Fabrication/characterization of multiferroic LuFe₂O₄ and BiFeO₃ and their dielectric properties

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**NANYANG
TECHNOLOGICAL
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**Fabrication/Characterization of Multiferroic LuFe_2O_4 and
 BiFeO_3 and their Dielectric properties**

Ren Peng

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2012

**Fabrication\Characterization of Multiferroic LuFe_2O_4 and BiFeO_3
and their Dielectric properties**

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School of Physical and Mathematical Sciences

A thesis submitted to Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

2012

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

Date

Ren Peng

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SUMMARY

Two emerging multiferroics LuFe_2O_4 (LFO) and BiFeO_3 (BFO) are fabricated and characterized in this thesis. The LuFe_2O_4 polycrystalline were fabricated by high temperature sintering. The pure phase LFO samples used in our works show similar properties with what was reported in literatures. For example, the para-ferri magnetic transition, large coercive field and spin glass like behaviors. In this thesis, the work focuses on the magnetocapacitance (MC) and magnetoelectric effect. With the help of electric circuit based curve fitting, it is demonstrate that the large dielectric constant and magneto electric effect are caused by the non-intrinsic interface effects. The large Magnetocapacitance effect comes from the Magnetoresistance effect of the interface or the bulk. A home made low temperature Magneto-electric effect measurement system was setup to investigate the magnetoelectric effect of the LFO sample. From our experiment, it is proved that these LFO samples with large extrinsic magnetocapacitance effect shows no large ME effect. Apparently observed signal may come from the improper shielding of the electromagnetic field from the alternating current source. The multiferroic BiFeO_3 thin films were synthesized with magneto sputtering systems. The growing conditions are optimized based on our system. It is found that while the Bi/Fe ratio is the most vital for the pure phase growth of BFO thin film, the ratio itself is very sensitive to almost every parameter of the deposition process. Fortunately, the reproducibility is very good for sputtering methods. It is also found that the Bi rich target as often used Pulsed Laser Deposition (PLD) method are not suitable for our sputtering system. Because the Bi/Fe ratio is larger than 1 even at

the 0.1 Pa which is the minimum possible controllable pressure in our system. Bi deficient with Bi/Fe=1/1.2 is most suitable. Although, the conditions that necessary for the intrinsic transport property is in contrary with the improvement of crystal quality. BFO samples with high quality and intrinsic transport properties can be obtained at optimized conditions.

The Dielectric responses of BFO are investigated on the samples that show intrinsic ferroelectric properties. The equivalent circuit base fittings are also used to explain the relationship between the phase transition and dielectric anomalies at low temperature.

Furthermore our efforts on the lower temperature and large bending angle in the sputtering growth show the coexistence of T and R like BFO on STO substrate. This provides an optional way to fabricate T like phase through mechanism of strain effects.

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Chapter One

Introduction

1.1 Background

Modern information technologies are based on tiny microelectronic devices such as transistors.(1) Despite of a bewildering range of architectures and applications, the fundamental principle of operation of all such microelectronic devices is the process of manipulating the motion of electrons using only their charge. Electrons however, in addition to having charges, also have spins. Today we lie on the verge of a technology revolution where both spin and charge are used to create Spintronic devices, which can overcome various difficulties in the present electronics using only charge degrees of freedom of electrons.

In particular, materials of which magnetization can be controlled with electric field or electric polarization can be manipulated by magnetic field would be fascinating and highly desired. Multiferroic and magnetoelectric materials with strong magnetism and ferroelectricity coupling are promising candidates for such operations. The materials that have been investigated include both composites and single phase materials.(2) Single phase multiferroics includes the Cr_2O_3 , Fe_3O_4 , Gd_2CuO_4 , Sm_2CuO_4 , KNiPO_4 , LiCoPO_4 , REMnO_3 and REMn_2O_5 et al.(3) The ME effects are generally measured in both direct way and indirect ways. In the direct measurement, the electric polarizations are manipulated by the magnetic field(4) or the magnetic

moments are reversed by electric field.(5) Most of the results shows weak magnetoelectric (ME) effects at low temperature.(3,6-10) Recently, large ME(H) signals have been measured in some new materials.(11) The indirect way is to measure the dielectric response near the magnetic phase transition temperature(2,12) or similarly, measure the magnetization near the ferroelectric transition temperatures.(2) In addition, it is proposed that samples with lower resistivity might cause misunderstanding in their electrical experiment results.(13)

1.2 Introduction to LuFe_2O_4

Charge ordering LuFe_2O_4 have become the target material of multiferroics due to its giant magnetocapacitance and ME(H) effect.(14) Diffraction experiments including neutron diffraction, (non)-resonant x-ray scattering, Anomalous X-ray Dispersion and Mössbauer spectroscopy et al, have revealed the spin, charge and orbital ordering in the RFe_2O_4 . And it is believed that a two-dimensional charge order occurs below 500 K,(5) the two-dimensional charge order state change to three-dimensional charge order state when the temperature is lower than 320 K which results in a net electric polarization. Meanwhile, the strong magnetic interactions between localized Fe moments develop as ferrimagnetic ordering below the Néel temperature $T_N \sim 240$ K.(6-8) At almost the same temperature the pyroelectric measurement showed a shoulder with about 20% percent of increase in the integration current.(15) The ac susceptibility indicates frozen glassy behavior when $T < 220$ K. Electric field induced resistance change at room temperature and electrically

controlled magnetization have also been discovered recently. (9, 10) All these results indicate a complex phase diagram and strong magnetoelectric coupling existing in the material system.

However these properties are under great debate. Its ferroelectric and charge ordering nature are exposed to doubt. The ferroelectric loop has never been observed even at low temperatures. Comparing with other oxide materials, the high conductivity may contribute a lot to the dielectric constant. Although, the large Magnetoelectric measurement may also be artifact, there is no detailed investigation on the possible origin of these phenomenon.

1.3 Introduction to BiFeO₃

On the other hand, it is well known that BiFeO₃ is the only room temperature multiferroic material that shows both weak canting ferromagnetism and intrinsic ferroelectricity. After years of research, the high quality epitaxial BFO thin films have been fabricated with many methods, which enable the study of intrinsic properties. The ferroelectric transition temperature (836°C) was determined by differential thermal analysis.(16) The Néel temperature of the R-like phase is around 384°C. (17) The real boost of BFO starts from the confirmation of its intrinsic ferroelectric property.(18) The epitaxial thin film (grown by PLD) shows much larger polarizations (50-60 $\mu\text{C}/\text{cm}^2$) and for the first time square like P-E loops are observed.(17) The thin films have been grown by many different methods, like the PLD (Pulsed Laser Deposition) (19), Liquid Phase Epitaxy (LPE), Sol gel(20) , chemical solution

deposition(21,22), Molecular Beam Epitaxy (MBE) (23) and Metal Organic Chemical Vapor Deposition (MOCVD)(24) are also used to grow BFO on substrates like on Si (with SRO buffer layer)(25) and on Pt/TiO₂ /SiO₂ /Si substrate(26). The 90° off-axial sputtering has been used in the BFO thin films growth, however the detailed growing conditions have never been revealed.(27-29) In this thesis, we report the effects of every sputtering parameter on the BFO growth and give detailed map for the growth of BFO epitaxial thin films. As the only room temperature multiferroic materials, the BFO was used as the antiferromagnetic (AFM) layer in spin valve devices. (30-33) The mechanism of exchange bias on BFO have been investigated.(34,35) It is noticed that, different from many leaky high-k materials, the BFO thin films can be quite insulating. Therefore intrinsic ferroelectric polarization can be measured on BFO thin films. However, so far the detailed investigations on dielectric property of BFO are still rare. The giant dielectric constant (as large as 10^4) have been observed in BFO ceramics in which the large values are attributed to hopping electrons at the electrode interface and grain boundaries.(36),(37) The dielectric properties of a In/BFO/LSMO capacitor also show obvious effects from the electrode interface.(38) This is similar to many other large dielectric materials like CaCu₃Ti₄O₁₂, LuFe₂O₄, LaMnO₃ *et al.* In literatures and our results on LuFe₂O₄, it is shown that both giant dielectric constant and magnetocapacitance can be attributed to the interfacial effects in leaky oxide.(39-41),(42) Therefore, although the leakage current can be suppressed in fabricated BFO thin films dramatically,(18, 28, 43) one should still be careful about the conclusions deduced from the dielectric results.

Furthermore, the low temperature transport properties are still rare, especially the dielectric properties of high resistive BFO. Recently, possible magnetic phase transition at low temperature was revealed by many other methods.(44) It is proposed that there may be several phase transitions at low temperatures for BFO.(45-49) The dielectric measurements based on BFO bulk materials have revealed that the elastic and dielectric anomalies at low temperature may be related to these transitions.(50) The electrical equivalent circuit fitting has been utilized to investigate the impedance spectroscopy (IS) of epitaxial BFO thin films above room temperature.(41)

In this thesis, the dielectric property of epitaxial BFO is measured below room temperature. The origins of the dielectric anomalies are clarified with equivalent circuit fitting. The results show that the dielectric anomalies at low temperature might be misleading for phase transition analysis if no electric circuit fitting is used. Furthermore, the physical significances of the Constant Phase Element (CPE) and the related capacitor conversion method are discussed based on the results at different temperatures and electric fields in BFO samples.

As mentioned above, the epitaxial BFO thin films have been grown on many different substrates, like the Si, STO, LAO, YAO and their related miscut substrates to control the domain structures. It is particularly interesting to find that, the low mismatch of LAO substrate lattice constant have induced c axis elongated T-like BFO, which shows larger polarizations. Although the T like BFO phase are mostly observed on LAO substrate, it is also synthesized at certain extreme conditions. The T like BFO

can also be fabricated on STO (001) substrate.(51) Therefore, it is also interesting to investigate the growth mechanism of the T-like BFO thin films.

1.4 Introduction to electric field based curve fittings on the Impedance Spectroscopy

The electric circuit based fittings can be traced back to the simple Debye equation.(193) Debye equation is firstly proposed to explain the dielectric properties of gases.(193) The impedance of the Debye response is a half circle in the Cole Cole plots. However, it is found that most of the dielectric responses in condensed matters are not exactly the same as the Debye equation. A series of empirical relaxation expressions have been proposed to parameterize the observed results. And, it is pointed out that all these dielectric response can be decomposed into circuits which contains a component called constant phase element (CPE) or Universal Dielectric Response (UDR).(193)

$$Y_{CPE} = A_0(i \cdot \omega)^s, 0 < s < 1$$

Since then, the electric circuit based fittings have become very useful for the analysis of dielectric response in solid state physics. For example, the methods were used to investigate the AC conductivity of La_2CuO_4 , in which it is found that the hopping mechanism may be different in different crystal direction.(194) Recently, it has been used to explain the large dielectric constant observed in LaMnO_3 , CdF_2 , $\text{SrNbO}_{3.41}$ et al. where the response of electrode interface, grain boundary and the bulk can be distinguished.(201-202)

1.5 Objectives

The main objective of this thesis includes fabrication of LuFe_2O_4 polycrystalline and epitaxial BiFeO_3 thin films (R like and T-like phase); Investigations on the transport and dielectric property of the fabricated materials.

1.6 Major contributions of the thesis

The major contributions achieved in this thesis are summarized as follows

- (1) Pure phase LuFe_2O_4 (LFO) bulk materials are fabricated, the low temperature dielectric property, magnetocapacitance and magnetoelectric effects are investigated
- (2) Epitaxial BiFeO_3 (BFO) thin films are grown on SrTiO_3 (STO) (001) and LaAlO_3 (001) substrates. The growing conditions are optimized to grow samples with higher crystalline quality.
- (3) Low temperature Impedance Spectroscopy of Rhombohedral like (R-like) BFO thin films are studied in detail, the relationship between the dielectric anomaly and the low temperature phase transition are discussed.
- (4) Successful growth of tetragonal like (T like) and R like phase BFO on STO (001) substrate with sputtering method. The appearance of T like BFO is not solely depending on the lattice or the existence BiO_x , which enables the growth of pure T-like phase on STO substrate.

1.7 Organization of the thesis

This thesis consists of eight chapters,

Chapter 1, gives an introduction of this thesis, the objectives, major contributions and organization of the thesis.

Chapter 2, includes the fabrication and basic characterization of LuFe_2O_4 bulk materials.

Chapter 3, investigates the magnetocapacitance (MC) effect of LuFe_2O_4 and its low temperature dielectric properties.

Chapter 4, focus on the growth condition optimization of BFO thin films, EDS and HRXRD are used to characterize the thin films.

Chapter 5, dielectric properties of BFO thin film are investigated from room temperature to 10K, equivalent circuit based fittings are carried out to explain the dielectric anomaly at low temperatures.

Chapter 6, sputtering growth of T like phase on the STO and LAO (001) substrate.

Chapter 7, magnetic Properties of BiFeO_3 thin films was measured by VSM, the exchange bias of NiFe/BFO structures on R like and T like BFO are compared.

Chapter 8, a summary of this thesis and future work are given.

Chapter Two

Fabrication and characterization of bulk LuFe_2O_4 Materials.

2.1 Introduction

Multiferroic materials with charge ordering induced ferroelectricity in RFe_2O_4 series compound have drawn much attention due to its colossal dielectric constants and magnetodielectric effects.(14),(15) Particularly, investigations on LuFe_2O_4 exhibit many interesting properties such as the electric field induced phase transition,(52) giant dielectric tunability,(53) giant magnetic coercivity,(54) giant magnetic anisotropy,(55) and spin glass like behaviours.(56) Therefore, LuFe_2O_4 , have been proposed to be a multiferroic system due to charge order. The crystals of these materials belong to the Rhombohedral system (space group $R\bar{3}m$), Figure 2.1(a).(57) It has a double layer structure with a triangular iron lattice within each layer as shown in Figure. 2.1 (b).(57) It is proposed that, the Fe-O double layer are in polar configurations,(14) and the polar Fe-O bilayer can be antiferroelectric stacking.(58) However, the detailed Fe^{2+} , Fe^{3+} arrangement was still not clear back then.

Figure. 2.1 The schematic diagram of LuFe_2O_4 structure (a) and the charge redistribution (b) between the layers and the interlayer charge ordering of bilayer FeO triangular lattice in LuFe_2O_4 .

2.2 Sample fabrication

The tube furnace was used to fabricate the LuFe_2O_4 polycrystalline samples in reduced atmosphere. The flow ratio of CO/CO_2 is kept at 7/3. The tube is made of corundum, which can be heated to as high as 1600 °C. An electronic flow meter was placed in front of the furnace tube to monitor the flow and a bubble flow meter was connected to outlet because of security concern. After careful grinding in agate mortar, the stoichiometric mixtures of Fe, Fe_2O_3 and Lu_2O_3 were pressed in a pressuring machine with maximum pressure of 25G Pa before the sintering.(52) The

pressed pellet ($\phi 10\text{mm} \times 10\text{mm}$) was firstly sintered at 575 K for 3 hour to remove the organic glues and then prepared by solid state reaction at 1600 °C for 3days.

2.3 x ray diffraction (XRD) and magnetic characterization

The pressed powder becomes solid pellet after sintering. Phase separation was observed at the surface of the $25\text{mm} \times 3\text{mm}$ samples. After sanding and polishing, pure phase LFO sample can be obtained. The sample structure was characterized by Philips Bruker D8 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=1.5406\text{\AA}$) in the locked coupled mode. The current and voltage for the x-ray tube are 40mA and 40 kV respectively. The sample surface was polished to eliminate any peak displacement. As shown in the lower graph of Figure 2.2, the X-Ray Diffraction (XRD) pattern of the LuFe_2O_4 polycrystalline shows that all the diffraction peaks can be indexed and the sample is pure phase. The upper graph is the measured result. The lower graph is the XRD pattern calculated from its crystal structure (R-3m) with ICSD FindIt software.

Figure 2.2. XRD patterns for the LuFe₂O₄ polycrystalline at room temperature. The upper graph shows the experimental data (Exp). The lower graph shows the pattern calculated from the R-3m structure. (Cal)

Figure 2.3 (a) The picture of the Physical Property Measurement System (PPMS);

and (b) a schematic of the VSM Install/Remove Wizard software.

The magnetic property of LuFe_2O_4 material is measured with the Physical Property Measurement System (PPMS), vibrating sample magnetometer (VSM). As shown in Figure 2.3 (a). The system is equipped with 9T Tesla vertical magnetic field. A small piece of LFO bulk sample was mounted at the center of the sample rod. Then the rod is placed into

the PPMS chamber and an automatic centering program is used to decide the precise position of the sample center to a precision of 0.1mm. Figure 2.3 (b) shows that the sample position is at 34.72mm. The operation principle for a vibrating sample magnetometer is that a changing magnetic flux will induce a voltage in a pickup coil. The pickup coil is seated at the bottom of the PPMS dewar.

Because of the charge ordering nature, the LFO shows spin glass like behaviour at low temperatures. Figure. 2.4 shows the temperature dependence of magnetization measured after zero field cooling and field cooling process in 100 Oe magnetic field. The M (T) curves indicate a phase transition from paramagnetic state to ferrimagnetic state at 240 K and a spin glass transition at about 225 K. The results are consistent with literatures.(56, 59-63)

Figure 2.4 Temperature dependence of magnetization, measured with the applied magnetic field of 100 Oe. ZFC and FC stand for zero-field-cooled and field-cooled magnetization, respectively.

2.4 Electric field induced phase transition in LuFe_2O_4 .

Recently, electric field induced resistance have been observed in a variety of transition metal oxides.(52). It is interesting because the switching phenomenon may have potential applications in memory devices. The I-V curve of the LuFe_2O_4 have also been investigated and are believed to show electric field induced phase transitions at higher electric field. The mechanism of this transition were attributed to the charge ordering broken down at higher voltage.(52) However, the joule heating also contributes to the transition at higher electric field.(165) We also carried out similar experiments. The I-V curve was measured with Keithley 2400 source measurement unit (SMU). Figure 2.5 (a) shows the I-V curve of the bulk LFO at 340K, 310K, 290K and 270K respectively. The typical size used in our experiment is $2\text{mm} \times 1\text{mm} \times 3\text{mm}$. In the measurement as shown in figure 2.5 (a), the pulse width is 20ms and the time interval between each pulse is 1s. The sample shows character that is similar to the insulator to metallic phase transition.(52) The phase transition becomes more obvious at lower temperatures.

Figure 2.5 (a) I-V curve of LuFe_2O_4 polycrystal at 340K, 310K, 290K and 270K. (b) I-V curve of LuFe_2O_4 polycrystal at 340K with different voltage pulse.

A simple method was used to check the possible contribution from joule heating. As shown in Figure 2.5 (b), comparing with the curves measured with 20ms pulse, the curves measured with 1ms pulse is less sharp at higher voltage. Similarly, with the same time interval, the curves measured with longer pulse time are stepper. These results indicate that the switching effects may be related to the Joule heating effects. Shorter pulse time and longer integration time will reduce the heating effects.

Chapter Three

Dielectric Investigation of LuFe_2O_4

3.1 Introduction

Giant dielectric constants have often been reported in RFe_2O_4 series materials.(15, 53, 63-69) The colossal dielectric constants is attributed to the freezing of the polar domains and antiphase boundaries of short-range charge ordering.(64) However it is also pointed out that the dielectric measurement of lossy dielectrics, like the RFe_2O_4 , may be misleading when the conductivity and polarizability co-exist.(70) The giant dielectric permittivity may be originated from the interface at electrode contacts, grain boundaries and hopping conductivity. The giant dielectric constant observed in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO), $\text{CdF}_2\text{:In}$, LaMnO_3 , was indicated to be extrinsic property due to the Maxwell Wagner (MW) effect.(39),(71) Detailed equivalent-circuit analysis has been utilized to explain the giant dielectric constant of many other materials including the charge ordering system like $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ and $\text{La}_{1-x}\text{Bi}_x\text{MnO}_3$.(72),(73)

Although the LuFe_2O_4 was proposed to be ferroelectricity below 320K, until now there is still no direct observation of convincing P-E loop reported at room temperature, probably due to its leaky nature. Our test on polycrystalline LuFe_2O_4 shows almost circular ferroelectric polarization vs electric field (P-E) loops at room temperature and banana like P-E loops at low temperatures which are comparable with the results in literatures.(11),(59)

The ferroelectricity established through the piezoelectric measurement is still under debate.(70) All these results indicate that a further investigation on the origin of the dielectric property in LuFe_2O_4 is quite necessary.

3.2 The measurement of impedance spectroscopy

The dielectric property of LuFe_2O_4 polycrystalline is measured with two point method by an Agilent E4980a LCR meter. The frequency is in the range of 20 to 2MHz. In order to improve the measurements, complete coaxial cable was used as the measuring circuit. The cable is interface with the multifunction probe, the sample is then inserted into the PPMS chamber. Labview program was used to control both the PPMS and LCR meter. The sample used for the dielectric measurement is polished by automatic polisher. 100 nm level sand papers are used. A rectangular sample is cut and polished for the dielectric measurement.

3.3 The equivalent circuit analysis of impedance spectroscopy

The equivalent circuit modeling is quite helpful in impedance spectroscopy (IS) analysis. The basic elements includes both lumped (R, C and L) and distributed elements.(74) In describing the frequency dependence of the dielectric response of gases, the Debye's formula are quite successful, formula (3.1).(75) The formula are originally derived from the quantum mechanism detail of the gas systems.(75) However the same frequency response can also be derived from the Maxwell-Wagner two layer model. In this model it is assumed that two R-C parallel circuits are

connected in series with each other.(75) Because the formula that can be used to describe the response are the same, the main characters are the same, as shown in figure 3.0, the Two layer model shows the Debye term (a peak) and the conductivity term in the dielectric loss part. Furthermore, if more RC layer is added into the circuit, more dielectric peaks can be introduced into the dielectric loss.(76) The Maxwell Wagner type relaxations are widely used to represent the interfacial effects.

$$\begin{aligned}\varepsilon' - \varepsilon'_\infty &= \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + \omega^2 \cdot \tau^2}, \\ \varepsilon'' &= \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{1 + \omega^2 \cdot \tau^2}\end{aligned}\quad (3.1)$$

Figure 3.0 the dielectric property of the typical Debye

As the development of Impedance Spectroscopy, it is noticed like response.(76) that

most of the response of solids cannot be explained by the Debye mechanism. However, the response from different systems follows another formula called the universal dielectric response (UDR) or more generally the constant phase elements (CPE), with the CPE impedance are represent as $Y_{CPE} = A_0(i \cdot \omega)^s, 0 < s < 1$. (39, 77)

3.4 Impedance spectroscopy of LuFe_2O_4

3.4.1 The effect of electrodes (a quick test)

It is suggested that different contacts and sample size can be used as a simple test of extrinsic contributions.(71) Therefore both silver paste and sputtered Au electrodes were utilized in our dielectric measurement. The dielectric constant measured with Au electrodes increases by more than one magnitude than that measured with silver paste electrode and the dielectric constant almost doubles for the same sample cut through the centre. These tests indicate that the electrodes affect the dielectric property significantly. As shown in the Figure 3.1 (a), the impedance spectroscopy of the same sample looks quite different between the silver paste and the sputtered Au electrode.

Figure 3.1. (a) Frequency dependent dielectric permittivity of LuFe_2O_4 ceramic at room temperature. Dotted curves and solid curves represent separately the result measured with silver paste as electrodes fabricated in a same process at two times; (b) inset: frequency dependent of dielectric permittivity measured with sputtered Au as electrode.

3.4.2 Detailed analysis with equivalent circuit fittings.

Similar to what was reported in literatures; both giant dielectric constant and the magnetocapacitance effect were observed in our experiments on LuFe_2O_4 . However, the measured value of the dielectric constant changes with different electrodes. Therefore, detailed equivalent circuit analysis is necessary to reveal the true nature of the large dielectric constant.

Considering the evident influence caused by different contacts, the fitting model for the IS analysis is designed as shown in the inset of Figure 3.2(a). The two parallel RC-circuits represent two interfacial effects, where $G_c C_c$ and $G_{gb} C_{gb}$ are the conductance and capacitance of the electrode contact and grain boundary of the polycrystalline materials.(42,78) The bulk property is modeled with three parts in parallel: (1) the trueDC conductance (G_{DC}), (2) the high frequency limit of the bulk capacitance (C_∞) and (3) Universal Dielectric Response (UDR). The UDR is frequently used in explaining the giant dielectric constant in the above mentioned literatures. As a common approach for the hopping conductivity, the UDR formula describes the AC response of localized charge carriers.(39),(79) The admittance of

the UDR part can be represented as $Y_{\text{UDR}} = G_0 \cdot \omega \cdot [1 + i \cdot \tan(s \cdot \pi/2)]$, $0 \leq s \leq 1$, where

$\omega = 2\pi \cdot f$ is the angular frequency of the test signal and i is the square root of -1. The

UDR model can be derived from the idea of Constant Phase Elements (CPE), a

more general phenomenological expression often used in IS fittings.(74,80-82)

The CPE admittance is defined as $Y_{\text{CPE}} = A_0(i \cdot \omega)^s$, $0 < s < 1$. The formula can be

written in expanded form as follows,

$$Y_{\text{CPE}} = A_0 \cdot \omega^s \cdot [\cos(s \cdot \pi/2) + i \cdot \sin(s \cdot \pi/2)] = A_0 / \cos(s \cdot \pi/2) \cdot \omega^s \cdot [1 + i \cdot \tan(s \cdot \pi/2)] .$$

Figure 3.2(a) The frequency dependence of the real part of dielectric permittivity at different temperatures. Inset of (a) The equivalent circuit used for fitting. (b) The frequency dependence of the imaginary part of dielectric permittivity of LuFe_2O_4 . Dots and lines are measured results and fitted results respectively.

The phase angle of the CPE impedance is independent of the frequency.(74, 80, 83, 84) Comparing with admittance representation of CPE and UDR , it is derived that the ac conductance G_0 in UDR model is not completely independent but related to s through $G_0 = A_0/\text{Cos}(s \cdot \pi/2)$.(80) The total impedance of the model is as follows,

$$Z^* = 1/(G_C + i \cdot \omega \cdot C_C) + 1/(G_{gb} + i \cdot \omega \cdot C_{gb}) + 1/\{G_0 \cdot \omega^s + G_{DC} + i \cdot [\tan(\frac{s\pi}{2}) \cdot G_0 \cdot \omega^s + \omega \cdot C_\infty]\} .$$

$\epsilon_\infty = L \cdot C_\infty / (A \cdot \epsilon_0)$ where A and L represent the contact area and sample length respectively. $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$, is the vacuum permittivity. In order to separate G_0 from s and avoid parameterization problem as s approach its limit value, the parameter A_0 is used in actual fitting.(80)

Figure 3.2 (a) and (b) shows the frequency dependence of complex dielectric permittivity at different temperatures between 300 K and 200 K. The real and imaginary parts are fitted simultaneously with all parameters unlock. The results are fitted well except at the range with frequency smaller than 200Hz. The fitting results and their temperature dependence are listed in Table. 3.1. Parameter s is temperature dependent and decreases with increasing temperature which is often found in CPEs .(80) This indicates that the CPE approach the property of a simple capacitor at low temperature ($s \rightarrow 1$).(82) The A_0 in CPE is temperature dependent and

increases when raising temperature. The calculated G_0 also increases with increasing temperature. The microscopy mechanism of CPE or UDR is still under debate. There is no unique origin for various systems.(80-82) In the case of LuFe_2O_4 sample, the CPE formula is probably caused by the hopping conductivity of localized charge carrier.(39, 79)

Table 3.1. Temperature dependence of fitting results for LuFe_2O_4 at different temperatures

Parameters	300 K	280 K	260 K	240 K	220 K	200 K
$G_C (\Omega)$	7.262×10^{-4}	3.129×10^{-4}	1.597×10^{-4}	5.079×10^{-5}	1.760×10^{-5}	4.120×10^{-6}
$C_C (\text{C})$	1.330×10^{-9}	1.323×10^{-9}	2.077×10^{-9}	1.736×10^{-9}	1.922×10^{-9}	1.450×10^{-9}
$G_{gb} (\Omega)$	1.980×10^{-3}	9.810×10^{-4}	2.357×10^{-4}	8.685×10^{-5}	2.163×10^{-5}	6.361×10^{-6}
$C_{gb} (\text{C})$	1.300×10^{-9}	1.295×10^{-9}	1.218×10^{-9}	1.154×10^{-9}	1.067×10^{-9}	1.242×10^{-9}
$A_0 (\Omega)$	9.730×10^{-6}	3.984×10^{-7}	1.395×10^{-7}	6.449×10^{-10}	2.616×10^{-10}	1.119×10^{-10}
$G_{DC} (\Omega)$	1.420×10^{-3}	4.940×10^{-4}	1.415×10^{-4}	4.262×10^{-5}	9.940×10^{-6}	1.991×10^{-6}
s	0.152	0.314	0.349	0.639	0.663	0.673
ϵ_∞	0	0	0	0	0	0
$G_0 (\Omega)$	9.453×10^{-6}	3.511×10^{-7}	1.190×10^{-7}	3.467×10^{-10}	1.322×10^{-10}	6.144×10^{-11}
Adjusted	0.99994	0.99998	0.99999	0.99997	0.99989	0.99989
R-Square						

The DC conductance of the electrode contact (G_C), grain boundary (G_{gb}) and the bulk (G_{DC}) all increase as the temperature increase. The conductance dependence on

temperature is consistent with its insulating feature. The interfacial capacitance (C_c) and (C_{gb}) shows weak temperature dependence above.(78) The intrinsic dielectric constant ϵ_∞ is zero at all temperatures. The adjusted R-Square is almost 1 for the data measured at different temperatures. This indicates that the same model is suitable for all temperatures. Other possible circuits without the grain boundary or the CPE have been tried. However, only the model considering all three components can fit the results well.

Figure 3.3 (a) The complex impedance plot at 300 K in logarithmic Scale. Solid lines and open symbols represent the total response and separated contributions from the three components respectively. Lower inset of (a) The complex impedance plot of the fitted result at 300 K in linear scale. Upper inset of (a) Enlarged part of the low frequency area of the complex impedance showed in the lower inset of (a). (b) The frequency dependence of the real part of the dielectric permittivity of LuFe_2O_4 at 300 K. (c) The frequency dependence of the imaginary part of the dielectric permittivity of LuFe_2O_4 at 300 K. The squares, triangular and circle dots represent contributions from electrode, grain boundary and bulk respectively.

The contributions from different components can be displayed separately. Figure 3.3(a) shows the logarithmic graph of the complex impedance ($Z-Z$) Plot at 300 K. The horizontal arrow indicates the direction of increasing frequency. The solid curves represent the measured results and the dots represent the contributions of the electrode contacts (squares), grain boundary (triangles) and the bulk (circles) derived from the fittings. In the logarithmic plot the solid curve bent towards the real axial and intercept at a non-zero value. This corresponds to two semi-arcs passing through the origin of the coordinates in linear scale as displayed in the lower inset of Figure.3.3 (a). The enlarged picture [upper inset of Figure 3.3(a)] of the low frequency part of the $Z-Z$ Plot [lower inset of Figure.3.3(a)] reveals a small arc proceeding to lower frequency region, indicated by the vertical arrow.(81) This arc is attributed to the bulk component.

The dielectric response from different components can be calculated from the decomposed Z-Z Plots. As an example, the real and imaginary parts of the complex dielectric constant at 300 K are shown in Figure.3.3 (b) and (c). The interfacial component shows almost frequency independent dielectric constant in the investigated frequency range, while the bulk component increases in exponential scale towards low frequency because of the response of the CPE. At high frequency end the total dielectric response shows the feature of bulk component. As the frequency decreases, the interfacial capacitance begins to dominate and the high dielectric plateaus are observed. The results are consistent with the prototypical model proposed by P. Lunkenheimer.(39)

Magnetocapacitance (MC) effects which have been used as a test of multiferroics is also doubtful considering the possible variation of parameters in the model mentioned above. As proposed by G. Catalan, a combination of magnetoresistance (MR) and the MW effect which have no connection with magneto-electric coupling can cause MC phenomenon.(13) It is also suggested that a large range of colossal dielectric materials shows interface-driven magnetocapacitance. To explore the origin of the MC effect in LuFe_2O_4 , we measured the “MR” and “MC” of the same sample in an elaborately controlled measuring process. The sample was firstly cooled down to 280 K at 3 K/min, and then the dielectric permittivity was measured while the magnetic field increased from 0 Oe to 2 Tesla at 100 Oe/s. The time interval between measurements is about 90 seconds and it takes about 1 hour before the magnetic field reach 2 Tesla. Then the magnetic field was decreased to zero in the same rate and the temperature

proceeded to 260 K. The same measuring process was taken at every measuring temperature. The sample was then heated to room temperature and waited for 3 days before carrying out resistance measurement in the same process. Both “MR” and “MC” are measured by two point method with the same current level.

Figure 3.4(a) shows the frequency dependence of the dielectric response measured in magnetic field at different temperatures. The dots are the measured data and the lines are the fitted results. For the data measured at zero fields, the fittings were carried out with all parameters unlocked. When fitting the result measured at non-zero fields, all the parameters except the three conductance (G_C, G_{gb}, G_{DC}) are fixed. Similar to the results measured at zero fields, the complex dielectric constants are fitted well with the same model. The total sample resistances $R_C + R_{gb} + R_{DC}$ at different magnetic fields are derived from the fitting and the MR is calculated as $MR = \frac{R_{(H)} - R_{(0)}}{R_{(0)}}$. To show the results at different temperatures clearly, the curves at 220 K, 240 K, 260 K and 280 K are shifted up vertically. From Figure 3.4 (b) one can see that the MR derived from the MC measurement (open symbols) has the same trend as the measured MR (solid symbols). This indicates that the MC in LuFe_2O_4 may be attributed to the variation of DC resistance. The temperature dependence of the resistance at zero fields was also derived, as showed in the inset of Figure 3.4(b). The fitted results (open symbols) are quite close to the measured resistance (solid symbols) in absolute values. The MR may be originated from both bulk and interface. The mixed valence of Fe atoms in LuFe_2O_4 may contribute to double-exchange MR.⁽¹³⁾ The nonlinear variation of resistance with magnetic field can be common in oxide materials because of the interaction between magnetic field and charge carriers at interface.⁽⁸⁵⁾

Figure 3.4 (a) The frequency dependence of the real part of dielectric constant measured at 280 K, 260 K, 240 K and 220 K with different magnetic fields. The measured and fitted data are shown in dots and lines respectively.

(b) The measured and fitted magnetoresistance during the same measuring process at 280 K, 260 K, 240 K and 220 K. The measured and fitted data are shown in solid and open symbols respectively. Inset of (b) the temperature dependence of the fitted and

measured resistance at zero fields.

In summary, detailed analysis of dielectric response has been performed in polycrystalline LuFe_2O_4 . We provided experimental evidence that the large dielectric constant in ceramic LuFe_2O_4 sample can be attributed to the interfacial effects at electrodes or grain boundaries and the AC response of Constant Phase Element in bulk. The MR effect originated from the interface or bulk can be responsible for the MC effect simultaneously. The equivalent circuit fitting showed that the Debye like dielectric response and MC can be modeled without any assumption of dipolar polarization. Further investigation including the leaky mechanism will be necessary to reveal the true character of charge ordering domains and multiferroic coupling in the RFe_2O_4 series materials.

3.5 The magnetic field induced voltage, Magnetoelectric effect (ME (H)) of LuFe_2O_4

The magnetoelectric effects which were firstly observed in Cr_2O_3 (195) have been viewed as a direct proof of the interaction between the magnetic and the electric order parameters. The voltage induced by the magnetic field from the sample can be expressed as:

$$P_i = \sum \alpha_{ij} H_j + \sum \beta_{ijk} H_j H_k + \dots$$

There are three methods that are used to measure the ME (H), they are: (1) the static method, (2) quasi static method and (3) dynamic methods.(86) In static and quasi static methods, the charge accumulated at the grain boundary will affect the results, therefore in order to measure the magnetoelectric effects in polycrystalline LuFe_2O_4 , dynamic methods

is used.

It is reported in the literature that the magnetic field can induce voltage as large as tens of mV from the LuFe_2O_4 sample.⁽¹¹⁾ The dynamic measurements were carried out on our LuFe_2O_4 samples with the same experimental setup mentioned in literature.⁽⁸⁶⁾ The diagram of the experiment setup is shown in Figure 3.5 (a). A Keithley 6221 current source are connected to the alternating current (AC) coil to provide AC magnetic field. The picture of the alternating current coil is shown in Figure 3.5 (b).

It is noticed from our experience that although the Lockin amplifier is used to reduce any noise signal from the environment, the experiment itself will generate large signal that are necessary to emphasize in respect of electric field shielding. Therefore the frontend of the multifunction probe are modified to meet these needs. A special cylinder was fabricated and installed into the sample holder of the Multifunction probe (Quantum Design). The cylinder also works as the electrical shieldings. The Cylinder was made of Al metal to be more sensitive to the high frequency electromagnetic radiations generated by the AC coils. The cylinder length are carefully machined to achieve close contact with the PPMS system's sample holder. The fabricated cylinder can be slide into the PPMS holder and the sample can be placed at the center of the cylinder. Our experiences indicate that tightener contact will further reduce the background signal form the AC oscillations. In order to avoid any possible of contact between the sample and the Al cylinder, another cylinder made of PTFE are inserted into the Al cylinder to avoid electric short with the sample

Figure 3.5 (a) AC magnet winded around a Al cylinder used for the ME (H) effects measurement; b) Schematical block diagram the ME(H) effects measurements.(86)

The circuit for the measurement is shown in figure 3.5 (a), the magnetic coil was winded around a hollow cylinder where the sample stays at the center, figure 3.5 (b). The winded coils were connected to the Keithely 2182 alternating current source. The magnitude of the AC magnetic field is calibrated with Gauss meter. The magnetic field at the center of the cylinder is more than 5 Oe. When the AC magnetic field is applied to the sample, a voltage can be induced from the sample. The voltages are then recorded through the lock in amplifier. Figure 3.6 (a) shows the test results of the equipment setup. When the system is connected to a Si substrate, the background noise of our experiment setup can be less than $10\mu\text{V}$ at room temperature and even smaller at lower temperature.

Figure 3.6 temperature dependence magnetoelectric (ME) effect for (a) Si test sample and (b) LuFe_2O_4

However, the bulk LuFe_2O_4 plate also shows similar response like the Si wafer, Figure 3.6 (b). No large ME effect was observed for our LuFe_2O_4 samples. Actually, many different pieces of samples have been measured even after poling at higher voltage, and it is found that none of them shows any evidence of large ME effect. Considering the leaky nature of the LuFe_2O_4 samples we doubt about the intrinsic value of the tens of mV can be achieved except the noise effects.

3.6 Conclusion

Recently, more literatures about LuFe_2O_4 have set more doubts on its charge ordering nature.(87-89) The dielectric results on LuFe_2O_4 single crystal further prove that, the large dielectric constant are not its intrinsic character.(89) The low resistivity is the main reasons that cause the high dielectric constant in these materials. Even the large magnetoresistance can be explained as the effect from the change of resistance with magnetic field. The most recent literatures on LuFe_2O_4 single crystal have revealed that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ bilayer may be nonpolar in nature. The dielectric properties of LuFe_2O_4 are also dominated by the electrode interfaces.(89) All these results set doubt on the ferroelectric nature of LuFe_2O_4 . Although many efforts have been made, until now there is no fabrication of LuFe_2O_4 samples with really large resistivity, probably because the fabrication of LuFe_2O_4 needs reduced gas environment, CO or H_2 , to guarantee the coexistence of Fe^{2+} and Fe^{3+} ions. At reduced environment oxygen vacancy may be formed in the samples. Efforts to reduce the residual conductivity may be necessary to further clarify the intrinsic property of the charge ordering structures.

Chapter Four

Synthesis and characterization of R-like BiFeO₃ thin films on STO (001) substrate

4.1 Introduction

The development of modern thin film growth technology has enabled the growth of high quality epitaxial thin films.⁽⁹⁰⁾ Many of the works about BFO thin films are based on Pulsed Laser Deposition methods.⁽⁹¹⁻⁹³⁾ On the other hand, magneto-sputtering have been used widely for the growth of many compounds in electronic industry. For example, the ZnO, silicon oxide, Al₂O₃ and many other dielectric or ferroelectric materials like BaTiO₃, LiNbO₃ and PbTiO₃ et al.⁽⁹⁰⁾ In this chapter, magneto-sputtering method are used to grow the BFO epitaxial films on STO (001) substrate. Energy Dispersion Spectroscopy (EDS) and X-ray diffraction (XRD) were used to characterize the compositions and structures of these thin films. The results are concluded as the function of deposition parameters like, temperature, pressure, RF power, target-substrate configurations (target-substrate distance and target bending angles) and target compositions. These results give detailed guidance for BFO thin films with sputtering method.

4.2. Synthesis of Rhombohedral like BiFeO₃ (R-like BFO) thin films on STO (001) substrate with sputtering methods.

4.2.1 Introduction to Magneto-Sputtering equipment.

Figure 4.1 (a) schematic graph of a sputtering system;(94) (b) the configuration of sputtering gun with respect of the substrate position

Figure 4.1 (a) shows the schematic graph of a sputtering system. The equipment is a three gun co-sputtering system from SKY Company (P. R. China). The system is composed of two chambers, the main deposition chamber and the loadlock chamber with anti-sputtering cleaning gun. Both chambers are equipped with mechanical and molecular pumps. The Radio Frequency (RF) power supply is the CESAR 136 generator. The vertical position of the sputtering gun can be adjusted in a range of 6.3cm. The 2 inch sputtering gun can also be bended between 0° (vertical) and 60 degree, as shown in Figure 4.1 (b). The maximum temperature for the heater of the system is 850 °C. Ar and O₂ gas flow are controlled by the gas meters with a precision of 0.1Pa. During the deposition, Ar gas is accelerated by high voltage and bombard on the target surface, the target material is then sputtered on to the substrate.

There are both advantage and disadvantage of the sputtering methods in oxide thin

films depositions. The advantages are, for example, environment friendly comparing with the CVD methods.(90) The gas used is only Ar and O₂ for the oxide growth. Comparing with the PLD methods, the sputtering have better reproducibility. Almost every parameter can be controlled precisely and no reproducibility problems from the Laser working gas or lens. Therefore it is easier to control the deposition conditions. The disadvantage of the sputtering methods in oxide thin film deposition is that there may be re-sputtering from the substrate which may influence the surface morphology.(90)

4.2.2 Magneto-sputtering deposition of BiFeO₃ thin films

(a) Target fabrication:

The targets are fabricated by sintering in air at 800 °C. The Bi₂O₃ and Fe₂O₃ powder were firstly grinded and then pressed in 2 inch mould before sintering. The target was sintered for two times, after the first sintering, the target is cracked with a agate pestle in the mortar, grinded and sintered again to increase the target hardness. Organic glue (Fluka Mowiol 20-98) is used to enhance the viscosity of the powders during pressuring process. The target was firstly heated to 300 °C to remove the organic glues. The sintering times are both 8 hours for the first and second high temperature sintering.

(b) Substrates preparation:

The substrates were cleaned by ultrasonic in Acetone, Ethanol and Distilled water subsequently. The backside of the substrate was then pasted to the sample holder with

silver paste to ensure the close contact.

(c) Growth procedure:

The substrate was heated to the target temperature, and then the Ar/O₂ gas was introduced into the main chamber. When the pressure is stable, starts to increase the RF power. When the plasma is stable, we open the target baffle and substrate baffle to start the deposition. It is noted that when increasing or decreasing the RF power, the target may be cracked. Therefore, it is better to adjust the power slowly.

4.3 Basic characterization and parameter optimization of BFO thin films growth

4.3.1 Energy Dispersion Spectroscopy (EDS) and High Resolution X-ray Diffraction (HRXRD) equipments

Energy Dispersion Spectroscopy (EDS) and High Resolution X-ray Diffraction (HRXRD) were used for the basic characterization when optimizing the growing conditions. The equipment used for the EDS measurement is the JEOL (Japan) Scanning Electron Microscopy. The electron accelerating voltage is 20kV. The Bi, M edge and Fe, K edge are used for the analysis. It is well known that the EDS is actually a Semi-quantitative method. Therefore, a standard bulk and a standard thin film sample are used for calibration. The HRXRD are measured with Rikagu (Japan) XRD system with Ge (002)×2 single crystal monochromators. The (001) peak of the STO substrate is at 46.45°. Optical slit of 2mm are used for our BFO samples, this enable that the incident light spot is less than 2mm. The x ray tube is the Cu_{Kα1} with

the wavelength of 1.5405952 Å. The x ray tube is set to 40kV and 30mA. Many sputtering parameters may influence the epitaxial growth of the BiFeO₃ thin films. These include the temperature, pressure, RF power, target composition and target configuration. The detailed evolution of composition and structure are given in following paragraphs. The EDS and HRXRD are complementary in optimizing the growth condition of BFO thin films. That is because, Bi deficient BFO thin film may also be pure phase from the HRXRD results, however the non stoichiometrical samples may be highly conductive.

4.3.2 The influence of temperature, pressure and RF power.

Figure 4.2 The relationship between the Bi/Fe mole ratio of BFO thin films and (a) Deposition pressure; (b) Substrate temperature; (c) O₂ flow; (d) RF power; (e) Target height; (f), (g), Deposition pressure and (h), O₂ flow.

It is indicated in the PLD method that the growth windows for BFO films are very narrow.(91, 93) The EDS results of our BFO films show that the Bi/Fe mole ratio is very sensitive to the growing parameters. As shown in Figure 4.2 (a), when the deposition pressure changes from 0.34 to 4 Pa, the corresponding Bi/Fe mole ratio varies from 0.85 to 1.80. This is consistent with literature.(93) In Figure 4.2 (b), the change of 10 °C in deposition temperature results in a Bi/Fe mole ratio variation of a few percents. Generally, the Bi/Fe mole ratio in thin films will decrease with increasing temperature. However, our results also show that at low temperatures the increase of temperature will firstly increase the content of Bi until 640 °C. Then, the content of Bi begins to decrease. At even higher temperature (above 720°C), the Bi

content increases again. It is learned from literatures that, the optimum substrate temperature is around 680 °C to 700 °C which lie at the decreasing range of the EDS results.(95,96) The increase of RF power will decrease the composition of Bi. However the change is less obvious in Figure 4.2 (d). Through the adjustment of other parameters, for example, increasing the power, or decreasing the target-substrate distance; the Bi/Fe ratio can be decreased while keeping the pressure at the same level. Figure 4.2 (f) and (g) also show the pressure dependence of the Bi/Fe mole ratio. Comparing with the Figure 4.2 (a), the Bi/Fe ratio has been greatly decreased. This is because the samples shown in figure 4.2 (f) are grown at a lower target position (-1cm) while the samples shown in figure 4.2 (a) are grown at higher target position (1cm). From figure 4.2 (e), we already know that the lower target height will decrease the Bi composition. Actually, the samples shown in figure 4.2 (f) are all pure phase BFO samples, the HRXRD results of these samples are shown in figure 4.4 (b). Several series of samples have been grown. The results show that the effects of pressure are robust and are irrelevant with other parameters except that the increase of Bi/Fe mole ratio become less obvious at higher pressures. In addition, the growing parameters for figure 4.2 (c) are 680 °C; RF power 70 W; target position, 0.5cm; total pressure 3.2 Pa . The growing parameters for the figure 4.2 (f) are: 680 °C; RF power, 40 W; target position, -0.5cm; total pressure 1.5 Pa. This is why the Bi/Fe mole ratio in figure 4.2 (h) are much small than in figure 4.2 (c).

In addition to the total pressure, the O₂/Ar flow ratio will also influence the Bi/Fe ratio. Figure 4.2(c) and Figure 4.2 (h) shows that the effect from change of O₂ flow on

the mole ratio can almost be negligible compared with the total pressure. Therefore, higher O₂/Ar flow ratio and lower total pressure can be used to increase the O₂ partial pressure. Besides, the target position which represents the target-substrate distance also provides another way for adjusting the mole ratio, as shown in Figure 4.2 (e).

Figure 4.3 HRXRD results of BFO thin films grown at different temperatures a); grown with different substrate-target distance b); grown at different RF powers c).

It is noticed from the EDS results that the Bi/Fe mole ratio is sensitive to almost every parameters of the sputtering equipment. However, it is found that the epitaxial BFO thin films can be fabricated even if the film is Bi deficient.(93) As shown in Figure 4.3 (a), when other conditions are the same and the growing temperature change from 550°C to 640°C, only peaks from BFO are observed in the HRXRD results. These correspond to the samples shown in Figure 4.2 (b). Similarly, Figure 4.3 (b) show that with Bi/Fe mole ratio changing from 0.87 to 0.75, the grown film is still pure phase. This is consistent with PLD growth of BFO thin film where the Bi deficient up to fifty percent can still sustain the pure phase growth.(93) Figure 4.3(c) shows the HRXRD results of samples in Figure 4.2(d) with Bi/Fe mole ratio changing from almost 1 to 0.97. The four samples are all pure phase since the RF power have minor effect on the Bi/Fe mole ratio. Actually, the FWHM of these four samples keep increasing with enhanced power which indicate that the temperature of 640°C is not

enough to sustain high rate growth, the adatoms have not enough time to diffuse on the surface.

All the EDS and HRXRD results shown above indicate that pure phase BFO thin film can be fabricated at a wide range of temperatures. It is also found that, at higher temperatures (700 °C), the increase of pressure will results in the formation of BiO_x. As shown in Figure 4.4, when other conditions are the same, the HRXRD results shown in figure 4.4 (a) are sample grown at 700 °C. BiO_x peaks can be observed at higher pressure. However, for the samples grown at 580 °C no BiO_x peaks can be observed even at 3.2 Pa, figure 4.4 (b).

Figure 4.4 HRXRD results of BFO grown at 700 °C (a), and at 580 °C (b) respectively.

Based on above principles, the optimized growth conditions can be decided depending on the requirement. Firstly, higher temperature (above 680 °C) is helpful in growing high quality thin films. Second, further increase of temperature will in favor of the formation of BiO_x . Lower pressure or higher power must be used to keep the right Bi/Fe ratio. Therefore, it is a contradiction to increase the deposition pressure and improve the crystal quality simultaneously. Actually with Bi rich target which is often used in literatures,(97-99) even if all the other parameters are adjusted to limited values that demonstrate minimum Bi composition (minimum target-substrate, higher power), pure phase BFO can only be grown at very low pressure, 0.2 or 0.1 Pa. Because of the high oxygen deficient, the sample is very leaky. Therefore, the Bi deficient targets are used in our sputtering system.

With the Bi/Fe mole ratio equal to 1/1.2, the optimized growth conditions are decided to be at around 700 °C. For the purpose of electric transport measurement, the sample can be grown at 1 Pa. Higher temperature will greatly reduce the pressure that is necessary to avoid BiO_x phase. The P-E loop of the optimized sample is shown in Figure 4.5 (a).

Figure 4.5 (a) electric polarization of BFO sample grown at 680°C; (b) the AFM results for the same sample as in (a); (c) HRXRD results of the sample grown at 740 °C (d), the AFM morphology results of the same sample as in figure (c).

The Atomic Force Microscope (AFM) used in our experiment is the Asylum Research MFP-3D. The morphology graph were measured in tapping mode with scanning size of 5 μ m by 5 μ m, the Piezoresponse Force microscope (PFM) results was recorded at the same area of the morphology results. The measurements are carried out in contact mode with Pt/Ti coated tips. The force constant of the tip is around 2-5 N/m. An AC voltage with peak of 4V and frequency of 10 kHz is applied to the tip. The amplitude and phase of the AC voltage are then recorded by the lock in amplifier.

Although the best P-E loop is observed at 680°C, the film surface for our sample is not the best at this temperature, as shown in Figure 4.5 (b). The surface roughness is around 3nm. When increasing the temperature to 740 °C. The pressure needed to obtain pure phase BFO decreased to 0.2Pa, as shown in Figure 4.5 (c) and (d). The sample roughness can reach below 1nm. The surface shows step bunching like morphology.

4.3.3 The influence of Bi highly deficient target and target bending angles.

4.3.3.1 Bi highly deficient target

For the deposition of BFO thin films, stoichiometric target are not necessary. Target with more Bi are most often used to compensate for the Bi evaporations. However, in our sputtering system, if the Bi rich target is used, the pure phase BFO films can only be synthesized at very low pressure. As shown above, the Bi/Fe mole ratio increases with deposition pressure very quickly. At certain conditions, (high temperature or low power) the pressure needed to fabricate pure phase BFO can reach as low as 0.1 Pa which is the minimum limit of our equipment. In order to increase the oxygen pressure to a tunable range, the target composition of 1/1.2 was used, as shown in above paragraphs. We further decreased the Bi content in the target. The Bi highly deficient targets with Bi/Fe equal to 1/1.5 and 1/2 were tried. Both EDS and HRXRD were measured for the samples fabricated with 1/2 target. The results for a series of samples grown at 660 °C are shown in Figure 4.6 (a). The Bi/Fe mole ratio increases

with increasing pressure. This is similar with the 1/1.2 target. As shown in Figure 4.6 (b), at higher pressure, there is no evidence of any other peak except the substrate STO (001) peaks. This is probably because of the films deposited on the substrate are too thin or totally amorphous.

Figure 4.6 (a) Pressure dependence of the BFO thin films grown with Bi highly deficient target at 660 °C; (b), HRXRD results of samples grown at 0.3 Pa, 0.5 Pa, 1.5 Pa and 2.5 Pa.

If increase the temperatures to 700 °C, shown in Figure 4.7 (a). There is no much improvement. However if increasing the power to 50 W, pure phase BFO can be

synthesized at 0.5 Pa, Figure 4.7 (b). We have also lowered the temperature to 620 °C.

At 620 °C, pure phase BFO can be fabrication up to 1 Pa, Figure 4.8.

Figure 4.7, HRXRD results of BFO thin films grown at 700 °C; (a) 25W (b) 50W

Figure 4.8 HRXRD results of BFO thin film grown on STO (001) substrate at 620°

C.

The above results indicate that, with the Bi highly deficient target, the pure phase BFO films can also be fabricated. However, the RF power has to be increased to get the pure phase BFO. Furthermore, the suitable deposition pressure range was not dramatically increase, still around 1Pa. Therefore, a Bi/Fe mole ratio of around 1/1.2 might be most suitable for our sputtering system.

4.3.3.2 The effect of Target-bending angle

As mentioned above, the sputtering gun in our system can move vertically and bend toward the substrate from 0° to maximum 60°, as shown in Figure 4.1 (b). All of the above results are at 40°. In addition, we have tried to grow the BFO thin films at 0° and 60°. The results show that, if the other parameters are adjusted accordingly, pure phase epitaxial BFO thin films can be fabricated at both bending angles. As shown in Figure 4.9 (a), pure phase epitaxial BFO can be fabricated at 0° configuration. (with

1/1.5 target and at low pressure and high power). Therefore we conclude that the bending angle might be not vital for the phase formation but might be important for the roughness and defects. As the pressure increase to 0.5Pa, the BiO_x impurity begin to appear which is consistent with the basic principle of BFO growth, Figure 4.9 (b). And if the target is changed to Bi/Fe equal to 1/2, as shown in Figure 4.9 (c), pure phase BFO can also be obtained at 0.5 Pa.

Figure 4.9 HRXRD results of samples grown at zero degree bending angle (a) grow at 50 W and 70 W.; (b) grown at 0.2 Pa and 0.5 Pa; (c) with mole ratio of Bi/Fe = 1/2 target.

Finally, very surprisingly, T like phase BFO are found on STO (001) substrate when growing with 60° bending angle. These results will be shown in Chapter 6.

4.4 Conclusion

Many parameters are varied to find the optimized conditions for the growth of BFO thin films. The EDS and HRXRD are used to characterize the thin films. Detailed principles for these parameters are given. It is found that the target composition, pressure and temperature are the three key factors in the growth. It is noticed that for a special equipment setup, the target composition is vital in high quality thin films growth.

Chapter Five

Dielectric properties of the Rhombohedral like (R like) BiFeO₃ thin films

5.1 Introduction

The conductivity of both BFO bulk (polycrystal and single crystal) have been greatly improved since the year 2000. With the development of modern technology in thin film growth it is possible to grow insulating BFO thin films. Therefore intrinsic ferroelectric polarizations can be measured on BFO thin films. On the other hand, the dielectric properties of BFO are still scarce, especially with the higher resistive samples. Giant dielectric constant ($\sim 10^4$) was also observed in BFO polycrystalline samples. A In/BFO/LSMO capacitor showed obvious large dielectric constant. (36),(37) In both case the large values can be attributed to hopping electrons at the electrode interface and grain boundaries.(38) These literatures remind us of many other large dielectric materials like CaCu₃Ti₄O₁₂, LuFe₂O₄, LaMnO₃ *et al.* In literatures and our previous results, it is shown that both giant dielectric constant and magnetocapacitance can be attributed to the interfacial effects in leaky oxide.(39-41),(42) Therefore, although the leakage current can be suppressed in fabricated BFO thin films dramatically,(18, 28, 43) one should still be careful about the conclusions deduced from the dielectric results.

In addition, although BFO is the most popular multiferroic material, the coupling between dielectric and magnetic property have rarely been demonstrated. Recently, several phase transitions at low temperatures have been reported for BFO.(45-49) The dielectric measurements based on BFO bulk materials have revealed that the elastic and dielectric anomalies at low temperature may be related to these transitions.(50) However, the origin of these transitions is far from clear. The electrical equivalent circuit fitting has been utilized to investigate the impedance spectroscopy (IS) of epitaxial BFO thin films above room temperature.(41) The situation at low temperature is still not clear. Therefore, in our research, the dielectric property of epitaxial BFO is measured from 300 K to 10K. The origins of the dielectric anomalies are clarified with equivalent circuit fitting. The results show that the dielectric anomalies at low temperature might be misleading for phase transition analysis if no electric circuit fitting is used. Furthermore, the physical significances of the Constant Phase Element (CPE) and the related capacitor conversion method are discussed based on the results at different temperatures.

5.2 Basic characterization of the BFO thin films.

As shown in chapter three, the conductance of the sample shows great influence on the dielectric response, because the interfacial effects may dominate in the leaky samples.(38) Therefore, care was taken to optimize the growth condition for samples that can sustain large enough electric field and show intrinsic ferroelectric behaviors. Two BFO epitaxial thin films named sample (A) and sample (B) are deposited on

Nb:STO (100) conductive substrates by magnetron sputtering at 680°C from a Bi deficient BFO target (Bi/Fe = 1/1.2). Details for synthesis and characterization are shown in Chapter three and four. The thicknesses of sample (A) and sample (B) were estimated to be 400nm and 140nm respectively by scanning electron microscopy (SEM) and high resolution x-ray reflectometry (XRR) methods. As shown in Figure. 5.1, the sample (A) used in the dielectric measurement shows only the (100) peaks with a full width at half maximum (FWHM) of about 0.5 degree. The ferroelectric hysteresis loops showed in Figure 5.2 indicate intrinsic ferroelectric hysteresis loops. The polarization can reach more than $70\mu\text{C}/\text{cm}^2$. The loops are not rectangles which indicate larger leaky current at high electric fields.(100-104) The horizontal shift of the polarization loops are due to asymmetric electrodes. The ferroelectric loops indicate the insulating character of the thin film.

Figure 5.1 HRXRD results of the epitaxial BiFeO₃ thin films. Full width at half maximum of the rocking curves is 0.5 degree.

Figure 5.2. Ferroelectric polarization of sample (A) measured at 1kHz.

5.3 Dielectric Properties of BFO thin films

5.3.1 Dielectric measurements

Figure 5.3. (a) Schematic diagram of the measuring setup and (b) Schematic diagram of the fitting model; R, the resistance. C, the capacitance. CPE, the constant phase element. G_{DC} , the conductance in parallel with the constant phase element.

The dielectric properties of BFO capacitors were measured with two-point method by an Agilent E4980a LCR meter in the frequency range of 20 to 2M Hz. The electric field used is about 10kV/cm which is much smaller than the coercive field of BFO ($\sim 100\text{kV/cm}$).⁽¹⁰⁵⁻¹⁰⁷⁾ The Pt top electrodes ($30\mu\text{m} \times 30\mu\text{m}$) were fabricated on the film surface by lithography and Pulses Laser Deposition (PLD). The electrodes are then connected to the coaxial cable with wire binding (Al-wire). The experimental setup is shown schematically in Figure. 5.3a.

5.2.2. Impedance spectroscopy at low temperatures.

Figure 5.4. Temperature dependence of (a) the measured capacitance and (b) dielectric loss tangent of sample A at selected frequencies of 1kHz, 5kHz, 10kHz, 50kHz, 100kHz and 500kHz. (c) temperature dependence of the measured capacitance

and (d) dielectric loss tangent at 1kHz (solid lines). Fitted results (square dots, black); the calculated results without R1-C1 (triangular dots); calculated results without CPE2-G2 (circular dots).

Figure 5.4a shows the temperature dependence of the AC capacitance at frequencies of 1k, 5k, 10k, 50k, 100k and 500k Hz. The measured capacitances keep decreasing gradually when decreasing temperature. As shown in Figure 5.4a, the decrease of capacitances are not linear, but with slope changes at certain temperatures. These changes in slopes, together with peaks in dielectric loss can be viewed as dielectrics anomalies. According to the Kramers-Kronig relations, anomaly in the capacitance will result in anomaly in the dielectric loss tangent.^(108,109) As demonstrated in Figure 5.4b, there are two peaks in the temperature dependent dielectric loss tangent at lower frequencies. The loss tangent can be smaller than 1 at room temperature with frequency higher than 1kHz. Small dielectric loss tangent also indicates that the sample used is insulating.⁽¹¹⁰⁾

Similar slope changes with this temperature range have been reported in both single crystalline and polycrystalline BFO. They are related to the ferroelastic phase transitions at low temperature.⁽⁵⁰⁾ Many other literatures have connected the anomaly in capacitance with certain phase transitions.^(108, 111-123) In the field of multiferroics, for example, the anomalies were often accompanied by antiferromagnetic transition,^(111, 121, 124-126) domain formation,⁽¹²⁷⁾ phase transition near the morphotropic phase boundary (MPB)^(128, 129) and many other magnetic phase transitions.^(114, 118, 119, 125, 130) However, many of these designations are in lack of detailed

analysis.

Figure 5.5. Frequency dependence of (a) the real part and (b) imaginary part of the complex impedance at 300K; the measured data (Dotted curve) ; CPE1-G1(green), R1-C1(blue) and R2-C2(cyan); Frequency dependence of (c) the capacitance and (d) the dielectric loss tangent calculated with fitting parameters from different components at 300K;

In order to recognize these anomalies, electrical circuits based curve fittings are carried out at every measured temperatures. The equivalent circuit used for the fitting is shown in Figure 5.1(b). At the first try of our fittings, many distributed components and their combinations are used. However, it is soon found out that the CPE model is necessary to fit the main feature of the measured results. Figure 5.5a and 5.5b show the dielectric response in impedance representations at 300K. In these graphs, the black dotted curve represents measured results. The solid curves (in red, blue and

purple) are contributions from different components which are calculated individually from the fitting parameters. These results show that the response from CPE1-G1 alone can already represent the main feature of the measured data. The discrepancy between the calculated response of CPE1-G1 and the measured Z' can be improved by the introduction of R1-C1 and R2-C2. We have also tried to include another CPE-G to replace any of these R-Cs. However, the results indicate that it is not necessary because the parameter n turns out to be 1 and the CPE is degenerated to a pure capacitance. The measured imaginary part of the impedance shows even smaller difference with the CPE1-G1.(110)

The impedance data can be transferred to many other forms, for example, the dielectric-loss tangent or the Module. The purpose of this is usually to show different components in a more straightforward way. In the results shown above (Figure 5.5.a and 5.5 (b) , if the impedance are translated to the dielectric constant and loss tangent (Figure 5.5c and 5.5d), the necessity to include R1-C1 and R2-C2 will becomes more obvious. As shown in Figure 5.5(c) and 5.5(d), the dotted curve labeled CPE1-G1+R1-C1+R2-C2 is the fitted results of the data at 300K which matches the measured data (solid line) quite well. The dotted curves labeled as CPE1-G1+R1-C1 and CPE1-G1 represent the calculated results from two and one component respectively. The measured capacitance show obvious discrepancy with the calculated results without R1-C1 and R2-C2, Figure 5.5(c). The dielectric loss tangent of CPE1-G1 is in reverse proportional with frequency. Therefore, R1-C1 and R2-C2 must be included in the model to fit the two dielectric loss peaks. It is demonstrated in

chapter three that two simple R-C components in series (Maxwell-Wagner type relaxation) can results in dielectric loss response that can be separated into the conductivity term (be reverse proportional to frequency) and the Debye term (characterized with dielectric maxmum.)(75) P. Lunkenheimer shows that the UDR model in series with an R-C can also generate similar response in dielectric loss tangent.(39) Therefore, the dielectric loss tangent indicate the existence of three different components at 300K.(76)

Figure 5.6.Frequency dependent of (a) capacitance and (b) dielectric loss tangent of sample A at temperatures between 300K and 70K. (c) the dielectric loss tangent calculated with fitting parameters from different components at 210K; (a) and (b) share the same legend.

When the temperature decrease, the dielectric constant and dielectric loss peaks change gradually with temperatures. Figure 5.6a and 5.6b show the frequency dependence of the dielectric response at several selected temperatures. The dotted lines indicate the measured data while the solid lines represent the fitted results. Above 210K, the model composed of three components can fit both the real and imaginary part perfectly. Furthermore, no simpler model can fit the feature of two dielectric loss peaks. The number of parameters is seven and the number of point in frequency range is fifty three which is much larger than the degree of freedom, six. The ratio of the number of freedom to the number of data point is comparable with in literatures.(39, 42, 131) At temperatures below 210K, the number of parameters increased by 3 because of the introduction of CPE2-G2. It is necessary to add this component in the fittings at lower temperatures because the third dielectric loss peak begins to appear at 210K. As shown in figure 5.6c, another dielectric loss peak is observed between the peak introduced by R1-C1 and R2-C2. Both simple R-C and CPE-G components have also been tried to fit the new relaxation at lower temperature. However, only CPE-G can give good fittings. A further examination shows that an inductor (L_0) in series with the CPE-G is necessary to represent the dielectric increase at high frequencies and low temperatures. The inductance comes from the contact leads. The capacitance of the experimental setup is below $5 \times 10^{-14} \text{F}$ which is much smaller than the minimum measured value in our results.(110)

Figure 5.7. Thickness dependence of the capacitance converted from the (a) CPE1-G1 unit and (b) capacitance of C1 and C2 for sample A (S-A) and sample B (S-B).

The above results shows that the 3 components model shown in Figure 5.1 (b) can fit our experiment successfully. However, the fitting did not show whether these components represent the BFO film or the interface. Besides, both ideal R-C and the CPE-G unit can be used to represent the interfacial component.(41) In order to distinguish the origin of different components, we measured dielectric response of the

sample B with different thicknesses at 300K. The capacitances of sample B are measured in both single and double capacitance, as shown in Figure. 5.1a. The current path of double capacitor includes two Pt-BFO interfaces, 2×140 nm BFO thin films and two BFO/Nb:STO interfaces. Therefore we can compare the fitting parameters with effective thickness of 140nm, 280nm and 400nm. The capacitances of the CPE-G ($C_{\text{converted}}$) are converted from the fitted parameters with a conventional method that is often used in the field of corrosion(132) and have been recently introduced to multiferroic thin films. The results shown in Figure 5.7a and 5.7b indicates that the capacitance converted from CPE1-G1 can be scaled with the thin films thickness. Therefore we attribute the CPE1-G1 to the thin film. Because $C = \epsilon_0 \cdot \epsilon_r \cdot \frac{A}{d}$, with A and d represent the electrode area and thin film thickness, the capacitance scales with sample geometry. In addition, different capacitors with the same thickness of 140nm in samples B were tested. The derived CPE capacitance can also be scaled with film thickness, as shown in Figure. 5.7(a). The derived capacitances do not precisely follow 1/d probably because there are conductive defects in the sample and the effective sample thickness may be a little different from the measured. The capacitances of R1-C1 and R2-C2 are comparable in Figure. 5.7(b). The results show that the capacitances in double capacitors of sample B are one half that of the single capacitor in both sample A and sample B and are independent of the film thickness. This is reasonable if they are attributed to the electrode interfaces, because there are two more interfaces for double capacitors. Two R-Cs are needed to model the interface effects probably because of the asymmetrical

electrodes.(110)

Table 5.1 Equivalent circuit fitting parameters for sample A at different temperatures with 95 % confidence intervals.(110)

Parameters	300k	250k	200k	170k	120k	70k
$A'_0 -1(s^n/\Omega)$	2.52283×10^{-11}	1.96478×10^{-11}	1.4022×10^{-11}	1.1427×10^{-11}	9.25791×10^{-12}	9.40417×10^{-12}
	$\pm 7.91919 \times 10^{-14}$	$\pm 3.73137 \times 10^{-14}$	$\pm 1.32213 \times 10^{-14}$	$\pm 1.96225 \times 10^{-14}$	$\pm 2.51291 \times 10^{-12}$	$\pm 9.61308 \times 10^{-13}$
$G_{DC} -1(1/\Omega)$	4.68849×10^{-8}	5.22814×10^{-9}	3.60172×10^{-10}	6.73036×10^{-11}	1.8239×10^{-17}	3.64539×10^{-10}
	$\pm 6.68875 \times 10^{-11}$	$\pm 7.1507 \times 10^{-12}$	$\pm 7.52798 \times 10^{-13}$	$\pm 1.34689 \times 10^{-12}$	$\pm 4.08915 \times 10^{-11}$	$\pm 1.01726 \times 10^{-10}$
n_1	0.93386±	0.94152	0.9614	0.97318	0.99257	1
	3.02009×10^{-4}	$\pm 2.23082 \times 10^{-4}$	$\pm 1.56222 \times 10^{-4}$	$\pm 2.25545 \times 10^{-4}$	± 0.00208	± 0.00803
$1/R_1 (1/\Omega)$	8.30207×10^{-5}	1.03828×10^{-5}	2.57048×10^{-7}	4.69926×10^{-8}	2.21529×10^{-9}	0
	$\pm 1.87818 \times 10^{-6}$	$\pm 2.45223 \times 10^{-7}$	$\pm 1.77869 \times 10^{-9}$	$\pm 1.07859 \times 10^{-9}$	$\pm 4.6977 \times 10^{-9}$	$\pm 3.29395 \times 10^{-10}$
$C_1/\epsilon_0(m)$	1267.00558	1744.1927	1119.94963	1282.86611	624.08539	87.64713
	± 19.87211	± 31.41825	± 7.16751	± 15.82284	± 856.23773	± 73.61639
$1/R_2 (1/\Omega)$	4.55756×10^{-4}	3.60133×10^{-4}	1.89409×10^{-4}	1.60393×10^{-4}	1.07445×10^{-4}	2.7154×10^{-5}
	$\pm 8.65729 \times 10^{-6}$	$\pm 5.00818 \times 10^{-6}$	$\pm 1.1715 \times 10^{-6}$	$\pm 1.14579 \times 10^{-6}$	$\pm 2.14071 \times 10^{-5}$	$\pm 2.50711 \times 10^{-6}$
$C_2/\epsilon_0(m)$	786.2611	859.66593	496.25695	470.22055	463.73445	133.61601
	± 9.10495	± 9.33391	± 2.91288	± 4.06753	± 111.69308	± 17.92593
$A'_0 -2(s^n/\Omega)$	N.A.	N.A.	4.11808×10^{-10}	8.96862×10^{-10}	5.36868×10^{-10}	2.2574×10^{-10}
			$\pm 6.91435 \times 10^{-11}$	$\pm 5.988 \times 10^{-11}$	$\pm 7.44948 \times 10^{-11}$	$\pm 2.27359 \times 10^{-11}$
$G_{DC} -2 (1/\Omega)$	N.A.	N.A.	8.69032×10^{-5}	1.96361×10^{-5}	1.43431×10^{-6}	1.55917×10^{-7}

			$\pm 4.71609 \times 10^{-6}$	$\pm 9.27084 \times 10^{-7}$	$\pm 3.53751 \times 10^{-7}$	$\pm 3.10532 \times 10^{-8}$
n_2	N.A.	N.A.	0.98193	0.86637	0.82817	0.78854
			± 0.01441	± 0.00563	± 0.00784	± 0.00621
$\epsilon_{\text{Converted}}$	449.85875	490.94744	540.2337	518.14978	563.03687	470.20871

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$$

Comparing the dielectric results of the two samples, we can conclude that the CPE based models can fit the measured result perfectly. As temperature decreases, a weak peak in dielectric loss appears and this feature cannot be fitted unless another component (CPE2-G2) is included in the model, as shown in Figure 5.1b. The fitting results of sample A and the corresponding confidence intervals (CI) are shown in table 5.1. A'_0 , G_{DC} and n are parameters of the CPEs. G_{DC} is the conductance in parallel with the CPEs. The parameters R_1 , R_2 and C_1 , C_2 represent the resistance and capacitance of the interface. The CI values are calculated from the fitted standard error (SE) of the fitting results within 95% precision. At higher temperature, the CI values are much smaller than the fitted parameters which indicate the uniqueness of these parameters. At low temperature the CI value becomes larger because of small dielectric response. It is noticed that the parameter n of CPE2 decreases when lowering temperatures. This is contrary to that of the CPE1. The conductance of the CPE2 is much smaller than that of CPE1, which indicates the formation of another region in the sample that is more conductive. The dielectric constants ($\epsilon_{\text{Converted}}$)

determined from the converted capacitance ($C_{\text{converted}}$) are larger than 400 even at low temperatures. As stated above, there are several possibilities that may cause the observed dielectric anomalies at this temperature for BFO. The fitting results reveal more information of the transition on the conductivity and inhomogeneities.(110)

5.3.3. Dielectric anomalies and Phase transition at low temperatures

With all these fitting parameters mentioned above, the dielectric response of any component or their combinations can be calculated at different temperatures. As an example the results at 1kHz are shown in Figure 5.4 (c) and 5.4 (d). The solid lines (black) represent the measured results while the square dots (black) represent the fitted results. The results fit well in the whole temperature range. There are two obvious dielectric loss peaks at around 70K and 210K, figure 5.4 (d). However, the calculated capacitance without the contribution from R1-C1 (triangular dots, blue) shows obvious discrepancy with the measured data below 210K. Accordingly, the dielectric loss peak at 210K disappears without the contribution of R1-C1. Similarly the CPE2-G2 (circles dots, red) are responsible for the dielectric loss peak at around 75K. It should be noticed that, although the CPE2-G2 is introduced to the fitting at 210K, the observable responses manifest themselves at much lower temperature. The capacitance calculated without CPE2-G2 only shows small discrepancy below 120K. The interfacial effects are responsible for the slope changes and the corresponding dielectric loss around 210K. This further indicates that the dielectric anomalies cannot be related to the phase transition directly. The equivalent circuit based curve fitting is

necessary to eliminate the extrinsic effects.(110)

5.3.4. Physical significance of the CPE parameters

The CPE have been widely used in the IS fittings in many different systems to get a better fit of the non-Debye like dielectric responses. Several different relations between the exponent n and the fractal dimension have been proposed with the CPE representing electrode interface.(133-136) The uses of CPE to represent the perovskite are reviewed recently in which the origin of exponent n is also believed to be the inhomogeneities in the system.(82, 137) In the case of ferroelectric materials the inhomogeneities may come from the domains. Similar to the situations in electrodes, there are also fractal dimensions and topological defects in the BFO thin films.(138, 139) Therefore it is nature to find CPE like behavior in the multi domain BFO thin films.

Furthermore, it should be noticed that there are actually two different forms of CPE expressions which are widely used in literatures. The common way that are often used in many commercial softwares do not include the G_{DC} in the CPE. (41) The admittance is as follows, $Y_{CPE} = A_0(j \cdot \omega)^n = A_0 \cdot \omega^n \cdot [\cos(n \cdot \pi/2) + j \cdot \sin(n \cdot \pi/2)]$. The second formula includes the G_{DC} into the CPE formula and the new expression of CPE becomes $Y_{CPE} = G_{DC}^{(1-n)} \cdot (A'_0)^n \cdot (j \cdot \omega)^n = G_{DC}^{(1-n)} \cdot (A'_0)^n \cdot \omega^n \cdot [\cos(n \cdot \pi/2) + j \cdot \sin(n \cdot \pi/2)]$. The parameter A'_0 is related to the previous parameter A_0 by $A_0 = (A'_0)^n / G_{DC}^{n-1}$.

In the case that the CPE-G represent the electrode interface, the second expression is believed to be more reasonable because the capacitance is closely related to the

charge transfer.(140) Schmidt first introduced the conversion method to multiferroic BFO and BMO thin films in which the CPE-G unit represent the thin films property.(41) But the necessities to use the second expression in the conversion methods are not clarified. In the following paragraph, we compare the fitting parameters in detail and give more evidence on the physical meaning of the second expression of CPE.(110)

Figure 5.8. The calculated impedance from the parameters at 300k with $G_{DC}=4.68849 \times 10^{-8}$, $A'_0=2.52283 \times 10^{-11}$ and n values between 0.1 to 1. real part (a); imaginary part (b).

Firstly, in order to convert the three CPE parameters to an idea capacitance, as what we did above, the second expression of the CPE have to be used.(140) When the G_{DC} is included in the CPE formula, the impedance of the CPE-G becomes

$$Z_{CPEG} = 1/[G_{DC} + G_{DC}^{(1-n)} \cdot (A'_0)^n \cdot (j \cdot \omega)^n] = 1/[G_{DC} + G_{DC}^{(1-n)} \cdot (A'_0)^n \cdot \omega^n \cdot [\cos(n\pi/2) + j \cdot \sin(n\pi/2)]]$$

The real (Z') and imaginary (Z'') part of the complex impedance can be separated. It is derived that the frequency at which the Z'' reach its maximum is independent of n and $\omega_{max} = G_{DC} / A'_0$.(132) The real part of the impedance is a constant for different n values at this frequency. Figure 5.8a and 5.8b demonstrate the calculated results from the fitting parameters at 300K with $G_{DC} = 4.68849 \times 10^{-8}$ and $A'_0 = 2.52283 \times 10^{-11}$. For different n values the $Z'' - \omega$ plots peak at the same ω_{max} and the corresponding $Z' - \omega$ intersect at this frequency with its conductance equal to half the G_{DC} . The converted capacitance is calculated through $C = A'_0 \cdot (\omega_{max})^{n-1}$. But for the first expression $\omega_{max}^n = G_{DC} / A_0$, the ω_{max} is frequency dependent. Therefore the conversion can only be carried out with the second expression. From these theoretical analyses, it is noticed that the effect of n can be separated from that of parameter G_{DC} and A'_0 . The conversion method actually provide a way to compare the dielectric properties of capacitors with different inhomogeneous. In the early work of A. K. Jonscher, the

$$G'_{AC} = A_0 \cdot \cos(n \cdot \pi/2) \cdot \omega^n = (A'_0)^n / G_{DC}^{n-1} \cdot \cos(n \cdot \pi/2) \cdot \omega^n = A'_0 \cdot (\omega_{Max})^{n-1} \cdot \cos(n \cdot \pi/2) \cdot \omega^n$$

is considered as the frequency dependent ac conductance which is certainly thickness dependent.(81) Therefore, both parameter A'_0 and $C_{converted}$ scales with sample thickness because $C_{converted} = A'_0 \cdot (\omega_{max}')^{n-1}$. In our results shown in Figure 5.7a, the

converted capacitances can be scaled with sample thickness because the ac conductivities of different capacitors are almost the same. Besides, $\omega_{\max} = G_{\text{DC}} / A'_0$, both dc and ac conductivities are fixed values in the sample. Therefore the $C_{\text{converted}}$ is only decided by the sample geometry.

Figure 5.9. The electric field dependence of (a) the capacitance and (b) dielectric loss tangent. Inset of (a) enlarged part of the electric field dependent capacitance.

Table 5.2 Equivalent circuit fitting parameters for electric field dependent dielectric response of sample A at 290k.

Parameters	0.5KV/cm	1 KV/cm	5 KV/cm	10 KV/cm	20 KV/cm
$A'_0 - 1$ (s^n/Ω)	2.44099×10^{-11}	2.48251×10^{-11}	2.97553×10^{-11}	3.4524×10^{-11}	3.38566×10^{-11}
$G_{DC} - 1$ ($1/\Omega$)	2.27885×10^{-9}	2.06226×10^{-9}	3.1162×10^{-9}	5.6346×10^{-9}	1.71868×10^{-8}
n_1	0.9003	0.8992	0.88986	0.88332	0.88424
$1/R_1$ ($1/\Omega$)	7.45333×10^{-7}	6.74381×10^{-7}	4.50605×10^{-7}	3.35854×10^{-7}	5.26999×10^{-7}
C_1/ϵ_0 (m)	255.718	253.93932	247.11305	232.01168	202.80115
$1/R_2$ ($1/\Omega$)	1.04063×10^{-5}	9.75473×10^{-6}	6.3855×10^{-6}	4.63614×10^{-6}	7.83045×10^{-6}
C_2/ϵ_0 (m)	319.93687	315.57112	280.14143	247.67219	276.6182
$C_{Converted}$ (F)	9.37332×10^{-12}	9.6672×10^{-12}	9.96518×10^{-12}	9.58691×10^{-12}	9.03983×10^{-12}

$$\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$$

In order to further validate the use of $C_{converted}$, we measured the electric field dependent impedance between 0.5kV and 20kV on sample A in the same capacitor at 290K, as shown in Figure 5.9a and 5.9b. The dielectric loss at low frequency increases dramatically with increasing electric fields. This is because the G_{DC} almost increased one magnitude with electric field, as shown in table 5.2. The inset of Figure 5.9a indicate that the measured capacitance also increase with electric field. This is consistent with the results of the dielectric nonlinearity in epitaxial BFO films.(105)

The other parameters also vary systematically with increasing electric field. However, the converted capacitances almost do not change with electric fields. The observed dielectric nonlinearity and the increase in dielectric loss tangent show that it is more

reasonable to include the parameter G_{DC} into CPE, because the conductance increases with electric field.(110)

5.4. Conclusion

We report the detailed study on the low temperature dielectric dynamics of the epitaxial BiFeO_3 thin films grown on Nb-doped SrTiO_3 substrate. The results indicate that, although the dielectric responses of our ferroelectric micro-capacitors come from both the thin film and the electrode interface, the contributions from the thin film dominate the dielectric response. The origins of the low temperature dielectric anomalies are investigated with electric circuit fittings. Although obvious dielectric anomalies are observed, they are not attributed to phase transition directly. Our fittings indicate that the interfacial effects can strongly influence dielectric response in temperature scale. A possible phase transition at 210K is revealed from analysis with dielectric loss tangent. The dielectric constants derived from the constant phase elements (CPEs) are more than 400 even at low temperatures. The physical significances of the CPE model are discussed.(110)

Chapter Six

Sputtering growth of T like phase on the STO and LAO (001) substrate

6.1 Introduction

The R like BiFeO_3 (BFO) thin film has demonstrated exciting properties in the mutual manipulation of electric and magnetic field. Recently, the c axis elongated BFO thin films have been discovered as the first large c/a ratio perovskite that shows larger ferroelectric property and further more obvious ferroelastic effects.(141) In the earlier literatures, this phase is named as tetragonal phase (T phase).(142) Later, it is found that the real symmetry of T phase is monoclinic.(143, 144) Furthermore, the so called bulk-like BFO thin films are also monoclinically distorted rhombohedral.(144, 145) Therefore, the R-like phase is used to represent the bulk-like BFO and the T-like phase to represent the c axis elongated phase in this thesis.(144) Although large polarizations are predicted for larger c/a ratio PbVO_3 and BiCoO_3 through first principles calculations,(146) only in BFO, ferroelectric polarizations have been observed. Since the discovery of T-like phase BFO in 2009.(142) The material has shown many useful characteristics. Recently, giant polarization values ($150 \mu\text{C}/\text{cm}^2$) have been observed in T-like BFO thin films as predicted by firstly principle calculations.(141) Large electric mechanical effects (5%) have been observed in mixed phase (T-like and R-like phase) BFO thin films.(147) Furthermore, the reduced

Néel temperature (~ 380 K) add more flexibility in the control of magnetic degree of freedom.(148)

Although the c lattice elongated BFO has shown superior property comparing with the R-like phase, the growth dynamics are still not fully understood. The c lattice elongated samples were initially fabricated through high temperature and high pressure methods.(149-151) Later, it was found that this phase can be stabilized through strains from the substrate, just like the conditions in PbVO_3 and BCoO_3 .(141) In the case of BFO, the T-like phase was believed to be induced by the smaller in-plane mismatch between T-like phase BFO ($a, b \sim 3.7 \text{ \AA}$) and LAO ($a \sim 3.79 \text{ \AA}$). (142) We noticed that most of the growing conditions of the T-like BFO are at temperatures higher than 680°C .(141, 143, 147, 152-155) As the thickness increases, R-like phase will begin to appear because of strain relaxations and then mixed phased BFO are formed. Because of the relative small surface roughness, the AFM topo-graphs show clearly the saw-tooth like morphology of the mixed phase area.(142) On the other hand, it was reported in a recent papers that large growth rate can induce the T-like phase transition in epitaxial BiFeO_3 thin films and form mixed phase BFO on STO (001) substrate.(51, 154) These works indicate another mechanism to provide the strains which is necessary for the growth of T-like phase. If the growth rate can change the growth mode to island growth, and thus cause the formation of T-like phase, the decrease of deposition temperature should also have the same effect. It is also reported that high growth rate or the BiO_x impurities, can induce T like phase on STO.(156) However, the pure T-like phase (without impurity) is rarely reported. We

find that at low temperatures, there might be another mechanism that causes the coexistence of these two phases. This might be another strategy in the growth of c elongated T-like phase.

6.2 Sputtering deposition of T-like BFO on LAO (001) substrate

The deposition of T-like BFO on LAO (001) substrate are based on the known parameters of R-like BFO in Chapter 4. The target composition is: Bi/Fe=1/1.2. It is found that the parameters for the deposition of T-like BFO on LAO are similar with that of R-like BFO on STO (001), which provides much convenience on the parameter optimization. Figure 6.1 (a) shows the HRXRD results of three T-like BFO samples on LAO substrate and at 720 °C. As the RF power decrease, the BiO_x peak can be observed at around 32° in 2 theta. (power 25W). At 40W the peaks from FeO_x begin to appear. The AFM results in Figure 6.1(b) show that at 720 °C the surface are full of large grains, which is in strong contrast with the morphology of BFO/STO grown at the same conditions and shown in Figure 4.5 (d).

A series of samples have been grown on LAO (001) substrates with different temperatures (620 °C to 710 °C). The HRXRD results from Figure 6.2 (f) shows that the thin films are mostly T-like BFO, with minor R-like phase. As temperature decreases, the BFO peak intensity decreases a lot and the FeO_x peak begins to appear. On the other hand, if the temperature is reduced to 580 °C, both T-and R like phases appear for very thin films. The film thickness is about 30 nm.

Figure 6.1. (a) HRXRD evolution of samples grown at 25W, 35W and 40 W; (b), (c), (d) AFM evolution of samples grown at 25, 35 and 40 W. The area size is 5 μm .

Figure 6.2 surface morphology of T-like BFO grown on LAO substrate and different temperatures (a) 710 °C; (b) 680 °C; (c) 660 °C; (d) 640 °C; (e) 620 °C.

Figure 6.3 HRXRD results of BFO thin films grown at 580 °C

The AFM results in Figure 6.2 (a - e) show that although the roughness improved at lower temperature, the crystal properties become worse. Therefore, similar to the situations on STO substrate, the optimized growing temperature should be at around 700 °C .For the growth on STO substrate, we can almost get step-flow like growth at 720 °C and the roughness is very low. For the growth on LAO, the situation is more complex. The deposition temperature was further increased and the pressure dependent surface evolutions were investigated at 740 °C degree. As shown in Figure 6.4, when the pressure is 0.3 Pa the surface morphology is full of valleys and hills. When the pressured is increased to 0.6 Pa and 0.8 Pa, the surface turns to step flow like growth. Although there are still valleys on the surface, the roughness on the flat part can be smaller than 1nm. At 1Pa, the surface is very rough with large outgrowth. Comparing with the HRXRD results in Figure 6.4 (e), it can be seen that, the large particles are caused by the formation of BiO_x . The evolution can be explained as

follows: at low pressure, the sample is Bi deficient. When the pressure increases, the Bi composition increase, until the formation of BiO_x , the outgrowth dominates the surface morphology. However, the growth windows are very narrow. The sample changes from Bi deficient BFO to with BiO_x impurity within 0.2 Pa. It is noticed that, even at the right Bi/Fe mole ratio (close to 0.6), there are deep valleys between the relative flat area. Similar morphology have been observed in the sputtering deposition of PbTiO_3 on STO substrate, and it is explained as the non-suitable O_2 partial pressure, which can lower the mobility of the surface atom.(157, 158)

Figure 6.4 (a), (b), (c), (d) morphology evolution of the BFO/LAO (001) samples grown at 740 °C as the deposition pressure increase from 0.3 Pa to 1.0 Pa; (e), HRXRD results of samples grown at 0.3 Pa to 1.0 Pa.

6.3 Sputtering deposition of T-like BFO on STO (001) substrate

In addition to the strains from LAO (001) substrate, it have been reported that, the high growth rate have caused the co-deposition of T-like and R-like BFO films.⁽¹⁵⁴⁾ However, it is indicated that the existence of BiO_x will also induce the T-like phase.⁽¹⁵⁶⁾ We tried to grow the BFO thin films with different growing conditions. It is found that at 60° bending angle, 620 °C and Ar/O_2 of 1/7, T like BFO are observed at total pressure of 1 Pa, 0.5 Pa on STO (001) substrate, figure 6.5. The HRXRD results show coexistence of T and R like phase although there are also BiO_x impurities. As the deposition pressure decrease, the BiO_x peak disappears leaving only the T- and R- like phase.

Figure 6.5 HRXRD results of BFO thin films grown on STO (001) substrate at different deposition pressure

In order to investigate the possible mechanism in the formation of these two phases, epitaxial BFO thin films on both STO (001) and LAO (001) substrate were fabricated at different temperatures and with Bi deficient target. The deposition rate of BFO films were kept at about 50nm/hour with radio frequency (RF)-sputtering power at 30W. The thicknesses of the BFO thin films are about 50 nm for all samples. The growing temperature of BFO films varies from 600 °C to 740 °C. The mole ratio of Bi and Fe are characterized with energy dispersion spectroscopy (EDS). The crystalline structures were characterized by high resolution x-ray diffraction reciprocal space mapping (RSM) (Rigaku, $\lambda = 1.5406 \text{ \AA}$). The RSM results are measured with the same Rikagu x ray diffraction system as we used for the HRXRD measurements. The details about the equipment have been described in Chapter 4, Page 40. When the RSM measurement is carried out, the STO (001) (46.46°) and LAO (001) (47.9°)

peaks are used as the central line, the measurement ranges are: 5° in omega and 12° in 2θ .”

Figure 6.6 the (002) ω - 2θ plane RSM of BFO films grown at (a) 600°C, (b) 620 °C, (c) 640°C and (d) 680°C respectively.

Figure 6.6 shows the (002) RSM of BFO films grown at substrate temperatures of 600 °C, 620 °C, 640 °C and 680 °C. For the 680 °C sample, the BFO film exhibits only one peak near 45° in 2θ scale. This is attributed to the R-like BFO phase. As the temperature decreases, the distribution of the peak shrink dramatically in omega scale and another peak at around 39° begin to appear. This corresponds to the c axis elongated phase (T-like phase) with a much longer out of plane lattice constant. The

peak intensity of the R-like phase decrease with lowering the growth temperatures and only T-like phase BFO is obtained at substrate temperature of 600 °C. It is noticed from the RSM results that, with the formation of the T-like phase at lower temperature, the distribution of the R phase in omega scale decreases dramatically, from about 2° at 680 °C to about 0.4° at 620 °C. Similarly the c elongated phase shows a distribution of about 2° at higher temperatures in omega scale. As temperature decreases, the distribution for this phase also decreases dramatically which indicates a much better epitaxial growth.

Figure 6.7 HRXRD 2θ - ω scan of the BFO films grown on (a) STO (001) substrate and (b) LAO (001) substrate at different growing temperatures. The positions of the T-like phase and R like phase are indicated by the arrows.

Figure 6.7 (a) shows the results of the high resolution X-ray diffraction (HRXRD) 2θ - ω scan of the above mentioned thin films. The results show that the relative ratios of the T-like phase and the R-like phase change continuously with temperature. At 680 °C, only R-like phase was observed. As temperature decrease the amount of T-like phase increases gradually while the R-like phase decreases. The thin film becomes completely T-like phase at 600 °C. The Full width at half maximum (FWHM) of the R-like phase in the sample grown at 640 °C is only 0.2 degree. All these results indicate that the large growth rate may be not a necessity for the T-like phase formation on STO substrate. Careful adjustment of growing parameter can lead to the growth of T-like BFO on STO substrate with improved crystalline quality.

It is well known that the formation of T-like phase is a strain induced process,^(156, 159-161) but it is still not very clear whether the strain comes from the substrate, the island growth or both of them. In order to clarify the effects of the two mechanisms, we grew BFO samples on LAO (001) substrates with the same conditions as on STO substrates. As a comparison, Figure 6.7 (b) shows HRXRD 2θ - ω scan of the BFO grown on LAO (001) substrate. Different from what is observed on STO substrate, almost pure T-like BFO are observed from the HRXRD results at all temperatures. Only very weak peak from R-like phase are observed. The peaks for the T-like BFO increase with temperature probably because the improved crystalline quality.

The difference on the two substrates can be explained if two independent source of strain are supposed. As mentioned in the literature,⁽¹⁵⁴⁾ the large growth rate may induce a high strain state during the growth process because the landing of newly

sputtered atoms is much faster than the diffusion of adatoms. While increasing of the growth rate will increase the amount of atoms landing on the substrate, lowering the temperature will decrease the diffusion of atoms. Both will cause the high strain state during growth. At a certain combination of temperature and growth rate, T-like phase BFO can be fabricated even on STO substrate. At high temperature only LAO can induce the T-like phase because of the lower in-plane lattice mismatch between LAO and T-like phase BFO. Similarly, it is also explained as the large compressive strain caused by the large mismatch between LAO and R-like phase. On the contrary, STO have a much larger lattice mismatch with T-like phase than with R-like phase and the strain caused by the island growth is greatly reduced at high temperature. Therefore, only R-like phase are obtained at high temperatures. However, at lower temperatures, the island growth caused strain can also induce the T-like phase on STO substrate independently. The strains are released through the formation of T-like phase, maybe this is why we get improved crystalline quality at lower temperature.

It is well known that the mole ratio of Bi/Fe may vary with growing temperatures.^(91, 93) In order to exclude the effects from composition variation, we measured the EDS for samples grown on STO substrate. The results indicate that the relative mole ratios of Bi/Fe are almost 1 comparing with the stoichiometric standard bulk sample and do not change with growing temperature.

Figure 6.8 (a), (c), (e), (g), (i),(k) atomic force microscopy topography images and (b), (d), (f), (h), (j), (l) in-plane PFM images of the BFO films on STO (100) substrate. For all samples, the height scale is 50nm and the in plane PFM scale is 20 V. All AFM and PFM images are $5 \times 5 \mu\text{m}^2$.

In order to further validate our speculations on the growth mode and to verify the ferroelectric nature of these samples, we measured Atomic Force Microscopy (AFM) and Piezoresponse Force Microscopy (PFM) on the samples grown on STO substrates, as shown in Figure 6.8. The AFM results indicate that the growth mode is islands growth where grains are formed all over the surface. The surface roughnesses of these samples decrease with increasing temperature until 660°C . At 660°C the grains size increase and begin to form blocks that tend to point at certain directions. This

indicates that the growth mode begin to change. Because of the higher diffusion rate of the atoms at higher temperatures (e.g. 620 °C), the strain caused by the island growth become smaller, and at some point of the substrate, the strain is not large enough to form the T-like phases. Therefore, R-like phase begin to appear and the amount of R-like phase increases with increasing temperatures. At 660°C only R-like peak is observed, as shown in Figure 6.7 (a). We further increased the substrate temperatures and much smoother surface is obtained at 740°C, (the partial pressure is adjusted for the sample grown at 740 °C in order to get BFO thin films with the same Bi/Fe mole ratio) as shown in Figure. 6.8 (h). The roughness of the sample reaches below 1nm. The HRXRD results of this sample are also shown in Figure. 6.7 (a) with an FWHM of 0.16 degree. The PFM results show obvious polarization contrast which indicates the ferroelectric character of these samples. We also repeated the growth on different temperatures and STO substrate, it turns out that the results can be repeated quite well. However, our results comparing with growth on LAO suggested that with the same sample growing conditions the island growth itself can induce the T-like phase BFO on STO.

6.4 Conclusion

BiFeO₃ thin films with a mixture of tunable R-like and c axis elongated low symmetry phase (T-like phase) BiFeO₃ are fabricated on STO (001) substrate through controlling of the substrate temperature. Almost pure T-like phase can be grown on STO substrate at 600 °C. Comparing with the situations on LAO (001), it is found that,

strains from the LAO substrate may be the only reason that induces the T-like phase at higher temperatures. At lower temperatures, the island growth induced strains alone can also generate T-like phase on STO substrate

Mixed phase BFO thin films can be obtained on STO (001) substrate through controlling of substrate temperature. Almost pure T-like phase are fabricated on STO substrate at 600 °C. Two independent ways of growing T-like phase are confirmed. While both ways are through the effects of strain, the first one is through the large strain caused by the large in plane lattice mismatch between LAO and R-like phase or the well match between LAO T-like phase. The other one is the island growth induced strain which may be a promising method to induce the c axis elongated BFO and provides more flexibility in tuning the ratio of R-like BFO to T-like phase BFO.

Chapter Seven

Magnetic Properties of BiFeO₃ thin films and exchange bias of NiFe/BFO structures

7.1 Introduction

The magnetic property of BiFeO₃ thin films have been a subject of long term debate in many aspects. For example, the origin of the weak ferromagnetic, the absolute value of the magnetic moment or whether there can be large ferromagnetism in BFO system.(18, 163-167) The bulk material is antiferromagnetic (AFM),(168) with spiral structure along the c axis (with a period of 65 nm).(169-172) However, It is still arguable whether the spiral structure is destructed or not in the thin film.(173, 174) It is generally accepted that the BFO thin films show weak ferromagnetic behavior at room temperature.(99, 175) Because of the antiferromagnetic nature of BFO, the exchange bias character was utilized to fulfill the multi-manipulate of the electrical and magnetic freedom.(176) In addition, through domain engineering, magnetization reversal was realized with exchange bias setups.(177) The R-like BFO shows weak ferromagnetism caused by spin canting. The Néel temperature is 643 K for the R like BFO(168), and around 380K for T like BFO.(178, 179) This temperature is higher than the Curie temperature of most of the Ferromagnetic materials. On the other hand, the T like BFO show much lower Néel temperature, around 380K.(180, 181) Furthermore, at lower temperature the BFO thin film shows

spin glass like behaviors.(47, 182-184)

7.2 Vibrating Sample magnetometer (VSM) measurement of BFO thin films

The magnetic properties are measured with the VSM option (Quantum Design) with a precision of 10^{-6} emu.(185) The equipment details are described in Chapter 2. It is noticed that the accurate measurement of weak ferromagnetism depends on the way to clean the sample and the proper use of VSM system. The possible artifact or errors from VSM are listed as follows:

1) The Quantum Design VSM option provides two kinds of sample holders. One is the copper rod, the other one is the quartz rod. The new rod is purely paramagnetic or diamagnetic. The Magnetizations response (M-H curve) of the clean quartz and copper rod are shown in Figure 7.1(a) and Figure 7.1(b), the results are independent of the centering position. The permittivity (χ) of the rod, (Moment $\mu = \chi H$) is just about 1×10^{-9} .

Figure 7.1 Magnetization curve of the (a) clean quartz rod; Magnetization curve of the (b) clean copper rod.

Figure 7.2 Magnetization curve of a contaminated copper rod.

However, the rod might be contaminated after repeated usage. Some magnetic particles left on the rod may cause artifact signals. Figure 7.2 shows the MH curve between 0 and 1T of a contaminated copper rod. When changing the centering position from 34mm to 38mm, the hysteresis loop changes from a ferromagnetic (or ferromagnetic) like MH loop to a reversed MH loop. The artificial signal can be as large as 4×10^{-6} emu. This is because there is a small amount of localized magnetic impurities on the sample holder located away from the center of the detection coils and in the negative part of the coil set response function. Hence, it is inverted $M \rightarrow -M$. (186) If this kind of rod is used, the VSM measurement can be ruined for the weak ferromagnetic materials. For example, if the centering position is decided to be 34mm, an artificial ferromagnetic signal is overlapped with the sample's intrinsic signal. On the contrary, if the centering position of 38mm is used, the sample's intrinsic signal will be cancelled by the reversed MH loop. A direct problem caused by this is that, the PPMS software cannot decide the precise centering position and worsens the measurement precision. However, if the rod is well cleaned and shows a linear MH

curves, the signals from rods are paramagnetic or diamagnetic. Therefore, these signals can be viewed as background signal and be subtracted through linear fitting of the high field part.

Another artifact comes from the deposition process. During growth, the substrate is pasted to the sample holder by silver paste. The sputtered Fe atoms will also contaminate at the side walls of the substrate. Therefore, the samples should be polished on the bottom and side walls and then ultrasonic cleaned in acetone before any magnetic measurement. The MH measurements are carried out at 300K. The magnetic field sweeps from zero to 1 Tesla and then sweep back to -1 Tesla. At the same time the magnetic moment are recorded. The typical MH curves of a 100 nm pure phase BFO thin films (R-like) are shown in Figure 7.3 (a), (b), (c), (d). Although, the absolute value is very weak, the experiment can be repeated very well. A lot of other samples have been measured and all of them show very weak ferromagnetism.

Figure 7.3 Magnetic field dependent magnetization of pure phase R-like BFO thin films (a), (c) before and (b), (d) after subtraction of signal from backgrounds. Temperature dependent magnetization of the R-like BFO thin film with cooling down field of 300 Oe (e) and 1000 Oe (f).

In addition, the temperature dependent magnetization was measured after zero field cooling (ZFC) and field cooling (FC) from 10K to 300K. These results show that, BFO thin films show spin glass like behavior at lower temperature, Figure 7.3(e) and

(f). However, different from what is shown in literatures, the temperature at which the ZFC and FC split almost does not change with magnetic field.

7.3 Exchange Bias (EB) of NiFe/BFO structures.

Figure 7.4 the MH curve of the NiFe/BFO (R like) structure at room temperature

Exchange bias is a phenomenon that occurs at the interface of two magnetic materials where the behavior of a hard anti ferromagnetic layer will pin the moment of a soft ferro(ferri)magnetic materials and cause shift of the magnetization curve in the soft layer.(196) The BFO thin films are ferromagnetic, therefore, it can be used as the hard layer in the exchange bias systems. Many ferromagnetic materials have been demonstrated to show exchange bias effect with BFO thin films.(30, 187-191) Furthermore, because the magnetic order and ferroelectric order in BFO are coupled with each other, the exchange bias can be tuned by the electric degree of freedom.(197-199) Recently, it is reported that the T like BFO thin film grown on the LAO substrate are also antiferromagnetic. Furthermore, its Néel temperature is only around 360K which is much lower than the R like BFO thin films ($T_N \sim 640K$). (200)

In our work, Ni/Fe thin films were grown on both R like BFO/STO (001) and the T like BFO/LAO (001). 5 nm Ni/Fe thin films were grown with a 6-Gun sputtering system with $\text{Ni}_{81}\text{Fe}_{91}$ target at room temperature. The substrate holder was modified and two piece of NdFeB magnet were installed to generate a parallel in plane magnetic field of about 200 Oe. Figure 7.4 shows that, the NiFe/(R-like) BFO shows negative exchange bias effect. The exchange field (H_{ex}) can be as large as 70Oe.

Figure 7.5 the MH curve of the NiFe/BFO (T like) structure at room temperature. (a) the MH curve measured after deposition. (b) after cooling down from 400K in 100 Oe; (c) after cooling down from 400K in -100Oe; (d) after cooling down from 400k in 100Oe again.

As shown in Figure 7.5a, the as grown NiFe/(T-like) BFO show similar exchange bias effects except that the H_{ex} become smaller. The sample was then heated to 400K

in the PPMS, and cooled down at 100 Oe magnetic field to 300K. The MH curve was measured again. This time the MH curve still shift toward the negative field. Subsequently, the sample was warmed up to 400 K again and -100 Oe field was applied and then cooled down to 300K at this field, as shown in Figure 7.5 (c). The MH curve shifted to positive field completely. The direction of the bias is depending on the direction of the cooling field. We repeat the same process with 100Oe, the MH shift to the negative field again. This is probably because the Néel temperature for the T-like phase is below 400K. When the sample is heated to 400K, the spins in BFO layer became random. The coupling between the BFO and NiFe was lost. As the sample cools down in -100 Oe magnetic field, the coupling was established again as in most common exchange bias systems.(192) The same procedure has been applied to R like BFO on STO substrate. However, the MH shift is always toward the negative field, Figure 7.4.

7.5 Conclusion

The magnetic properties of BFO thin films were characterized with VSM (Quantum Design PPMS). It is shown that the thin films only demonstrate very week ferromagnetic property at room temperatures. It is demonstrated that the NiFe alloy/BFO thin films structures grown with sputtering methods shows obvious exchange bias. The exchange bias shown on the T like BFO can be tuned by the high temperature warm up (to 400K) and field cooling process (1T). These also indicate that the Néel temperature of the T like BFO is lower R like BFO.

Chapter Eight

Summary and future work

8.1 Summary

Two emerging multiferroics, LuFe_2O_4 and BFeO_3 are fabricated and characterized in this thesis. The LuFe_2O_4 polycrystalline were fabricated by high temperature sintering. The pure phase LFO samples used in our works show similar properties with what was reported in literatures. For example, the para-ferri magnetic transition, large coercive field and spin glass like behaviors. In this thesis, the work focuses on the magnetocapacitance (MC) and magnetoelectric effect. With the help of electric circuit based curve fitting, it is demonstrate that the large dielectric constant and magneto electric effect are caused by the non-intrinsic interface effects. The large Magnetocapacitance effect comes from the Magnetoresistance effect of the interface or the bulk. A homemade low temperature Magneto-electric effect measurement system was setup to investigate the magnetoelectric (ME) effect of the LFO sample. From our experiment, it is proved that these LFO samples with large extrinsic magnetocapacitance effect shows no large ME effect. Apparently observed signal may come from the improper shielding of the AC electromagnetic field from the alternating current source.

The multiferroic BiFeO_3 thin films were synthesized with magneto sputtering systems. The growing conditions are optimized based on our system. It is found that

while the Bi/Fe ratio is the most vital for the pure phase growth of BFO thin film, the ratio itself is very sensitive to almost every parameter of the deposition process. Fortunately, the reproducibility is very good for sputtering methods. It is also found that the Bi rich target as often used in PLD method are not suitable for our sputtering system. Because the Bi/Fe is larger than 1 even at the 0.1 Pa which is the minimum possible controllable pressure in our system. Bi deficient target with Bi/Fe=1/1.2 is most suitable. Although, the conditions that necessary for the intrinsic transport property is in contrary with the improvement of crystal quality. BFO samples with high quality and intrinsic transport properties can be obtained at optimized conditions. The Dielectric responses are investigated on the BFO samples that show intrinsic ferroelectric properties. The equivalent circuit based fittings are also used to explain the relationship between the phase transition and dielectric anomalies at low temperature.

Furthermore our efforts on the lower temperature and large bending angle in the sputtering growth show the coexistence of T and R like BFO on STO substrate. This provides a optional way to fabricate T like phase through mechanism of strain effects.

8.2 Future work.

Our experimental works on the dielectric and magnetoelectric effects have set great doubt on the polar nature of the LFO bulk samples. However, there is still lack of direct proof on the real insulating samples. The mechanisms of leakage current are still not quite clear. The epitaxial thin films at grown at optimized growth conditions

may solve these problems. In addition, the charge ordering configuration of other materials in the RFe_2O_4 series are not investigated yet.

We have demonstrated the low temperature dielectric response of BFO thin films at low temperature. The abundant dielectric features are explained in quantity. Therefore, further investigations are necessary to reveal the true nature of phase transition at low temperatures for both R and T like BFO thin films. The relatively larger dielectric constants indicate that BFO can work as dielectric insulating layer. The lower Néel temperature makes it more convenient in the application of exchange bias. Furthermore, the new strategy to grow c elongated BFO samples may stimulate the application in other c axis elongated materials.

Author's Publications

1) S. C. Li, P. Ren, B. C. Zhao, B. Xia, and L. Wang

Room temperature ferromagnetism of bulk polycrystalline $(\text{In}_{0.85-x}\text{Sn}_x\text{Fe}_{0.15})_2\text{O}_3$: Charge carrier mediated or oxygen vacancy mediated? Appl. Phys. Lett. 95, (2009) 102101. cited 7 times as of Jul. 2012

2) B.M. Wang, P. Ren, Y. Liu, L. Wang

Enhanced magnetoresistance through magnetic-field-induced phase transition in Ni_2MnGa Co-doped with Co and Mn. J. Magn. Magn. Mater. (2010) 322 715
cited 6 times as of Jul. 2012

3) Yang Wang, Yu Sui, Peng Ren, Lan Wang, Xianjie Wang, Wenhui Su and Hong Jin Fan

Correlation between the Structural Distortions and Thermoelectric Characteristics in $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ (A = Ca and Sr) Inorg. Chem. 49 3216 APR 5 2010

4) Yang Wang, Yu Sui, Peng Ren, Lan Wang, Xianjie Wang, Wenhui Su and Hongjin Fan

Strongly Correlated Properties and Enhanced Thermoelectric Response in $\text{Ca}_3\text{CO}_{4-x}\text{MxO}_9$ (M = Fe, Mn, and Cu)
CHEMISTRY OF MATERIALS 22 (2010) 1155

5) P. Ren, Z. Yang, W. G. Zhu, C. H. A. Huan, and L. Wang

Origin of the colossal dielectric permittivity and magnetocapacitance in LuFe_2O_4

J. Appl. Phys. 109, (2011) 074109 Cited 5 times as of Jul.2012.

6) B. M. Wang, Y. Liu, P. Ren, B. Xia, K. B. Ruan, J. B. Yi, J. Ding, X. G. Li, and L. Wang

Large Exchange Bias after Zero-Field Cooling from an Unmagnetized State

Phys. Rev. Lett. 106, 2011 077203 Cited 9 times as of Jul.2012

7) Peng Ren, Peng Liu, Bin Xia, Xi Zou, Lu You, Junling Wang, Lan Wang

Dielectric dynamics of epitaxial BiFeO_3 thin films

AIP Advances 2, 2012 022133.

8) Peng Ren, Soon Khuen Cho, Peng Liu, Lu You, Xi Zou, Bao Min Wang, Junling Wang, Lan Wang

Temperature controlled c axis elongated low symmetry phase BiFeO_3 thin film on STO substrate

AIP advances, 3, 2013, 012110

9) Azat Sulaev, Peng Ren, Bin Xia¹, Qing Hua Lin, Ting Yu, Caiyu Qiu, Shuang-Yuan Zhang, Ming-Yong Han, Zhi Peng Li, Wei Guang Zhu, Qingyu Wu, Yuan Ping Feng,

Lei Shen, Shun-Qing Shen, and Lan Wang

β -Ag₂Te: A topological insulator with strong anisotropy (submitted to Physical Review Letter, under review)

10) Bin Xia, Peng Ren, Azat Sulaev, Peng Liu, Shun-Qing Shen, Lan Wang

Indications of surface dominated transport in single crystalline nanoflake devices of topological insulator Bi_{1.5}Sb_{0.5}Te_{1.8}Se_{1.2}

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