + d)$. Depending on the polarity of the polarization, oscillation of the cantilever could be in phase (0° difference) or out of phase (180° difference) with respect to the AC driving field. As a consequence, domains with different polarization orientations will exhibit contrasts in the phase images, even if they may have the same amplitude. However, instead of recording phase images only, we normally use images that contain information from both the amplitude and phase signals to investigate the domain structures of BFO thin films.

Figure 3.4 Interpretation of the domain contrasts in (a) out-of-plane and (b) in-plane PFM images in (001)-oriented BFO thin films with eight possible polarization variants. The color of each polarization variant represents the tone of corresponding domain in the PFM images. 71° , 109° and 180° domain walls can be determined depending on the angles between the polarization variants.

The interpretation of the contrast in PFM images of BFO thin films is illustrated in Figure 3.4. As mentioned above, (001)-oriented BFO epitaxial films have eight possible polarization variants along the $\langle 111 \rangle$ body diagonals, half of which have normal polarization component pointing upwards, while the rest half are pointing in the opposite

direction. Thus, they are totally out of phase in the out-of-plane PFM images, with upward-pointing domains showing yellow tone and downward-pointing domains exhibiting purple tone.

If we consider the in-plane projection of all polarization variants, they lie along the four possible $\langle 110 \rangle$ directions. Since the scan is performed with the cantilever along one of the $\langle 110 \rangle$ axes, four polarization variants will have the in-plane polarization component parallel to the long axis of cantilever, which produces a “buckling” effect on the cantilever instead of the lateral torsion. Thus, ideally no in-plane piezoresponse signal can be detected for these domain variants, giving rise to a brown tone in the PFM images. However, practically this “buckling” effect usually affects the out-of-plane signals, inducing a crosstalk in out-of-plane PFM images [118-119]. As for the rest four polarization variants with in-plane components perpendicular to the long axis of the cantilever, they will display yellow or purple tone respectively, depending on the polarities. To distinguish the in-plane orientations of the four variants with brown tone, we can simply rotate the sample by 90° and scan the cantilever along another $\langle 110 \rangle$ axis. By analyzing the out-of-plane and in-plane contrasts for each domain, the polarization vectors can be determined to delineate the configurations of the polarization variants. According to the angles between the polarization variants, three different types of domain walls can also be identified, as schematically indicated in Figure 3.4.

3.1.2 Experimental Procedure

BFO thin films were epitaxially grown directly onto STO (001) or DyScO₃ (DSO) (110)_o substrates without bottom electrode by PLD. The film growth procedures used here

are similar as those in Chapter 2, except that the substrates were adhered to the substrate heater using silver paste to improve the heat transfer. This method was proved to be effective in eliminating the cracks formed in BFO films under high oxygen pressures (Chapter 2, Figure 2.8). The growth temperature and oxygen pressure were fixed at 700 °C and 100 mTorr, respectively. Note that the oxygen pressure used here is much higher than those used in Chapter 2 for pure phase BFO. However, no excessive Bi oxides were observed in the resulting films. This is because the improved thermal contact between the heater and the substrate gives rise to much higher actual temperature of the substrate, which makes the reevaporation of the excessive Bi easier. The laser fluence was adjusted to be constant around 1 J/cm², while the target-to-substrate distance was fixed at 5 cm. The thicknesses of all the films were maintained to be around 50 nm.

In order to tailor the ferroelectric domain structure of BFO thin films, a couple of factors such as target composition, deposition rate and substrate miscut angle were varied to study their effects on the domain formation. For target composition, the Bi content is varied from 0.4 to 1. Film growth rate was adjusted by changing the laser frequencies, ranging from 5 Hz to 10 Hz. For substrate vicinality, STO substrates with different miscut angle along [100] or [110] direction were used for deposition. When studying one parameter, the rest were fixed. The details of the deposition parameters are summarized in Table 3.1.

After film deposition, the surface morphology and the ferroelectric domain structures were imaged using PFM (Asylum Research MFP-3D). The measurements were conducted under contact scan mode using Pt/Ti coated tips with a force constant of 2~5 N/m. Using the substrate edge ([100] direction) as the reference, the sample position is

adjusted so that the cantilever is directed towards [110] direction. During scan, an ac voltage of $V_{pp} = 4$ V was applied to the tip with a frequency of 10 kHz to drive the film into oscillation, whose amplitude and phase were then picked up by a lock-in amplifier. The details about the contrast interpretation of the domain patterns of BFO epitaxial thin films are referred to the last section.

Table 3.1 List of the deposition parameters used for tuning the domain structures of BFO thin films.

Invariable Parameters	Substrate Temperature	Oxygen Pressure	Laser Fluence	Target-to-substrate distance
Parameter values	700 °C	100 mTorr	~ 1 J/cm ²	5 cm
Variable Parameters	Target Composition (Bi _x FeO ₃)	Laser Frequency (film growth rate)	STO Miscut Angle	
Parameter Range	x = 0.4, 0.6, 0.8, 1	5 Hz, 7 Hz, 10 Hz	No miscut, 0.2° along [110], 0.2° along [100], 2° along [100]	
Other Fixed Parameters	Laser Frequency = 5Hz, Substrate miscut 0.2° along [100]	Bi _{0.6} FeO ₃ target, Substrate miscut 0.2° along [100]	Bi _{0.6} FeO ₃ target, Laser Frequency = 5Hz,	

3.1.3 Ferroelectric Domain Engineering during BiFeO₃ Growth

The growth temperatures for most ferroelectric thin films are above the Curie temperature T_C . Consequently, paraelectric-ferroelectric phase transitions will occur upon slowly cooling through T_C , accompanied by the domain formation. However, the growth temperatures for BFO thin films are typically lower than its T_C . Therefore, the ferroelectric domains have already formed during deposition. As the growth environment in PLD are thermodynamically nonequilibrium, the resultant domain structures are

significantly influenced by the deposition conditions, which provides us an opportunity to control the domain patterns via tuning the deposition environment. Additionally, the substrate may serve as a template, assisting in the domain engineering at the nanoscale.

3.1.3.1 Domain Control through Target Composition

As discussed in Chapter 2, the Bi yield from a stoichiometric BFO target is much higher than Fe during laser ablation. Under proper temperature and oxygen pressure, excess Bi will escape from the film surface, leaving a stoichiometric BFO film. However, the ferroelectric domain structures formed under such conditions are irregular and accompanied by cracks on the surface (Chapter 2, Figure 2.8). Consequently, it is a natural thought to use a Bi-deficient target to balance the yield difference between Bi and Fe instead of tuning temperature and oxygen pressure.

In this study, BFO targets with four different Bi contents (0.4, 0.6, 0.8 and 1) were used for film deposition, with all the rest parameters fixed at constant (Table 3.1). The corresponding ferroelectric domain patterns are illustrated in Figure 3.5. All the samples show no contrast with a yellow tone in the out-of-plane PFM images, indicating all polarization pointing upwards. For the in-plane domain structure, the stoichiometric target gives rise to mosaic-like domain pattern with considerable randomness (Figure 3.5 (a)). As the Bi concentration in the target decreases, the resulting domain structures become more and more regular, characterized by stripe-like domain patterns as shown in Figure 3.5 (b) & (c). However, when the Bi content decreases to 0.4, the domain pattern exhibits significant randomness again (Figure 3.5 (d)). As demonstrated in the oxygen pressure dependence study in Chapter 2, Bi deficiency would cause random pinning of the

ferroelectric domains by defect-dipoles, leading to disordered domain patterns, which might be the case in $\text{Bi}_{0.4}\text{FeO}_3$ target. Therefore, the optimized domain structure is obtained at a Bi/Fe ratio of 0.5 to 0.6 in the target. This is consistent with the Bi/Fe ratio of a stoichiometric target surface after long-time ablation, which may produce a Bi/Fe yield close to 1. Combining the out-of-plane and in-plane polarization orientations, it can also be inferred that the regular stripe patterns are comprised of 71° domains, in agreement with previous reports [35,38,120].

Figure 3.5 Influence of the target composition on the domain structures of BFO thin films. (a)-(d) in-plane domain patterns of (001)-oriented BFO thin films deposited by targets with different Bi/Fe ratios. The insets are the corresponding out-of-plane PFM images with uniform yellow tone, indicating all the polarizations are pointing upwards.

Our compositional control of the domain structures using Bi-deficient targets is in striking contrast with the commonly accepted idea that Bi-rich target should be used to compensate for the loss of volatile Bi. The problem basically stems from the large difference in the ablation yields of Bi and Fe, which is usually neglected in PLD. If we use a stoichiometric target, although the excessive Bi-oxide impurities can be eliminated by adjusting the thermodynamic environment during growth (i.e. by reducing the oxygen pressure or increasing the temperature), the film quality is usually deteriorated, especially in term of domain structures, which impedes the successive exploration for functional applications of BFO thin films.

3.1.3.2 Domain Control through Film Growth Rate

Figure 3.6 Influence of the film growth rate on the domain structures of BFO thin films. (a)-(c) Topography and (d)-(f) corresponding in-plane domain structures of BFO (001) films with decreasing growth rate. (g) XRD θ -2 θ patterns and (h) rocking curves of (001) peak of BFO films with different growth rate. (i) Correlations among surface roughness, out-of-plane lattice constant and FWHM of (001) peak in (001)-oriented BFO thin films.

In addition to the target composition, the film growth rate is also critical in controlling the domain structure. As mentioned previously, PLD is a highly nonequilibrium and noncontinuous deposition technique. Between the laser pulses, there is a latent period for the adatoms to rearrange to the energetically favorable positions. However, if the growth rate is too fast for the adatoms to rearrange, the film growth mode will change from two-dimensional to three-dimensional. In this study, the influence of film growth rate on

the domain structures of BFO thin films was investigated. The growth rate was adjusted by varying the laser frequency, which is considered to be linearly proportional to the deposition rate. Three laser frequencies were used, namely 5, 7 and 10 Hz, which correspond to film growth rates of ~ 0.8 , ~ 1.1 and ~ 1.6 nm/min, respectively. $\text{Bi}_{0.6}\text{FeO}_3$ target was chosen for deposition with substrate temperature of 700 °C and oxygen pressure of 100 mTorr (Table 3.1).

As shown in Figure 3.6 (a)-(c), the topography of BFO films grown on (001)-oriented STO is usually featured by a crisscross structure, with the edges parallel to [100] or [010] direction. At high growth rate of ~ 1.6 nm/min, the formation of three-dimensional islands complicates the local electrical and mechanical boundaries, leading to a complex mosaic-like domain structure. By gradually decreasing the growth rate to ~ 1.1 nm/min and finally ~ 0.8 nm/min, the film surface becomes smoother and the growth mode changes from three-dimensional towards two-dimensional. Consequently, the domain structure becomes well-ordered 71° domain patterns (Figure 3.6 (d)-(f)). By examining the crystal structure and crystallinity in details using XRD, it is revealed that the BFO (001) peak shifts from 21.94° to 21.80° upon reducing the growth rate from ~ 1.6 nm/min to ~ 0.8 nm/min. This suggests an expansion of the c lattice constant from 4.048 Å to 4.074 Å. Furthermore, rocking curve of the (001) peak shows smaller full width at half maximum (FWHM) and higher intensity, which indicates a better crystallinity of the film. The correlations among surface roughness, BFO lattice constants and film crystallinity can be understood based on the structural relaxation of epitaxial film induced by three-dimensional island growth. Such three-dimensional growth mode produces free-standing islands, which partially relieve the compressive epitaxial strain from the

substrate. Thus, the out-of-plane c lattice constant will decrease when the surface becomes rougher. Certainly, inferior crystallinity is also expected in this case. Reducing the growth rate will drive the deposition process closer to equilibrium, resulting in atomic-flat film surface and fully strained coherent interface. The highly-coherent BFO films with regular stripe domains can serve as a good platform to study the functionalities of BFO and its exchange coupling with a ferromagnetic layer.

3.1.3.3 Domain Control through Substrate Vicinality

Using vicinal substrates is the most widely reported method to engineer the ferroelectric domain structure in BFO thin films [30,104,121-122]. After proper chemical and heat treatments, a miscut substrate can generate highly-ordered steps on the surface, which may serve as the nucleation sites for adatoms during film growth. This topographic anisotropy will favor certain domain variants while suppressing others. In this way, with less domain variants, well-ordered domain structures can be obtained. To study the substrate vicinity effect on the domain structures of BFO thin films, a series of (001)-oriented STO substrates with various miscut angles along [100] or [110] direction were selected for film deposition. According to previous optimization process, $\text{Bi}_{0.6}\text{FeO}_3$ target and a laser frequency of 5 Hz were used in the film growth. The rest parameters are referred to Table 3.1.

Figure 3.7 Influence of the substrate vicinality on the domain structures of BFO thin films. (a)-(d) Topography and (e)-(h) corresponding in-plane domain structures of BFO (001) films grown on STO substrates with various miscut angles.

Figure 3.7 demonstrates the evolution of the topography and in-plane domain structure with different miscut angles along different crystallographic axes. For films grown on exact STO with no miscut, the topographies are extremely flat, whereas the domain patterns are characterized by random combinations of two-variant stripe domains with all 4 structural variants present. When the miscut angle is 0.2° along $[110]$ direction, the ferroelectric domain pattern is well represented by two sets of stripe domains interlaced with each other, and the structural variants are reduced to 3. Surface morphology shows little anisotropy except for slightly increased roughness compared with no miscut case. If the miscut angle is still 0.2° , however, along $[100]$ direction, the amount of one set of stripe domains is greatly reduced while the other becomes dominant, which means that 2 structural variants are prevailing with minor third variant. Nevertheless, the corresponding topography still shows no preferred alignment of the step edges, probably due to the small miscut angle. Once the substrate vicinality increases to 2° along $[100]$

direction, well-aligned steps are apparent on the film surface. The related domain pattern is completely dominated by one set of stripe domains, leading to a BFO film with only 2 structural variants.

Figure 3.8 Schematic illustration of the energetically favorable and unfavorable domain configurations of (001)-oriented BFO films grown on STO substrates with miscut along [100] and [010] directions, respectively.

To understand the influence of substrate vicinality on the domain structures, all possible domain configurations in BFO film need to be carefully examined. Because the BFO films grown on (001) STO typically only exhibit upward-pointing polarization, our analysis can be reduced to four structural variants as demonstrated in Figure 3.8. There are four possible combinations to form 71° stripe domain patterns. For an exact STO with no miscut angle, all the combinations are energetically degenerate from symmetry consideration. Thus, all four possible structural variants are equally distributed in the BFO films as shown in Figure 3.7 (e). However, by introducing substrate vicinality, such

degeneracy can be lifted. Due to the existence of atomic step edges, certain domain variants will become energetically more favorable [104]. As schematically illustrated in Figure 3.8, if the miscut lies along [100] direction, the P_2 and P_3 domains are preferred because the rhombohedral tilt of the unit cell matches the downhill miscut direction, which is more effective to relieve the shear strain and reduce the system energy. On the other hand, the formation of P_1 and P_4 domains are prohibited in this case, because the rhombohedral distortion is against the step edge. If the substrate miscut is towards [010] direction, similarly, only the combination of P_1 and P_2 domains will be stabilized. A miscut in between the [100] and [010] directions leads to a competition between these two combinations. In case of miscut along [110] direction, these two sets of stripe domains are equally favorable. Thus, equal amount of them combine to form the domain pattern in Figure 3.7 (f). The minor extra domain variant in Figure 3.7 (g) is due to the small miscut angle of the substrate, which has relatively less step edges to induce anisotropy in strain relaxation. By simply increasing the miscut angle to 2° , the extra domain variant can be totally eliminated, giving rise to ideal two-variant stripe domains (Figure (h)).

The step edges of a vicinal substrate act as atomic-scale templates, introducing external anisotropy energy to selectively stabilize certain ferroelastic variants. This breaks a new path to engineer the domain architecture and tune the percentage of each structural variant. With reducing domain variants and ordered domain patterns, the theoretical model can be greatly simplified, facilitating the following study on the magnetoelectric coupling in BFO-based heterostructure.

3.1.3.4 71° and 109° Domain Patterns on Orthorhombic Substrate

Another approach to induce the anisotropic elastic energy is to use orthorhombic substrates. Through symmetry breaking of the substrate lattice, the in-plane lattice of BFO film along the two orthogonal in-plane axes will be subjected to different stress field, causing a preferred growth of some domain variants. As presented in the work by Chu *et al.* [123], 71° or 109° stripe domain patterns can be obtained in BFO films grown on DSO substrates by modifying the relevant electrical boundary conditions. The presence of a metallic bottom electrode is effective in screening the bound charges of the polarization, thus stabilizing a fully-poled 71° stripe domain pattern. However, if the bottom electrode is removed, 109° stripe domain pattern with alternating out-of-plane polarization components will become energetically favorable so as to minimize the depolarization energy.

In contrast to their method, we manage to obtain both 71° and 109° stripe domains in BFO films on bare DSO substrates simply by varying the target composition, similar to what we have demonstrated in tuning the domain structures on STO substrates. In this study, BFO epitaxial thin films were grown on (110)_o-oriented DSO substrates using Bi_{0.8}FeO₃ and Bi_{0.4}FeO₃ target at a laser frequency of 5 Hz. The other invariable parameters are given in Table 3.1.

When using a Bi_{0.8}FeO₃ target, 71° stripe domains are dominant in the BFO films. With decreasing Bi content in the target, 109° stripe domains begin to appear and become dominating when the Bi/Fe ratio in the target reduces to 0.4. As shown in Figure 3.9 (b) & (c), the 71° stripe domain pattern is featured by two domain variants with all the out-of-plane polarization components pointing upwards, whereas in case of 109° domains,

alternating contrast can be observed in both the in-plane and out-of-plane PFM images (Figure 3.9 (e) & (f)), consistent with the theoretical model described previously. If we recall the domain structure of BFO on STO, 71° stripe domains prevail with upward-pointing out-of-plane polarization component. In fact, by reducing the Bi content in the target, we did observe the emergence of downward-pointing domains. Combining these two separate observations suggests a universal mechanism that underpins the self-poling effect in ferroelectric thin films.

Figure 3.9 (a) & (d) Topography, (b) & (e) In-plane domain patterns and (c) & (f) Out-of-plane domain patterns of BFO films grown on DSO substrates with 71° and 109° stripe domains, respectively.

Based on our preliminary results, the preferred orientation of the out-of-plane polarization is tentatively attributed to the interplay between the orbital reconstruction at the film-substrate interface and the charged point defects, namely Bi and oxygen vacancies, which produces considerable internal field during film growth. An in-depth study is currently underway to gain a better understanding of these phenomena.

3.2 In-plane Ferroelectric Domain Switching in BiFeO₃ thin films

Ferroelectric switching mechanisms in BFO thin films are critically important to the coupling between ferroelectric and antiferromagnetic order parameters, which underpins the potential magnetoelectric applications. However, the polarization switching process in conventional vertically-sandwiched capacitors cannot be investigated directly. Consequently, planar-electrode capacitor is proposed to facilitate the ferroelastic switchings which are effective in altering the antiferromagnetic orders [124-125]. Additionally, the evolution of ferroelectric domain structures can be monitored in situ by PFM. The following section will focus on the polarization switching behavior in planar BFO capacitors, aiming to decisively control the ferroelectric domains using electric field. Since the ferroelectric polarization and antiferromagnetic spins are intimately coupled, the successful manipulation of the ferroelectric domains by electric field will lay a solid foundation for the ultimate goal of electrical control of ferromagnetism.

3.2.1 Introduction to Polarization Switching Mechanisms in BiFeO₃ thin films

The most important characteristic of ferroelectrics is the switchable spontaneous polarization. Multiferroics such as BFO enable electrical control of magnetic order parameter due to the close interaction between electric and magnetic orders. Such novel effect has great significance from both fundamental and application points of view. However, the switching process in BFO needs to be thoroughly investigated and decisively controlled first. ,

For rhombohedrally distorted BFO, three distinct switching events, namely 71°, 109° or 180° switching can take place under an electric field, depending on the rotation angle

of the polarization vector. Among them, 71° and 109° switchings are also accompanied by a change in the elastic distortion of the unit cell. Accordingly, they are termed as ferroelastic switchings. They also lead to the corresponding rotation of the magnetization plane and consequently the spin orientation. On the contrary, 180° switching only involves the reversal of the polarization vector, so it is purely ferroelectric in nature with no change in the antiferromagnetic order. Therefore, in our pursuit of electrically controllable magnetic devices, ferroelastic switchings in BFO thin films are highly desirable. The 180° switching should be suppressed.

In early studies of the polarization switching dynamics in (001)-oriented BFO thin films, all of the three switching events have been observed by PFM under conventional vertically stacked structures, where the AFM probe acts as a movable top electrode [30,126]. The results suggest that 180° switching is more favorable under low electric field while at higher field 71° and 109° polarization rotations become dominant. Recent work [127] on the ferroelastic switching of single-domain continuous BFO film as well as isolated BFO island reveals that though 71° switching has lower activation energy compared to 180° switching, it is still energetically unfavorable due to the large elastic energy induced. In order to stabilize the ferroelastic switching, isolated island-like capacitors are proposed, which, however, is limited by the fabrication techniques. Another way is to create new mechanical boundary conditions which can accommodate the large strain incurred by the ferroelastic switching. This scenario is quite common in the electrical “writing” process using an AFM tip, though unintentionally. Because the electric field generated by the nano-size AFM tip is highly nonuniform and spread with both in-plane and out-of-plane components, proximate domains outside the “writing” area

may also be switched by the stray field to release the electrical and mechanical energy. It is reported that by playing with the lateral motion and the applied bias of the scanning probe, ferroelastic switching in BFO thin films can be deterministically controlled to form regular 71° stripe domain patterns [128]. However, this method requires complicated scanning setup and the switching process is not straightforward.

3.2.2 Experimental Procedure

Based on previous results on domain engineering during film growth, optimized conditions were exploited to produce the films with smooth surface and ordered domain structures for electrical switching experiments. 60 nm-thick BFO epitaxial thin film was deposited on (001)-oriented STO substrate by PLD using $\text{Bi}_{0.6}\text{FeO}_3$ target and a laser frequency of 5 Hz. STO substrate used here has a 0.2° miscut along [110] direction (substrates with other miscut angles have also been tried, resulting in similar results). The rest parameters were fixed the same as listed in Table 3.1.

After BFO deposition, 40 nm Pt electrodes were patterned on top using photolithography lift-off process. The pattern consists of two electrode pad separating by a small gap, with different channel widths ranging from 1.4 μm to 8.8 μm (Figure 3.10). Taking the substrate edge ($\langle 100 \rangle$ directions) as the reference, the Pt electrode edges can be align at different angle with regard to the $\langle 100 \rangle$ directions during photolithography patterning. Afterwards, the measurements of ferroelectric properties and the domain switching were carried out using a commercial ferroelectric tester (Precision LC, Radiant Technologies). Meanwhile, the domain evolutions of BFO films can be visualized by PFM. The experimental method for PFM can be found in Chapter 3, Section 3.1.2. The

spatial distribution of the electric field of the planar capacitor was simulated using commercial finite element software (COMSOL Inc.).

3.2.3 Ferroelectric Properties of Quasi-planar Capacitors

The fundamental drawback of the vertically stacked configuration is the overwhelming out-of-plane component of the electric field, which promotes the 180° polarization reversal. Planar-electrode capacitor has been developed, which prevents the out-of-plane polarization switching due to the absence of a bottom electrode. Furthermore, under the horizontal geometry, the switching dynamics in BFO can be examined in-situ by PFM. Instead of using the coplanar electrodes embedded in the film as reported in the literature [124,129], we deposited Pt electrodes directly on top of the BFO film, similar to a single-unit interdigitated electrode pair.

The experimental setup is schematically shown in Figure 3.10 (a). The bias is applied to the Pt electrodes to switch the BFO film within the channel while the domain structures can be accessed by PFM simultaneously. Since the film and the electrodes are not in the ideal coplanar geometry, it is essential to find out the electric field distribution in the film. With the aid of finite element simulation, spatial distribution of the electric field can be visualized in a contour plot, as depicted in Figure 3.10 (b), where only the in-plane field component concerned is shown. Whereas the field near the electrode edges is highly concentrated, majority of the BFO film within the channel region is subjected to a relatively homogeneous electric field, which controls the in-plane switching of the polarization. Therefore, such device structure can be regarded as a quasi-planar capacitor.

Figure 3.10 (a) Sketch of the device layout of a quasi-planar BFO capacitor. (b) Cross-sectional view of in-plane electric field distribution of a 1.4- μm -wide capacitor under 1 V bias, simulated using finite element analysis. The relative permittivities of BFO and STO used in the simulation are 80 and 300, respectively.

When measuring the in-plane ferroelectric hysteresis loops of thin films, due to the very small capacitor area, the polarization switching current is usually overwhelmed by the parasitic capacitances that originate from the circuit elements and stray field into the air and substrate. As a result, planar interdigitated electrode arrays with repeated unit cells are commonly used to increase the effective area. In contrast, we managed to obtain the remanent hysteresis loop in a single-pair quasi-planar-electrode capacitor by subtracting the linear extrinsic contributions.

Figure 3.11 (a) Dual-pass voltage waveforms in remanent hysteresis measurement. The remanent hysteresis loop is obtained by subtracting the non-remnant component from the total switched polarization. (b) The deduction of remanent hysteresis loop of a 5.3- μm -wide capacitor using the method described in (a). (c) Remanent hysteresis loops of a 5.3- μm -wide capacitor measured using different voltages. (d) PUND measurements of quasi-planar BFO capacitors with different channel widths using 0.1 ms voltage pulse.

The remanent hysteresis loop measurement is based on a dual-pass field sweeping process (Figure 3.11 (a)). In the first voltage cycle, the preset pulse (green) and the measuring triangle wave (black) are of opposite polarity, which ensures both the remanent ferroelectric polarization and extrinsic contribution to be recorded. In the subsequent voltage cycle, the measuring wave (red) follows the polarity of the preset pulse (green), obtaining only the extrinsic component. Subtracting the extrinsic contribution from all the polarization measured allows the remanent-only hysteresis loop to be constructed. The deduction of a remanent hysteresis loop is exemplified in Figure 3.11 (b). Voltage-dependent hysteresis loops for a capacitor with 5.3 μm channel width exhibit

remarkable squareness with little coercive field (E_c) dispersion, suggesting a single-crystal-like coherent switching behavior (Figure 3.11 (c)). Furthermore, Positive-up-negative-down (PUND) pulse test enables accurate assessment of the remanent polarization (P_r) for capacitors with different channel widths (Figure 3.11 (d)). It is worth noting that the larger the channel width, the sharper the switching curve. This is consistent with the fact that electric field distribution is more uniform in capacitors with wider channels under quasi-planar geometry.

We were able to correlate the ferroelectric properties with the channel width which is essentially equivalent to the thickness of a vertically sandwiched capacitor. The relationship is depicted in Figure 3.12 (a). The remanent polarizations of all capacitors show a value of $48 \pm 3 \mu\text{C}/\text{cm}^2$. The slight reduction in narrow-channel capacitors may result from the incomplete switching of the polarization due to the relatively large field inhomogeneity. The in-plane polarization value in BFO thin films have never been reported before. However, through simple geometric deduction from the spontaneous polarization vector (P_s) in BFO, the in-plane polarization component along [100] direction (P_1) can be obtained according to the following equation [42]:

$$P_1 = \sqrt{P_s^2 - P_3^2} / \sqrt{2},$$

with P_3 being the out-of-plane polarization projection, which is measurable in stacked capacitors of (001)-oriented BFO thin films. Based on the polarization rotation model, the out-of-plane polarization P_3 was estimated to be $75 \mu\text{C}/\text{cm}^2$ in fully strained BFO on STO (001) substrate. Together with the intrinsic polarization $P_s = 102 \mu\text{C}/\text{cm}^2$, P_1 can be calculated to be $\sim 48.9 \mu\text{C}/\text{cm}^2$, in excellent agreement with our experimental result, which implies that solely in-plane component contributed to the measured polarization.

Figure 3.12 (a) Plots of capacitor's channel width versus remanent polarization P_r and nominal coercive field E_{cn} . (b) Amended effective coercive field E_{ce} of quasi-planar BFO capacitors with varying thicknesses (channel widths). Solid line shows the Kay-Dunn scaling fit of data in this study (red symbols) and from literature (black symbols).

The nominal coercive field (E_{cn}), defined as voltage divided by channel width, reduces monotonically with the channel width. However, the average electric field within the channel region taking into account the nonuniformity, namely the effective coercive field (E_{ce}), is more appropriate for the analysis, which is plotted in Figure 3.12 (b). A good linear fit with a slope $k = -0.62 \pm 0.03$ can be obtained by combining our E_{ce} data and those from literature [34,41,89,121,130], consistent with the scaling factor of $-2/3$ in the semiempirical coercive field scaling law, $E_c \propto d^{-2/3}$ [131]. Our experimental results happen to bridge the gap in the thickness range, indicating that the scaling law holds from nanoscale thin films to micron-size bulk samples.

3.2.4 Domain Switching Dynamics in Quasi-planar Capacitors

The planar device allows us to observe the domain switching dynamics across the thickness of the capacitor directly, which remains elusive in vertically-sandwiched capacitors. The in-plane domain structure of as-deposited (001) BFO thin film on STO is featured by a network comprised of two sets of 71° stripe domains, with the out-of-plane

polarization pointing upwards (Figure 3.13 (a)). Based on the rule of contrast interpretation in in-plane PFM images, the polarization arrangement in each domain can be resolved, as illustrated in the insets of Figure 3.13.

Figure 3.13 In-plane and out-of-plane (inset) ferroelectric domain structures of a quasi-planar BFO capacitor (a) in as-grown state, (c) & (d) after electrical poling with opposite bias and (b) at the intermediate stage during poling. The inset also schematically illustrates the corresponding in-plane domain configuration. The AFM cantilever is scanning along [110] direction in all PFM images. The marking in the red circle serves as an aid for the reader; domain merging region is denoted by blue circle.

When an electric field larger than the coercivity is applied, the original stripe domain network is converted to a highly-aligned single stripe domain pattern (purple/brown) composed of only two polarization variants. The average domain size increases from

~100 nm to ~170 nm, indicating that the domains reach a new equilibrium state after electric switching. Once the electric field is reversed, the domain pattern is largely preserved, with totally different contrast (yellow/brown). As expected, the net polarization follows the direction of the applied electric field. Throughout the switching process, the out-of-plane PFM images remain in the same tone, implying that only in-plane polarization rotations take place to form the regular 71° stripe domains. Therefore, in such planar-electrode configuration, only 71° or 109° ferroelastic switchings are permitted, whereas the 180° reversal is prohibited.

By scrutinizing the domain structures of the two fully-poled states, we confirm that the stripe domain switching is accomplished by 90° rotation of the polarization vector in each domain without creating new domains, which represents a 71° switching event. For example, from the polarization state in Figure 3.13 (c) to that in Figure 3.13 (d), the purple-tone domains convert to brown-tone ones while the brown-tone ones changes to yellow-tone ones. (The marking inside the red circle serves as an aid to locate the same position.) Domain coalescence or branching also exists during the polarization switching, as indicated by the blue circle, probably due to the nonuniform field at the electrode edges. Nevertheless, the coherent nanoscale domain switching is consistent with the macroscopic polarization hysteresis measurement results, providing more insights into the polarization switching in the quasi-planar capacitors.

The coherent polarization rotation is further corroborated by the domain arrangement at certain intermediate stage during switching, as shown in Figure 3.13 (b). Two stripe domain blocks with opposite net polarization directions are separated by one straight boundary running through the capacitor perpendicularly. This boundary consists of a

series of small 71° domain walls that split each stripe domain, confirming the 71° switching path during domain growth. Such intriguing domain pattern coincides well with the artificial domain structure created by advanced PFM “writing” method [128]. According to a recent report, the activation energy for 71° switching is the lowest one among the three switching schemes owing to the shortest switching path [127]. As a consequence, 71° polarization rotation becomes the predominant mechanism in the capacitor switching. Due to the magnetoelectric coupling in BFO, in-plane 71° switching will result in corresponding changes of antiferromagnetic spins. Quasi-planar BFO structure thus provides an ideal platform to manipulate the multifunctional properties of BFO using electric field, opening up the way for future applications.

Voltage dependence experiments have also been carried out to shed more light on the domain evolution during switching. The capacitor was first poled into one remanent state as the starting point (Figure 3.14 (a)), which is followed by applying gradually-increased reverse field pulses (100 μ s). Below the threshold field for nucleation, the domain pattern remains unchanged (Figure 3.14 (b)). However, once the bias increases to the proximity of the coercive field, a large portion of the capacitor is switched to the opposite polarity, which coexists with the residual domains (Figure 3.14 (c)). Further increase of the bias leads to a complete switching of the capacitor (Figure 3.14 (d)). Such domain switching behavior seems to be consistent with the classic switching dynamics in ferroelectric thin-film capacitors, where the nucleation of reversed domains is followed by the fast forward propagation of domains across the film and finally, the relatively slow sideways growth of domains [92]. In the case of a quasi-planar capacitor, the forward growth of opposite domains is achieved by creating 71° domain walls in each stripe domain.

Subsequently, these 71° domain walls will move laterally, leading to complete reversal of all the domains. Our pulse width dependence study ranging from 100 μs to 100 ms shows similar switching characteristic. Unfortunately, we are not able to observe the domain nucleation and forward growth stages, probably because their speeds are beyond the lower limit of the pulse width available in our equipment. The switching dynamics in capacitors with planar electrodes is worth further detailed investigations.

Figure 3.14 Voltage dependent switching dynamics of ferroelectric domains in a quasi-planar BFO capacitor. (a) Starting state. (b) After applying 25 V pulse. (c) After applying 28 V pulse. (d) After applying 30 V pulse. The voltage pulse width is fixed at 1 ms. Corresponding domain configurations are depicted in the insets of (a) & (d).

Finally, we have also studied the angular dependence of domain switching by applying the electric field at different angles from the main crystallographic axis of BFO thin films. The purpose of this electric field angular dependence study is to better manipulate the domain structure in order to facilitate the exploration for electrical control of magnetism.

In our previous work, the electrode edges are parallel to one of the $\langle 100 \rangle$ axes so that the electric field is along the other $\langle 100 \rangle$ axis, normal to the stripe domain arrays. By intentionally patterning the electrodes at various angles, the electric field can be applied away from the $\langle 100 \rangle$ direction.

Figure 3.15 Dynamic switching of quasi-planar BFO capacitors with varying angles between electrode edge and $[100]$ direction. (a), (d), (g) As-grown state; (b), (e), (h) after electric poling to one direction; (c), (f), (i) after reverse electric poling for capacitors with angles of 0° , 20° and 45° , respectively. Relevant in-plane domain configurations are schematically illustrated in (j).

As demonstrated in Figure 3.15 (a)-(c), the 0° case is exactly what we have described above with the net polarization of the single stripe domain following the electric field direction. However, when the angle increases to 20° , the other set of stripe domain starts to appear since the electric field is no longer perpendicular or parallel to the domain stripes (Figure 3.15 (d)-(f)). The percentage of the newly emerging stripe domains scales up with the rotation angle, as shown in the 45° case (Figure 3.15 (g)-(i)). The formation of two types of stripe domains can be understood by projecting the field vector onto the

two $\langle 100 \rangle$ axes. Based on the polarization configurations for each type of stripe domain listed in Figure 3.15 (j), it can be found that the net polarization of each stripe domain is indeed in line with the two orthogonal components of the electric field, respectively. Ideally, the amount of each stripe domain should be proportional to the magnitude of the field projection along the corresponding axis. As for angles from 45° to 90° , it is identical to those from 0° to 45° considering the system symmetry.

When the electrical field is parallel to one of the main axis, the net in-plane polarization can be switched without modifying the domain pattern. Subsequently, if we place a ferromagnetic layer on top of BFO, the magnetic domain patterns should remain unchanged since it follows the antiferromagnetic thus the ferroelectric domain patterns of BFO through exchange coupling at the interface. When the planar electrode edges are rotated away from the $\langle 100 \rangle$ directions, the domain pattern will be altered by the external bias, leading to possible changes in the ferromagnetic domain pattern.

3.3 Conclusions

In this chapter, we have demonstrated: first, the ability of engineering ferroelectric domain structure in-situ during BFO film growth and second, the capability of switching the ferroelectric domains ex-situ using external field. Such deterministic control over the ferroelectric domains implies the possibility of manipulating the antiferromagnetic order parameter in BFO and is critical for the following investigation of the coupling effect in BFO-based magnetoelectric devices.

For the domain engineering during film growth, a series of variables were investigated in detail, including target composition, film growth rate, substrate vicinality and substrate anisotropy. The findings can be briefly concluded as follows:

- (i) Using BFO targets with different Bi content, the domain patterns of the BFO films can be tuned. The optimized domain pattern is obtained at a Bi content of 0.6. Higher or lower Bi content in the target will lead to more disorder domain structures.
- (ii) The film growth rate can be adjusted by changing the laser frequency. With gradually decreased growth rate from ~ 1.6 nm/min to ~ 0.8 nm/min, the surface morphology becomes smoother and the associated domain structure evolves from disordered mosaic-like to regular stripe-like patterns.
- (iii) By playing with the substrate vicinality, the number of structural variants present in the films can be controlled. All four structural variants are found coexisting in the films grown on zero-miscut STO (001) substrates. This number can be reduced to three if the substrate has a 0.2° miscut angle along [110] direction. Given that the 0.2° miscut is along [100] direction, one of the three structural variants will be greatly suppressed. Finally, increasing the miscut angle to 2° along [100] gives rise to ideal two-variant stripe domain pattern.
- (iv) Orthorhombic substrates like DSO with anisotropic in-plane lattices further enable us to obtain stripe domains with different types of domain walls. Using BFO target with high Bi content ($\text{Bi}_{0.8}\text{FeO}_3$), 71° stripe domains prevail in the films. If $\text{Bi}_{0.4}\text{FeO}_3$ target is being used, 109° stripe domains will become dominating.

As for the domain switching using electric field, planar device layout was used to facilitate direct observation and future experiments on electrical control of magnetism.

The findings are summarized below:

- (i) Macroscopic ferroelectric properties can be obtained for planar capacitors with channel width in the range of 1.4 μm to 8.8 μm . The measured remanent polarizations and coercive fields agree well with theoretical predictions.
- (ii) Microscopically, highly-aligned 71° stripe domains can be obtained under electrical switching. The polarization reversal is achieved through 71° elastic polarization rotation.
- (iii) Electric field was applied at different angles with respect to the $\langle 100 \rangle$ axes in the planar BFO capacitors. When the field angle is zero, the switched domain patterns will be maintained under bias voltages with opposite polarities. If the field angle is changed to 20° or 45° , the domain patterns can be totally modified after opposite electric fields are applied.

To sum up, for the domain engineering during film growth, the optimized stripe domain patterns are obtained using $\text{Bi}_{0.6}\text{FeO}_3$ target and a growth rate of ~ 0.8 nm/min. Stripe domains with less structural variants can be achieved using STO substrate with 2° miscut along $[100]$. Such ability of tuning the ferroelectric domain structure of BFO films provides us an extra degree of freedom in study the exchange coupling between LSMO and BFO layers in the following chapter. Besides, the manipulation of the ferroelectric polarization using planar capacitor help us establish the device basis for future electrical control of ferromagnetism.

Chapter 4 Electrical Control of Ferromagnetism in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ Heterostructures

In this chapter, we proceed to the central question of this dissertation, that is, whether it is possible to control ferromagnetism by an external electric field. To realize this ultimate goal, LSMO/BFO heterostructures were fabricated, whose magnetic properties were first examined to unravel its relationship with the underlying BFO layer. A strong magnetic anisotropy in LSMO induced by the ferroelectric stripe domains of BFO is observed, which confirms the strong exchange coupling at the LSMO/BFO interface [132]. We then construct a prototypical device and attempt to switch the local ferromagnetism of LSMO by applying an electric field to the underneath BFO film. Preliminary results confirm the possibility of electrical manipulation of magnetism at room temperature, opening up a pathway to electrically writable magnetic devices.

4.1 Introduction

We have demonstrated the capability to manipulate the ferroelectric domain structures of BFO in Chapter 3, and the inherent coupling between multiple ferroic orders in BFO has been well established recently. However, the negligible macroscopic magnetization of BFO restricts its direct applications in logic or memory devices. To circumvent this issue, an additional ferromagnetic LSMO layer is deposited onto BFO thin film. It is expected that the finite magnetic moment of LSMO will follow the antiferromagnetic order of BFO upon electrical switching through the exchange coupling of the interfacial spins.

The exchange coupling between ferromagnetic and antiferromagnetic layers is a purely interfacial effect, in which the surface spin configuration plays a crucial role. Ideally, compensated or uncompensated surface should give rise to dramatically different coupling effects and magnetic behaviors following the classical model of exchange bias introduced in Chapter 1 [59]. However, this intuitive picture never succeeds in interpreting the experimental observations. The complete theory could be much more complicated, involving other factors such as surface roughness and orbital reconstruction.

Figure 4.1 Schematic showing the spin configurations on (001), (110) and (111) surfaces of BFO, respectively. Both (001) and (110) surfaces possess fully compensated spins, whereas the (111) surface is fully uncompensated.

Despite the lack of a complete theory of exchange coupling effect, it is still necessary to study the magnetic response of LSMO on BFO surfaces with different spin arrangements, which can be achieved by depositing the films on substrates that are cleaved along different crystallographic planes. BFO possesses a G-type antiferromagnetic order. In the absence of the spin cycloidal modulation, the spins on the $\{111\}$ planes are ferromagnetically coupled and between the adjacent $\{111\}$ planes, they are antiferromagnetically coupled. Under such spin arrangement as schematically shown in Figure 4.1, the spins on the $\{100\}$ and $\{110\}$ surfaces are fully compensated while that on the $\{111\}$ surface are completely uncompensated. According to the classic model of

exchange coupling, we should observe exchange bias only in the (111)-oriented LSMO/BFO heterostructure.

4.2 Experimental Procedure

LSMO and BFO epitaxial thin films are deposited on STO single crystal substrates by PLD using $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ target and $\text{Bi}_{0.6}\text{FeO}_3$ target, respectively. The detailed film growth parameters are summarized in Table 4.1.

Table 4.1 List of the deposition parameters used for BFO and LSMO growth by PLD.

Deposition Parameters	Substrate Temperature	Oxygen Pressure	Laser Frequency	Laser Fluence	Target-to-substrate Distance
BFO	700 °C	100 mTorr	5 Hz	$\sim 1 \text{ J/cm}^2$	5 cm
LSMO	700 °C	300 mTorr	3 Hz	$\sim 1 \text{ J/cm}^2$	6 cm

In orientation-dependent study, LSMO films were first deposited on (001), (110) and (111)-oriented STO substrates, which was followed by the BFO grown on top of LSMO. The resulting stack structure is BFO/LSMO/STO with the thicknesses of BFO and LSMO to be 40 nm and 10 nm, respectively. In the following sections, BFO films were grown before LSMO onto STO (001) substrates, giving rise to LSMO/BFO/STO bilayers. The thickness for BFO is typical 60 nm and for LSMO is 30 nm. In the meantime for LSMO deposition, usually a single layer of LSMO was also grown on bare STO as a reference for comparison.

Structural analyses of the heterostructures were carried out using XRD (Shimadzu 6000). The surface morphology and ferroelectric domain structures were characterized by PFM (detailed experimental setup and methodology are referred to Chapter3, Section

3.1.2). Measurements of magnetic properties were performed using superconducting quantum interference device magnetometer (Quantum Design) and VSM (LakeShore 7400).

4.3 Growth and Characterizations of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ Heterostructures

In a classic ferromagnetic/antiferromagnetic system, the magnetic properties of the ferromagnetic layer are strongly affected by the spin interactions at the interface. Exchange bias and exchange enhancement are two common manifestations of the exchange coupling effect. The magnetic properties of LSMO are closely related to the strongly correlated electrons that are vulnerable to external perturbations. When LSMO is deposited on BFO, it is interesting to see how the multiple ferroic orders of BFO will affect its magnetic properties.

4.3.1 Orientation-Dependent Magnetic Properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ Heterostructures

To investigate the effect of substrate orientation on the exchange coupling between LSMO and BFO layers, BFO (40 nm)/LSMO (10 nm)/STO stack structures were fabricated with (001), (110) and (111) orientations. The magnetic hysteresis loops are measured at different temperatures from 10 K to 300 K, as shown in Figure 4.2 (a)-(c). Surprisingly, all three samples display similar magnetic behaviors, with a Curie temperature near 300 K. Compared with single-layer LSMO on STO, the bilayer samples show greatly increased coercive fields as shown in the inset of Figure 4.2 (b), which indicates the exchange enhancement from random pinning of the ferromagnetic spins. The coercivities all decrease monotonically as temperature increases due to the vanishing

coupling strength (Figure 4.2 (d)). This agrees with the behavior reported for the CoFe/BFO system [71]. However, there is no observable loop shift along the field axis, which indicates that exchange bias is absent in all samples even if field cooling is performed from above the Curie temperature of LSMO. This is likely due to the fact that the Néel temperature of BFO is higher than the Curie temperature of LSMO. Besides, in such top-pinned exchange-coupled systems, the magnetic property of the LSMO is inevitably affected by the substrate underneath. Furthermore, the domain structure of BFO is not well controlled. Fortunately, based on the domain engineering approaches established in Chapter 3, we push the research forward by depositing LSMO on top of BFO films with distinct domain patterns, aiming to elucidate how the multiferroic orders in BFO affect the ferromagnetism of LSMO on top.

Figure 4.2 Temperature dependent magnetization hysteresis loops of (a) (001), (b) (110) and (c) (111) oriented BFO/LSMO bilayer samples. (d) The relationship between film coercivity and temperature for all three orientation samples.

4.3.2 Effect of Structural Relaxation in BiFeO₃ Films on the Magnetization of La_{0.7}Sr_{0.3}MnO₃/BiFeO₃ Heterostructures

Figure 4.3 (a), (b) and (d) In-plane ferroelectric domain structures of BFO films in LSMO/BFO heterostructures. The inset shows the corresponding topography after LSMO growth. (c) Corresponding magnetization hysteresis loops of LSMO/BFO heterostructures with various BFO domain structures.

As demonstrated in Chapter 3, Section 3.1.3.2, the ferroelectric domain structures of BFO thin films can be tuned by varying the film growth rate, giving rise to either mosaic-like or stripe-like domain patterns (referred to Figure 3.6). Taking advantage of this tunable ferroelectric domain patterns, LSMO epilayers (30 nm) were then deposited on BFO films (~60 nm) with different domain structures as shown in Figure 4.3 (a) & (b). The surface morphologies after LSMO growth (insets of Figure 4.3 (a) & (b)) follow those of the BFO underneath. Consistent with our previous results, LSMO films on BFO

with random ferroelectric domains typically exhibit rougher surfaces. Surprisingly, the magnetization of LSMO films on BFO with stripe domains reaches 400 emu/cc, which is four times as large as that of LSMO on BFO with mosaic domains (Figure 4.3 (c)).

Intuitively, one may attribute the dramatic difference to the distinct domain structures of BFO or the interface roughness. However, we noticed that some bilayer samples with stripe domain BFO also display reduced magnetization despite even smoother topographies (Figure 4.3 (d)). Therefore, the diverse magnetizations observed in LSMO/BFO heterostructures are not directly related to the ferroelectric domains of BFO.

Figure 4.4 (a) & (b) XRD θ - 2θ patterns of LSMO/BFO heterostructures shown in Figure 4.3 (d) & (b) before and after LSMO growth. (c) XRD θ - 2θ patterns of LSMO/BFO heterostructures with different strain relaxations. (d) Correlation between BFO and LSMO c lattice constant and the magnetization of LSMO layers. The saturated magnetization of single layer of LSMO grown on bare STO is indicated by red dash line.

By analyzing the XRD patterns of the samples before and after LSMO deposition, we discover that in some samples (especially those with already relaxed BFO) the BFO peaks

shift to higher degrees after LSMO growth (Figure 4.4 (a)), indicating the occurrence of structural relaxation in BFO. This could be due to the prolonged thermal history during LSMO growth at a high temperature of 700 ° C for 30-60 mins. On the contrary, other samples (especially those with fully strained BFO) show no sign of lattice relaxation after deposition of LSMO layer (Figure 4.4 (b)). Combining the XRD (Figure 4.4 (c)) and magnetization data, we notice a direct correlation between the out-of-plane c lattice constant of BFO (also c lattice constant of LSMO) and the saturation magnetization of LSMO (Figure 4.4 (d)).

As shown in the Table 4.2, bulk BFO has a lattice constant of 3.96 Å, larger than STO. Thus, BFO epitaxial thin film grown on (001)-oriented STO is subject to a -1.4% compressive strain, leading to elongated c lattice constant of ~4.07 Å under in-plane fully-strained state (in-plane lattice constant equals to STO, i.e. 3.905 Å). This c lattice constant value is consistent with our experimental results for fully-strained BFO thin films, which can be further validated through the following equation [133]:

$$\nu = 1 / (1 - \frac{2\varepsilon_{xx}}{\varepsilon_{zz}})$$

where ν is the Poisson's ratio, ε_{xx} is the in-plane biaxial strain and ε_{zz} is the out-of-plane lattice strain. The ε_{zz} for $c = 4.07$ Å is calculated to be 0.027. Taking the Poisson's ratio $\nu = 0.49 \pm 0.01$ in BFO thin films [134], the ε_{xx} can be obtained to be -0.0145 ± 0.0006 . Thus, the in-plane lattice constant of the BFO film is estimated to be 3.903 ± 0.002 Å, in good agreement with the lattice constant of STO substrate.

For the LSMO film grown on STO, it is subject to a 0.6% tensile strain as bulk LSMO has a smaller lattice constant (3.88 Å) than STO. If the LSMO are grown on top of fully-strained BFO, the encountered strain is similar to the case of being grown directly

on STO. However, if the in-plane strain in BFO films is partially relaxed, meaning the in-plane lattice constant becomes larger than STO, the c lattice constant of BFO films will start to decrease, as indicated by the arrow in the XRD patterns in Figure 4.4(c). This is accompanied by the decrease of the c lattice constant of LSMO films because they are facing a larger tensile strain caused by BFO. As illustrated in Figure 4.4 (d), the LSMO films on partially relaxed BFO (c lattice constant $< 4.07 \text{ \AA}$) show inferior magnetizations, which gradually increases to the saturation value of LSMO on STO when the underlying BFO approaches the fully strained state (c lattice constant $= 4.07 \text{ \AA}$). Such a relationship explains the distinct magnetic properties of LSMO grown on different BFO films. The BFO with mosaic domain structure is generally related to a rougher surface and significant structural relaxation as described in Chapter 3, Section 3.1.3.2. Consequently, LSMO layers on top exhibit reduced magnetizations. The BFO with stripe domain structure usually (with some exceptions as shown in Figure 4.3 (d)) shows better structural coherence with the substrate and a fully strained in-plane lattice, leading to enhanced magnetization in LSMO.

Table 4.2 List of lattice parameters of BFO, LSMO and STO adapted from literature [28,34,133-134].

Films or Substrate	BFO	LSMO	STO
Bulk lattice constant (in pseudocubic unit cell)	$3.96 \text{ \AA}$	$3.88 \text{ \AA}$	$3.905 \text{ \AA}$
Misfit Strain to STO	-1.4%	+0.6%	0
c lattice constant with in-plane lattice fully strained to STO	$\sim 4.07 \text{ \AA}$	$\sim 3.85 \text{ \AA}$	$3.905 \text{ \AA}$

Essentially, the dramatic change of magnetization of LSMO layers originates from the different strain state caused by the structural relaxation of underlying BFO layers. The strain dependent magnetic properties of LSMO have been studied extensively [133,135-137]. And it is believed to be closely related the Jahn-Teller distortion which describes the lifting of the degeneracy of the Mn e_g orbitals due to the geometric distortion of the MnO₆ octahedrons. It is well known that the electronic and magnetic behaviors of LSMO are governed by the double-exchange hopping of the Mn e_g electrons across the Mn³⁺-O²⁻-Mn⁴⁺ chains, leading to a ferromagnetic alignment of the spins. However, if a tensile strain exists in the LSMO film, it will cause a biaxial distortion that increases the Jahn-Teller splitting of the e_g orbitals [138]. Consequently, the electron hopping between Mn³⁺ and Mn⁴⁺ ions will be inhibited, resulting in decreased Curie temperature of the LSMO. Early first principle calculations have predicted that large tensile strain ($c/a \sim 0.97$) in LSMO will induce a competition between ferromagnetic state and A-type antiferromagnetic state [139-140]. In case of LSMO/BFO bilayer on STO, the LSMO is always subject to a tensile strain. However, on fully strained BFO, the strain state in LSMO is close to that on bare STO with a in-plane biaxial strain of +0.6%, which gives rise to comparable saturated magnetization of 420 emu/cc. For LSMO on partially relaxed BFO thin films, greatly reduced magnetization is observed due to much larger tensile strain that suppresses the ferromagnetic order. For the case that LSMO is under largest tensile strain, its c lattice constant is 3.837 Å, corresponding to $\varepsilon_{zz} = -0.011$. Considering the Poisson ratio ν of LSMO thin films is 0.37 ± 0.01 [133], the in-plane biaxial strain ε_{xx} can be estimated to be 0.0094 ± 0.0004 , namely $\sim +0.9\%$. This result means that with the increase of the in-plane tensile strain from +0.6% to +0.9%, the

saturated magnetization of LSMO at room temperature decrease from 420 emu/cc to 90 emu/cc. Such great modulation in the saturated magnetization within only 0.3% biaxial strain change is actually quite surprising. However, because the measurements were carried out at room temperature, which is very close to the Curie temperature T_c of LSMO thin films (~ 350 K for LSMO on STO), the measured saturated magnetizations are very sensitive to the T_c shift induced by strain-mediated Jahn-Teller effect. For example, the saturated magnetization will reduce to nearly zero, if the T_c decrease by 50 K. To our knowledge, the LSMO grown on DSO substrate has a tensile strain of +1.6%, which is the closest to +0.9% case. Under such strain, the T_c is reduced to ~ 280 K with no saturated magnetization at room temperature [133]. This partially supports our assumption of the strain effect on the measured magnetization of LSMO films.

It is clear that the different saturation magnetizations observed in LSMO grown on BFO films with various domain structures are due to strain effect. Even though this offers another avenue to tune the magnetization of LSMO films, we still need to find other evidences that confirm the exchange coupling between the multiferroic orders of BFO and the ferromagnetism of LSMO.

4.4 Exchange Coupling between $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and Stripe domain BiFeO_3

The electrical control of magnetism in LSMO relies on the exchange coupling between its ferromagnetic order and BFO's antiferromagnetism, the later is again linked to the ferroelectric order. In the following sections, we demonstrate the robust exchange coupling in the LSMO/BFO heterostructure from both a general collective behavior and a local microscopic picture. From the findings in last section, we have learnt that the

magnetization of the LSMO layer is greatly affected by the strain state of the BFO thin films. To eliminate the extrinsic effect caused by the strain relaxation, fully-strained BFO thin films will be used in the following studies to further explore the exchange coupling effect in the LSMO/BFO heterostructure. Furthermore, in order to simplify the physical model, BFO films with less domain variants are desirable. Based on the domain engineering method established in Chapter 3, Section 3.1.3.3, the structural variants in BFO thin films can be reduced by introducing substrate vicinality. However, if the miscut angle of the STO substrate is too large, the topographic anisotropy from the substrate may prevail across BFO to LSMO, overwhelming the exchange coupling effect. Consequently, (001)-oriented STO substrate with a small miscut angle ($\sim 0.35^\circ$) along [100] was chosen to reduce domain variants while minimizing the substrate topography contribution. Consequently, 60-nm BFO thin film was first grown on STO. After that, 30-nm LSMO films were deposited onto this BFO film and the same STO substrate simultaneously as a reference. These are termed as the bilayer and single layer samples, respectively. The detailed deposition parameters and subsequent experimental procedures are described in Section 4.2. For the angular related measurements, the [100], namely, the miscut direction can be identified based on the well-aligned terraces from the topography of the STO substrate. Subsequently, the orthogonal axis can be identified as [010].

4.4.1 Uniaxial Magnetic Anisotropy in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Induced by Ferroelectric Stripe Domain of BiFeO_3

Figure 4.5 (a)-(d) Topographies of STO substrate, LSMO/STO, BFO/STO and LSMO/BFO/STO samples, respectively. The height scales are 2 nm in (a) and 5 nm in (b)-(d). (e) & (f) In-plane and out-of-plane domain structures of BFO layer in the LSMO/BFO heterobilayer, respectively. The phase scale is 180° in the PFM images.

As shown in Figure 4.5 (a), the STO substrate displays atomically-flat surface with 60-70 nm wide terraces after a brief heat treatment, in accordance with the miscut angle. After BFO deposition, although the flat terrace feature of the STO is not maintained, the BFO film still exhibits a very smooth surface with roughness below 0.5 nm (Figure 4.5 (c)). Owing to the anisotropy resulted from the substrate vicinality, the in-plane domains of the BFO is mainly comprised of two variants forming a single stripe, but with minor extra variants nonetheless (Figure 4.5(e)). The out-of-plane polarization components all point up as shown in Figure 4.5 (f), implying that the observed domain structure is mainly 71° domains. The topographies of the LSMO films basically preserve those of the underneath layers. While the surface of LSMO/BFO bilayer shows no obvious topographic anisotropy (Figure 4.5 (d)), the well-aligned step edges in LSMO single layer is clearly visible (Figure 4.5 (b)).

Figure 4.6 (a) M–T curves of LSMO single layer and LSMO/BFO bilayer samples measured under field cooling condition. The cooling and measuring fields are both 100 Oe. The inset shows the zoom-in dM/dT –T curves around Curie temperature. (b) Temperature dependence of coercive field of LSMO single layer and LSMO/BFO bilayer samples. The inset is the magnetization hysteresis loop of both samples at 10 K. (c) Comparison of XRD θ - 2θ patterns of LSMO/BFO heterostructure before and after LSMO growth. No obvious BFO relaxation is observed.

Figure 4.6 (a) & (b) shows the relevant magnetic properties of both the single layer and bilayer samples, which were measured with magnetic field applied along the film plane.

The magnetization versus temperature (M - T) curves were recorded at 100 Oe under field cooling condition. The Curie temperatures of the films determined from the peaks of dM/dT versus T curves are 338 K for the single layer LSMO and 344 K for the bilayer LSMO/BFO, respectively (inset of Figure 4.6 (a)). Such an enhancement in Curie temperature of the ferromagnet has been observed before in exchange coupled ferromagnetic/antiferromagnetic systems with T_N higher than T_C [141]. BFO has a Néel temperature of 643 K, which is much higher than the Curie temperature of LSMO. Therefore, when the temperature exceeds the T_C of LSMO, the ferromagnetic order can still be preserved due to the pinning of the interfacial spins by the antiferromagnetic BFO. An apparent decrease in the magnetization can be seen in the bilayer sample. However, the XRD patterns show negligible relaxation of the BFO lattice after LSMO growth (Figure 4.6 (c)). One possible explanation could be the in-plane shear strain induced by the ferroelastic distortion of BFO, which affects the ferromagnetic coupling of LSMO through Jahn-Teller distortion [138]. Further study is needed to fully unravel the underlying mechanism. The exchange coupling between LSMO and BFO is evident by the greatly increased coercive field compared to that of the LSMO single layer (Figure 4.6 (b)). Temperature dependence of the exchange enhancement is similar to our previous results, exhibiting decreasing coupling strength with rising temperature.

When the magnetic field is applied along the two orthogonal in-plane $\langle 100 \rangle$ directions, obvious magnetic anisotropies are present in the hysteresis loops for both samples (Figure 4.7 (a)). However, their easy axes are perpendicular to each other. It is along $[100]$ direction in the LSMO/BFO bilayer sample and along $[010]$ direction in the LSMO single

layer sample, which points to totally different origins for the anisotropy. The anisotropy persists from 10 K all the way to room temperature.

Figure 4.7 (a) Magnetization hysteresis loops of LSMO single layer and LSMO/BFO bilayer samples measured along [100] and [010] directions at 10 K respectively. Magnetic anisotropy is visible in both samples. (b) Angular dependent M_r/M_s and H_c curves of both samples measured at 300 K. Solid lines are theoretical fits. (c) Schematic drawing of the in-plane ferroelectric domain configuration of BFO layer and the angular measurement geometry. (d) Large scan (8 μm * 8 μm) of the in-plane domain structure of the underlying BFO film used in the study. Imperfect region of stripe domains and extra domain variants (purple tone) are enclosed in blue lines. The phase scale is 180° .

To gain more insight into the underlying mechanisms, angular-dependent tests were carried out to measure the remanent magnetization (M_r) and coercive field along different azimuthal angle ϕ with respect to the miscut [100] direction at room temperature (Figure

4.7 (c)). 180° periodic oscillations were observed in all curves as shown in Figure 4.7 (b). However, there is a 90° phase shift in the angular dependence of M_r and H_c of single layer and bilayer samples, confirming that their magnetic easy axes are rotated by 90° .

There could be various sources for the magnetic anisotropy in LSMO, e.g. magnetocrystalline anisotropy, shape anisotropy, stress anisotropy and so on [142]. Here, based on the topography of the single layer LSMO on STO (Figure 4.5 (b)), shape anisotropy arose from the step edges is clearly visible. In order to reduce the magnetostatic energy, the magnetic moments in LSMO will prefer to align parallel to the step edges, giving rise to a magnetic easy axis normal to the miscut [100] direction. This result is in good agreement with the widely-reported magnetic anisotropy caused by substrate vicinality [143-145].

In contrast, the surface morphology of the LSMO/BFO bilayer displays no apparent topographic anisotropy (Figure 4.5 (d)). This raises the question about the origin of the anisotropy in LSMO. In such a typical ferromagnetic/antiferromagnetic system, naturally we will think of the exchange anisotropy, which is mediated through the coupling of the interfacial spins. Since the ferroelectric and antiferromagnetic orders in BFO are inherently coupled [26-27], the antiferromagnetic spin configurations can be derived from the corresponding ferroelectric domain patterns obtained via PFM. As mentioned above, the BFO film is dominant by two-variant 71° stripe domains. The corresponding polarization arrangement is schematically shown in Figure 4.8, where the in-plane polarization vectors (green arrows) align in a head-to-tail zigzag fashion, leading to a net polarization towards [100] direction. Through the magnetoelectric coupling in BFO, the antiferromagnetic spins tend to lie in an easy magnetization plane normal to the

polarization direction with a six-fold degeneracy of the easy axes under rhombohedral symmetry [50]. Fortunately, such degeneracy can be lifted by external substrate strain that lowers the crystal symmetry. BFO grown on (001) STO is subject to a compressive strain, causing the unit cell to elongate along [001] axis. According to the magnetostrictive effect, the spins will favor to align in the out-of-plane direction, thus adopting the $\langle 112 \rangle$ axes, which aligns with the polarization vectors when projecting onto the (001) plane [51]. Due to the one-to-one correlation between polarization and spin easy axis, the antiferromagnetic spin arrangement (blue arrows in Figure 4.8) can be determined to follow the zigzag pattern of ferroelectric polarizations.

Figure 4.8 Schematic illustration of the microscopic coupling mechanism at the LSMO/BFO interface. Local polarization and spin configurations are indicated by arrows. The top right corner shows a zoom-in picture of spin coupling in a single domain region.

Both collinear coupling and perpendicular (spin-flop) coupling models have been proposed to explain the exchange coupling at the ferromagnetic/antiferromagnetic interface [59,63]. For our LSMO/BFO heterostructure, both models give the correct conclusion in interpreting the magnetic anisotropy of the LSMO layer. However, for the fully compensated (001) BFO surface, the spin-flop coupling model is more reasonable,

because of the small canting-induced net moments (purple arrows) resulted from the Dzyaloshinskii-Moriya interactions, as demonstrated in the top right corner of Figure 4.8. Because of the exchange coupling, the ferromagnetic spins in LSMO (red arrows) will mimic the zigzag alignment of the antiferromagnetic spins in BFO. In order to lower the demagnetizing energy, the spins in LSMO will tend to connect in the head-to-tail arrangement, forming 90° Néel walls. There are, however, two opposite net magnetization directions that are energetically degenerate. Therefore, only uniaxial magnetic anisotropy is observed in the LSMO layer, instead of a unidirectional alignment of the spins. The magnetic easy axis is parallel to the net polarization direction, which provides a possible route to change the magnetic anisotropy of LSMO via switching the ferroelectric domains of BFO electrically.

Quantitative analysis was also carried out to support the microscopic coupling model proposed above. As we know, for the ideal uniaxial magnetic anisotropy, the angular dependence of the remanent magnetization should obey a $|\cos\phi|$ function with no remanence along the hard axis. However, this is slightly different from what we observed in the angular dependent curve, which displays a finite value of 0.28 for the M_r/M_s along the hard axis (Figure 4.7 (b)). This discrepancy can be attributed to the imperfection of the stripe domain patterns. As shown in Figure 4.7 (d), extra domain variants forming stripes (purple domains) perpendicular to the dominant one (yellow domains) exist, which will induce anisotropy along [010] direction. Additionally, branching and interruption of the dominant stripe domains will also cause disorder in the spin alignment. By summing up the total imperfect domain areas, we obtain a ratio of ~ 0.25 , which is in accordance with the magnetic remanence along the hard axis. As for the angular behavior of the

coercive field, it can be well described by the Stoner-Wohlfarth model, indicating a coherent magnetization rotation during switching [146].

Figure 4.9 (a) In-plane ferroelectric domain pattern of BFO with equal amount of two sets of stripe domains. **(b)** The corresponding angular dependent M_r/M_s and H_c curves of LSMO layer grown on top of BFO film shown in (a).

Finally, LSMO layer was also deposited on BFO film with two sets of stripe domains (Figure 4.9 (a)) to validate that the uniaxial magnetic anisotropy is indeed introduced by the stripe domains of BFO. Because the two sets of stripe domains exist in nearly equal quantity, their effects on inducing the magnetic anisotropy are comparable along the two orthogonal in-plane $\langle 100 \rangle$ directions, thus cancelling out with each other (leading to a weak 45° modulation). Indeed, no significant anisotropy is detected in the magnetic properties (Figure 4.9 (b)).

4.4.2 Local Correlation between Ferroelectric Domains of BiFeO₃ and Ferromagnetic Domains of La_{0.7}Sr_{0.3}MnO₃

We have demonstrated that the exchange coupling between LSMO and BFO leads to the uniaxial magnetic anisotropy observed macroscopically. However, it will be more incisive to establish a direct correlation between the ferroelectric and ferromagnetic domains at the nanometer scale. By combining PFM and magnetic force microscopy

(MFM), the ferroelectric domains of BFO and ferromagnetic domains of LSMO can both be visualized and analyzed together, as shown in Figure 4.10.

Figure 4.10 (a) & (c) Topographies of BFO film and after growing LSMO on top scanned at the same location. (b) & (d) Corresponding in-plane ferroelectric domain pattern of BFO and magnetic domain pattern of LSMO, respectively. (e) Large scan of the magnetic domain pattern of LSMO at a different location. (f) A zoom-in scan of (e). The height scale is 5 nm in (a) & (c). The PFM phase scale is 180° in (b). The MFM phase scale is 3° in (d), (e) and (f). Polarization vectors are denoted by blue arrows, while possible spin configurations are indicated by red arrows.

The domain structure of BFO was first captured before the LSMO growth at a specific location (Figure 4.10 (a) & (b)). Subsequently, after depositing the LSMO layer, we traced back to the same location to obtain the MFM image (Figure 4.10 (c) & (d)). As shown in Figure (a) & (c), the topography features of BFO are maintained after LSMO deposition. However, the magnetic domains in LSMO and the ferroelectric domains of BFO do not match exactly. By looking at a larger picture, we notice that the ferromagnetic domain of LSMO exhibits stripe-like features running perpendicular to the ferroelectric stripe domains (Figure 4.10 (e)). The stripes are parallel to the magnetic easy

axis of LSMO as describe above. To explain the origin of these stripes, recall that the two opposite directions along the easy axis of LSMO are degenerate. Thus, domains with net magnetic moments pointing to opposite directions will form to reduce the demagnetizing energy. This leads to a domain wall that is parallel to the easy axis, and perpendicular to ferroelectric stripe domains of BFO underneath. These domain walls appear bright in MFM images since MFM only senses the stray fields that originate from the domain walls in samples with in-plane magnetization. However, we cannot decisively figure out the exact spin configuration within each domain.

Interestingly, if we zoom into a smaller area in the MFM image, a finer domain structure with modulation width and direction matching that of the ferroelectric domain of BFO underneath is clearly visible (Figure 4.10 (f)). This finer domain patterns can be attributed to the stray field that comes from the 90° Néel walls of the zigzag-aligned spins in LSMO, which should match the antiferromagnetic (thus the ferroelectric) domains of BFO (Figure 4.10 (b)). Although precise spin arrangements in the magnetic domains remain unknown, the domain patterns from both PFM and MFM studies unambiguously point to a strong correlation between local ferroelectric order in BFO and ferromagnetic order in LSMO, in good agreement with the exchange coupling model we have demonstrated. We are now well prepared to explore the possibility of electrical switching of local ferromagnetism.

4.5 Preliminary Results of Electrical Switching of Local Ferromagnetism in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BiFeO}_3$ Heterostructures

Figure 4.11 (a) Sketch of the device layout and experimental setup for electrical switching of ferromagnetism in a LSMO/BFO heterostructure. (b) Cross-sectional view of the device structure and the corresponding electric field distribution within the BFO layer.

To realize the electrical control of magnetism, a feasible device design is crucial. Based on the quasi-planar device introduced in Chapter 3, we add a LSMO slab into the channel area on top of BFO for the electrical switching experiment. This way, when the ferroelectric domains of BFO are switched, the magnetic domains of LSMO can be observed in-situ. Since LSMO itself can serve as electrodes, the device preparation turns out to be relatively easy. We first grow a continuous LSMO layer on BFO film. Then, a layer of photoresist is spin-coated on top of LSMO, followed by standard photolithography to pattern the device structure. Finally, the unwanted surrounding LSMO can be etched away by chemical method, leaving a well defined device pattern as sketched in Figure 4.11 (a). Afterwards, an electric field is applied to the LSMO

electrodes at the two sides to switch the ferroelectric domain of BFO within the channel. Note that the LSMO pad in the middle of the channel is very effective in screening the electric field beneath it due to its excellent conductivity (Figure 4.11 (b)). According to our finite element simulation, the field strength in BFO beneath the LSMO pad will be reduced by one order of magnitude. Therefore, much higher field is required to successfully switch the polarization of BFO.

Figure 4.12 Dynamic switching of the ferromagnetic domains of LSMO using electric field in LSMO/BFO heterostructure. Corresponding topography, in-plane ferroelectric domain structure of BFO and ferromagnetic domain structure of LSMO (a) in as-grown state, (b) after first electrical switching and (c) after second electrical switching back. The height scale, PFM phase scale and MFM phase scale are 80 nm, 180° and 3° respectively. Red circles indicate domain areas that can be reversibly switched by electric field, whereas blue circle denote the domain area with no significant change upon electric poling.

Figure 4.12 shows the topography, in-plane PFM and MFM images of the as-prepared device. The pristine domain structure of BFO consists of two sets of 71° stripes. Following our discussion in Chapter 3, we intentionally patterned the electrode to form a 45° angle with respect to the stripe domains. Due to the absence of the anisotropy in the

ferroelectric domains of BFO, the MFM image of LSMO exhibits a relatively random magnetic domain pattern.

An electric field pointing to the right electrode was first applied to switch the ferroelectric domains of BFO. As shown in Figure 4.12 (b), part of the ferroelectric domains are switched, especially those located near the electrode edges. The corresponding magnetic domain patterns also display obvious changes in certain areas, as indicated by the red circles. However, domains that remain intact are also observable (area inside the blue circle). Upon the second electrical switching with a reverse bias, the ferroelectric domains are partially changed again (Figure 4.12 (c)). And it is observed that the ferromagnetic domains enclosed by the red circles switch back to the original state. Unfortunately, due to the large voltage applied, the device is partially broken down, which prevents further electrical switching experiments. However, clear changes in local ferromagnetism are detected during the electrical switching of the ferroelectric polarization of BFO, though the manipulation is far from perfect at this moment.

Many issues still exist in regard of the electrical control of magnetism using LSMO/BFO heterostructures. First of all, because the ferroelectric stripe domains of the as-grown BFO form a crisscross pattern, the magnetic domains of LSMO display significant randomness instead of single stripe-like features due to the absence of the anisotropy. The disorder complicates our further investigations. Secondly, in contrast to the example presented in Chapter 3, the domain switching in BFO is incomplete, presumably due to the large channel width and the conducting LSMO pad within the channel. To achieve a deterministic control of local ferromagnetism, we have to find out whether or not the inhomogeneous and greatly weakened electric field can effectively

switch the whole BFO film right beneath the LSMO pad. Thirdly, the exchange coupling strength between BFO and LSMO at room temperature is a keystone to the electrical control of magnetism, yet still an open question to date [73]. Last but not least, parasitic contributions like magnetostrictive effect need to be deconvoluted from the pure magnetoelectric/exchange coupling effect, since the in-plane polarization rotation in BFO is dominated by ferroelastic switching events with accompanying strain. Only after resolving these issues, can reliable electrical manipulation of magnetism be realized in the LSMO/BFO heterostructure.

4.6 Conclusions

In this chapter, an in-depth investigation on the exchange coupling of LSMO/BFO heterostructures was performed, which was followed by the first attempt to electrically switch the local ferromagnetic domains in LSMO. The important findings can be concluded as below:

- (i) It is found that the saturated magnetization of the LSMO is greatly influenced by the structural relaxation of the BFO films underneath through the strain-mediated Jahn-Teller effect. For LSMO grown on fully-strained BFO thin film, the saturated magnetization is close to that of single layer LSMO on STO with a value of ~ 420 emu/cc. The increase of in-plane tensile strain by 0.3% will reduce the saturated magnetization to 90 emu/cc.
- (ii) A strong uniaxial magnetic anisotropy was observed in LSMO deposited on BFO thin films with two-variant ferroelectric stripe domains. The easy axis lies along the net polarization direction of the ferroelectric stripe domains. Through local MFM

analysis, a direct correlation between the ferroelectric domains of BFO layer and the ferromagnetic domains of LSMO layer can be found. These observations were then explained by a microscopic coupling model that details in the exchange coupling between the antiferromagnetic spins in BFO and the ferromagnetic spins in LSMO at the hetero-interface.

- (iii) A LSMO/BFO planar device was fabricated to launch the first attempt to switch the local ferromagnetism in LSMO using electric field. Preliminary results demonstrate the possibility of electrical modification and recovery of the ferromagnetic domains.

Chapter 5 Summary and Future Work

5.1 Summary

The objective of this work is to achieve electrical control of magnetism by combining the magnetoelectric coupling in BFO and exchange coupling between LSMO and BFO. We started by optimizing the deposition condition to grow high quality, phase-pure BFO epitaxial films. We then demonstrated a series of methods to tune the ferroelectric domain structure during and after the BFO growth. By using a quasi-planar-electrode configuration, we can manipulate the domain structure of BFO with an electric field. Following the fabrication of highly coherent LSMO/BFO heterostructures, we discovered a uniaxial magnetic anisotropy in LSMO, which is induced by the anisotropy in the ferroelectric stripe domains of BFO thin film. The local correlation between the ferroelectric domains of BFO and the ferromagnetic domains of LSMO further corroborates the existence of a strong exchange coupling between the two films. Finally, we have demonstrated electrical control of local ferromagnetism using a prototype LSMO/BFO quasi-planar device.

To conclude, our findings can be summarized as follows:

- (i) The difficulty of growing phase-pure BFO thin films by PLD arises from the volatility of Bi element. Contradicting to the common belief that excess Bi is needed in the target to compensate for Bi loss, we found that the laser ablation yield of Bi from the target is much higher than Fe, thus a Bi-deficient target is more appropriate for PLD deposition of BFO. However, using a stoichiometric target, the Bi/Fe ratio in the film can still be tuned through substrate temperature

and oxygen pressure during deposition. Higher substrate temperature and/or lower oxygen pressure promotes Bi evaporation from the substrate surface and destabilizes the Bi-rich phases, and vice versa. By fixing the temperature at 700 °C and varying the oxygen pressure from 1 mTorr to 20 mTorr, a series of phase-pure BFO thin films can be obtained. However, the Bi/Fe ratio in the film decreases with reducing oxygen pressure, leading to deteriorated ferroelectric properties. The best ferroelectric properties were obtained in films grown at 20 mTorr, however, with cracks formation on the surface. This indicates that a further optimization and engineering of the ferroelectric domain structures are highly desirable.

- (ii) By tuning the target composition and the film growth kinetics, we can change the ferroelectric domain structures of BFO epitaxial thin films from a disordered mosaic pattern to an ordered stripe pattern. For the target composition, the optimized domain pattern was obtained using target with a Bi content of 0.6. By decreasing the film growth rate from ~1.6 nm/min to ~0.8 nm/min, the domain structure of BFO thin films will change from mosaic-like to stripe-like patterns. Furthermore, by introducing the substrate vicinality in STO, the number of structural variants in resulting BFO films can be adjusted: from all four variants present on exact STO substrate, to three variants on STO with 0.2° miscut along [110] direction and finally to two variants if the miscut is 2° along [100] direction. Last but not least, by using orthorhombic substrate like DSO, specific domain walls can be selectively grown. For example, using $\text{Bi}_{0.8}\text{FeO}_3$ target, 71° stripe

domains can be acquired. However, use of $\text{Bi}_{0.4}\text{FeO}_3$ target will result in 109° stripe domains.

- (iii) Quasi-planar capacitors were fabricated to achieve manipulation of the ferroelectric domains by external field, which is crucial to the electrical control of antiferromagnetic order. After electrical switching, highly-aligned 71° stripe domains were observed. The ferroelectric switching was accomplished mainly through 71° polarization rotation. Angular dependent switching experiments further enhance our capability of domain manipulation. When the field is applied along $\langle 100 \rangle$ axes, the switched domain patterns will be preserved under biases with opposite polarities. However, if the field is applied at an angle of 20° or 45° with regard to $\langle 100 \rangle$ axes, the domain patterns can be totally modified upon reversing the bias.
- (iv) In the (001)-oriented LSMO/BFO heterostructures, the magnetization of LSMO is strongly affected by the strain state of the underlying BFO layer via Jahn-Teller effect. LSMO grown on BFO with two-variants stripe domains exhibits uniaxial magnetic anisotropy due to the exchange interaction between the ferromagnetic spins of LSMO and the antiferromagnetic spins of BFO at the interface. The easy magnetic axis coincides with the in-plane net polarization direction of the stripe domains. The strong coupling is further corroborated by the local correlation between the ferromagnetic domains of LSMO and the ferroelectric domains of BFO. A microscopic coupling model was introduced to successfully explain the observed phenomena.

- (v) Preliminary experiments reveal undoubtedly changes of ferromagnetic domains in LSMO upon application of an electric field to the underneath BFO film. The change of ferromagnetic domains can be subsequently recovered by reversing the electric field.

5.2 Future Work

Research activities on BFO-based systems continue to increase rapidly. Exotic functionalities such as conducting domain walls [105], strain-induced morphotropic phase boundary (MPB) [147], photovoltaic effect [106,148] and photostrictive effect [149] have been discovered in multiferroic BFO in addition to the magnetoelectric effect. What's more appealing for applications is the capability to control all these functionalities by an electric field. Inspired by these intriguing observations, we propose a couple of topics to be investigated in the near future:

- (i) As demonstrated in Chapter 3, the quasi-planar capacitor provides an ideal platform to study the polarization switching dynamics in BFO and other ferroelectrics [124-125,129], which cannot be accessed directly in the conventional vertical stack configuration. Detailed study in this area can improve our understanding of the switching mechanism of ferroelectric capacitors, which involves domain nucleation, forward growth and lateral growth. However, due to the limitation of pulse width of our current equipment, only the slowest lateral growth step can be resolved. Future investigation should exploit shorter voltage pulse to visualize the switching process at different time scale. Switching studies that involve different types of domain walls

and stability of ferroelastic switching should also be addressed, which will lead to a better control of ferroelectric domains of BFO by electric field.

- (ii) Uniaxial magnetic anisotropy was observed for LSMO deposited on BFO with 71° stripe domains. However, the effect of different types of domains on the exchange coupling between LSMO and BFO remains unclear. Martin *et al.* [71] reported that 109° domain walls are the origin of the exchange bias in the CoFe/BFO system due to the enhanced ferromagnetic moments at the domain wall. If this is true, we should be able to reproduce the exchange bias in the LSMO/BFO system. Through domain engineering, we can obtain different domain structures in BFO, including 71° , 109° stripe domains and even single domain. This offers us another degree of freedom to manipulate the exchange coupling effect between LMSO and BFO.
- (iii) From our preliminary results, switching the ferroelectric domains of BFO indeed induce changes in the ferromagnetic domains of LSMO. However, the degree of control is far from satisfactory. Two issues need to be solved to achieve deterministic electrical control of ferromagnetism at room temperature. First, we have to confirm whether or not the ferroelectric domains of BFO beneath the LSMO can be fully switched under the partially screened electric field. If not, alternative device architectures have to be explored. Secondly, the strength of exchange coupling between LSMO and BFO at room temperature needs to be investigated. The Curie temperature of LSMO is very close to room temperature, giving rise to vanishing ferromagnetic order, which may lead to a relatively weak exchange coupling effect. Therefore, high T_C ferromagnetic oxides such as Fe_3O_4 and NiFe_2O_4 should be explored as the substitutes for LSMO.

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