GROWTH, CHARACTERIZATION AND APPLICATIONS OF MULTIFUNCTIONAL FERROELECTRIC THIN FILMS

Bo Xiao
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GROWTH, CHARACTERIZATION AND APPLICATIONS OF
MULTIFUNCTIONAL FERROELECTRIC THIN FILMS
A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy at Virginia Commonwealth University.

by

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# Table of Contents

Table of Contents .................................................................................................................. ii  
Acknowledgement ................................................................................................................. v  
List of Tables ....................................................................................................................... vi  
List of Figures ..................................................................................................................... vii  
Abstract ................................................................................................................................ xi  
Chapter 1 Introduction ........................................................................................................... 1  
  1.1 Ferroelectricity ............................................................................................................. 1  
  1.2 Perovskite oxides: PbZr_{1-x}Ti_{x}O_{3} and Ba_{x}Sr_{1-x}TiO_{3} ........................................... 5  
  1.2.1 Lead Zirconate Titanate (PZT) .............................................................................. 6  
  1.2.2 Barium Strontium Titanate (BST) ......................................................................... 8  
  1.3 Organization of the dissertation ................................................................................. 10  
Chapter 2 Sputtering growth of ferroelectric thin films ....................................................... 13  
  2.1 RF magnetron sputtering ............................................................................................ 13  
  2.2 Epitaxial growth of ferroelectrics ............................................................................... 16  
    2.2.1 Epitaxial growth of PZT thin films ..................................................................... 17  
    2.2.2 Epitaxial growth of BST thin films ..................................................................... 20  
Chapter 3 PZT thin films on STO substrates ....................................................................... 22  
  3.1 Preparation of SrTiO_{3} substrates .............................................................................. 23  
  3.2 RF sputtering growth of PZT thin films ..................................................................... 25
3.3 Characteristics of PZT thin films .................................................................26

3.3.1 Structural properties of PZT thin films .........................................................26

3.3.2 Dielectric and ferroelectric properties of PZT thin films..............................28

3.4 Pyroelectric properties of PZT thin films .......................................................32

3.4.1 Introduction of pyroelectric coefficient .........................................................33

3.4.2 Experimental setup for pyroelectric coefficient measurement.....................35

3.4.3 Pyroelectric coefficient and figure of merit ..................................................41

Chapter 4 BST Thin Films .......................................................................................47

4.1 BST epitaxial growth on STO substrates .........................................................48

4.2 Strain induced structural properties of BST thin films ....................................49

4.3 Theoretical calculation of strain in BST thin films .........................................52

4.4 Strain enhanced ferroelectric properties .........................................................53

4.5 Temperature dependence of dielectric properties in strained BST ...............54

4.6 Dielectric constant in strained BST thin films .............................................60

4.6.1 Dielectric constant as a function of $c/a$ ratio ...........................................60

4.6.2 Thermodynamic calculation of strained BST thin film ...............................61

Chapter 5 Integration of ferroelectric & semiconductor materials .....................66

5.1 Introduction .........................................................................................................66

5.2 Integration of PZT and GaN ............................................................................67

5.2.1 Bridge layer deposition by oxide molecular beam epitaxy .........................68

5.2.2 PZT deposition on GaN with a double bridge layer of PbTiO$_3$/PbO ............70

5.2.3 Structural properties of PZT thin films on GaN ........................................71
5.2.4 Electrical and ferroelectric properties of PZT thin films on GaN ....................... 75

5.3 Asymmetric hysteresis loop and theoretical analysis ............................................. 76

5.4 Epitaxial growth of BST thin films on sapphire substrate ........................................ 83

5.4.1 BST sputtering growth and MgO/ZnO bridge layer prepared by MBE ............... 84

5.4.2 Structural properties and epitaxial relationship ................................................. 87

5.4.3 Electrical properties of BST thin film .............................................................. 92

Chapter 6 Ferroelectric field effect transistor .............................................................. 94

6.2 MFS structure ferroelectric field effect transistors .................................................. 95

6.1.1 PZT Thin film preparation on AlGaN/GaN HFET ............................................. 96

6.1.2 Structure properties of PZT films on AlGaN/GaN ............................................. 97

6.1.3 Fabrication of PZT ferroelectric FET .............................................................. 98

6.1.4 Electrical characteristics of PZT/AlGaN/GaN ferroelectric FET ....................... 99

6.2 MFMS structure ferroelectric FET ...................................................................... 103

6.2.1 PZT thin film preparation .............................................................................. 104

6.2.2 Structural properties of PZT thin films ......................................................... 105

6.2.3 Electrical characteristics of MFMS FeFET ...................................................... 106

6.3 Comparison of MFS and MFMS structures ......................................................... 108

Chapter 7 Summary ..................................................................................................... 111

REFERENCE ............................................................................................................. 116
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List of Tables

Table 3. 1 Lattice constants of PZT and STO ................................................................. 23
Table 3. 2 RF magnetron sputtering conditions of PZT thin films .............................. 25
Table 3. 3 Dielectric constant of PZT thin films on different substrates ..................... 31
Table 3. 4 Primary, secondary and total pyroelectric coefficients of various materials.
   (Units are nC/cm²·K) .................................................................................................. 35
Table 4. 1 RF magnetron sputtering deposition conditions ........................................ 49
Table 4. 2 Parameters in the transition strain calculation ............................................ 58
List of Figures

Figure 1. 1 Typical hysteresis loop of a ferroelectric material ......................................................2
Figure 1. 2 Paraelectric polarization versus electric field.................................................................3
Figure 1. 3 Free energy as a function of polarization: (a) ferroelectric phase and (b) paraelectric phase ........................................................................................................................................4
Figure 1. 4 Perovskite structure in cubic phase.................................................................................6
Figure 1. 5 PbZrO$_3$-PbTiO$_3$ phase diagram .................................................................................8
Figure 1. 6 Critical temperature vs. concentration phase diagram of Ba$_x$Sr$_{1-x}$TiO$_3$..........10
Figure 2. 1 Schematic diagram of a multisource rf sputtering system.................................15
Figure 2. 2 Configuration of rf magnetron sputtering.................................................................16
Figure 2. 3 Dependence of crystalline structure of PZT thin films.............................................17
Figure 3. 1 AFM surface morphology of (a) as-received and (b) etched STO substrate.....25
Figure 3. 2 HRXRD $\omega$ rocking curve of the (001) PZT reflection. Inset is a $2\theta$-$\omega$ pattern of epitaxial PZT film on STO substrate .....................................................................................27
Figure 3. 3 $\Phi$ scan pattern of asymmetrical (101) reflection of epitaxial PZT film and STO substrate ........................................................................................................................................28
Figure 3. 4 Diagram of a PZT/STO capacitor structure...............................................................29
Figure 3. 5 Dielectric constant ($\varepsilon$) vs dc bias of 300 nm PZT film on STO substrate ......30
Figure 3. 6 P-E hysteresis loops of PZT thin film on Nb doped STO substrate ..................32
Figure 3. 7 Schematic diagram of the pyroelectric coefficient measurement system..........36
Figure 3. 8 Pyroelectric current response with changing temperature as a function of time. The inset shows current variation for the whole cooling-heating cycle..........................38

Figure 3. 9 Temperature dependence of pyroelectric coefficient of the PZT/STO: Nb heterostructure..............................................................................................................42

Figure 3. 10 P-E hysteresis loops of a PZT thin film on Nb-doped STO substrate measured at 260 K (dashed) and 360 K (solid). Inset (1) shows the temperature dependence of remanent polarization in the PZT films and inset (2) is a close up of the +P, region..44

Figure 4. 1 X-ray diffraction spectrum of BST thin films: (a) symmetric (001) 2θ-ω scans and (b) asymmetric (011) 2θ-ω scans .................................................................50

Figure 4. 2 Lattice parameters (c, a) and c/a ratio of epitaxial BST thin films with different thickness.................................................................................................................52

Figure 4. 3 strain (x12, x3) of epitaxial BST thin films with various thickness ...............53

Figure 4. 4 P-E hysteresis loops of BST thin films measured at 300 K..........................54

Figure 4. 5 Room-temperature dielectric constant versus electric field of BST thin films measured at 1 MHz .................................................................56

Figure 4. 6 Out-of-plane dielectric constant in strain BST films as a function of temperature and film thickness. The inset is the dielectric constant as a function of c/a ratio at 300 K.................................................................57

Figure 4. 7 Theoretical in-plane and out-of-plane transition strain of BST films as a function of temperature.................................................................59
Figure 5.1 RHEED patterns of PbO and PbTiO$_3$ grown on GaN: (a) GaN [1 100], (b) GaN [1 1 2 0], (c) PbO parallel to GaN [1 1 00], (d) PbO parallel to GaN [1 1 2 0], (e) PbTiO$_3$ parallel to GaN [1 1 00] and (f) PbTiO$_3$ parallel to GaN [1 1 2 0]..................................70

Figure 5.2 X-ray diffraction patterns of (a) PbTiO$_3$/GaN, (b) PZT/PbTiO$_3$/PbO/GaN and (c) PZT/GaN structures ................................................................................................73

Figure 5.3 XRD pole figure scan of Pb(Zr$_{0.52}$,Ti$_{0.48}$)O$_3$ on (0001) GaN with a double PbTiO$_3$/PbO bridge layer ..................................................................................................74

Figure 5.4 P-E hysteresis curve of Pb(Zr$_{0.52}$,Ti$_{0.48}$)O$_3$ on Si-doped GaN.........................76

Figure 5.5 Diagram of Sawyer-Tower circuit for P-E measurement........................................77

Figure 5.6 Schematic of a physical model for a ferroelectric capacitor with a dielectric layer and interface charges ($\sigma_i$: interface charge density at the dashed line)..............78

Figure 5.7 Simulated P-E hysteresis loops of a ferroelectric capacitor: (a) without dielectric layer and interface trapped charge, (b) only with dielectric layer, and (c) with both dielectric layer and interface trapped charges.........................................................82

Figure 5.8 Measured P-E hysteresis loops of (a) PZT/(001) STO:Nb(001) and PZT/PTO/PbO/GaN/c- sapphire. The insets shows the structures of the ferroelectric capacitors .................................................83

Figure 5.9 RHEED patterns of MgO and ZnO grown on a-sapphire: (a) ZnO [1 1 2 0], (b) ZnO [1 1 00], (c) MgO parallel to ZnO [1 1 2 0], (d) MgO parallel to ZnO [1 1 00].......86

Figure 5.10 2θ-ω scan of the epitaxial BST/MgO/ZnO film on a-plane sapphire substrate .............................................................................................................88
Figure 5. 11 \( \Phi \) scan patterns of asymmetrical reflections of (a) ZnO (10\( \overline{1} \)2) and \( a \)-sapphire (10\( \overline{1} \)3), (b) BST (011), ZnO (11\( \overline{2} \)2) and \( a \)-sapphire (11\( \overline{2} \)3) ..............................................90

Figure 5. 12 In-plane epitaxial relationship between BST/MgO (001) and ZnO (0001) ....91

Figure 5. 13 C-V measurement of BST/MgO/ZnO/\( a \)-sapphire. ...........................................93

Figure 6. 1 Schematic diagram of the PZT/AlGaN/GaN ferroelectric field effect transistor .................................................................96

Figure 6. 2 X-ray diffraction 2\( \theta \)-\( \omega \) scan of the PZT thin film on the AlGaN/GaN/c-plane sapphire substrate .........................................................................................................................98

Figure 6. 3 Fabrication flow of the ferroelectric FET.................................................................99

Figure 6. 4 \( I_D-V_{DS} \) characteristics of the AlGaN/GaN field effect transistors without (a) and with (b) PZT layer..................................................................................................................101

Figure 6. 5 \( I_D-V_{GS} \) transfer characteristics of the field effect transistors .......................102

Figure 6. 6 Schematic of MFMFET structure AlGaN/GaN ferroelectric MODFET........104

Figure 6. 7 XRD 2\( \theta \) pattern of PZT on AlGaN/GaN heterostructure .....................................106

Figure 6. 8 \( I_D-V_{DS} \) characteristic of AlGaN/GaN ferroelectric MODFET.........................107

Figure 6. 9 \( I_D-V_{GS} \) transfer characteristic of AlGaN/GaN ferroelectric MODFET .........108
Abstract

GROWTH, CHARACTERIZATION AND APPLICATIONS OF MULTIFUNCTIONAL
FERROELECTRIC THIN FILMS

By Bo Xiao, Ph.D

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University.

Virginia Commonwealth University, 2009

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Ferroelectric materials have been extensively studied theoretically and experimentally for many decades. Their ferroelectric, piezoelectric, pyroelectric, dielectric and electro-optical properties offer great promise in various applications such as non-volatile random access memory devices, non linear optics, motion and thermal sensors, and tunable microwave devices. Advanced applications for high dielectric constant insulators
and nonvolatile memories in semiconductor industry have led to a meteoric rise of interest in the ferroelectrics recently.

As most studied and technically important ferroelectric materials, lead zirconate titanate (PZT) and barium strontium titanate (BST) are widely investigated to understand their properties for potential device applications. Using radio frequency magnetron sputtering, single crystalline PZT and BST thin films have been achieved on SrTiO3 substrates, and been characterized for their structural and electrical properties. Eyeing their different potential applications, ferroelectric, pyroelectric and dielectric properties of PZT and BST thin films were studied. In addition, the introduction of bridge layers (nucleation or buffer layers) grown by molecular beam epitaxy (MBE) has been employed to facilitate the heterostructure growth of PZT thin films on GaN and BST thin films on sapphire substrates. Highly (111)-oriented perovskite PZT thin films were achieved on silicon-doped GaN (0001)/c-sapphire with a PbTiO3/PbO oxide bridge layer. And (001)-oriented BST thin films were grown on a-plane sapphire with an MgO/ZnO bridge layer.

This dissertation also discusses the realization of PZT ferroelectric field effect transistors (FeFET). Two different 1T FeFET structures were successfully fabricated and their electrical properties were examined. Ferroelectric behavior was observed in the plot of source-drain current versus gate voltage where it exhibited a large counterclockwise hysteresis with 50% current modulation.
Chapter 1 Introduction

Decades of studies have been directed to ferroelectrics since 1920, the discovery of ferroelectricity in Rochelle salt. But early work did not attract much attention since the composition of Rochelle salt is slightly changed against dehydration either in vacuum or in dry air. In 1935, potassium dihydrogen phosphate (KDP) and the isostructural dihydrogen arsenate were reported for the ferroelectric behavior which broadened the horizon in ferroelectrics. Further studies led to the discovery of ferroelectric perovskite oxide barium titanate ($\text{BaTiO}_3$) in early 1940s and subsequent other perovskite materials, with much simpler crystal structures and more stable ferroelectric properties by comparison. The perovskite oxides then became the most important and fundamental ferroelectric materials and also paved the way to the industrial applications for ferroelectrics. During recent two decades, the breakthrough in the ferroelectric theory, the first principle model provided a perspective approach to analyze material properties accurately and quantitatively. In addition, the demand of high dielectric constant and nonvolatile memories in the booming semiconductor industry raised great interest and motivated a renaissance of ferroelectrics.

1.1 Ferroelectricity

Ferroelectric materials possess a spontaneous polarization produced by the asymmetric arrangement of ions in the crystal structure. The direction of this polarization
in ferroelectric materials can be switched by applying electric field. Although many crystals exhibit the property of spontaneous polarization, the switching along the applied electric field presents the ferroelectricity an unambiguous definition in comparison of many polar materials, for an instance, wurtzite GaN, ZnO and so on, whose spontaneous polarization remains unchanged with an applied electric field.

The switching of polarization with an applied electric field is the essential property of ferroelectrics. Thus measuring the change of polarization has been developed and defined as the Polarization-Electric field ($P$-$E$) hysteresis loop measurement where the polarization is plotted against the electric field. As illustrated in Figure 1.1, the value of polarization remains nonzero even without the electric field, which is known as remnant polarization $P_r$. But the direction of polarization is changed when the reversed electric field is higher than the coercive electric field $E_c$.

![Figure 1.1 Typical hysteresis loop of a ferroelectric material](image)

Figure 1.1 Typical hysteresis loop of a ferroelectric material
The P-E hysteresis loop is a typical and unique behavior of ferroelectric materials in the ferroelectric phase where materials demonstrate this behavior below a certain temperature, known as the Curie temperature ($T_c$). Most ferroelectric materials undergo ferroelectric to paraelectric phase transition at $T_c$. In the paraelectric phase, there is no remanent polarization in the materials, and the polarization exists only under an applied electric field. When the electric field is removed, the polarization returns to zero as shown in Figure 1.2.

![Figure 1.2](image-url) Paraelectric polarization versus electric field

The ferroelectric behavior and phase transition was investigated by Devonshire who developed a phenomenological theory to explain those behaviors based on Ginzburg-Landau theory. The basic principle of the theory is that the free energy ($G$) of
ferroelectrics, in the absence of stress but subject to an external electric field \((E)\), can be expressed as a power series of polarization:

\[
G(T, P_i) = F(T, P_i) - E_i P_i, i = x, y, z
\]

where \(F\) and \(P_i\) are the free energy and polarization, respectively. Since the contribution from the higher order is negligible in this power series, the power series can be truncated at the sixth order. Thus the equation sometimes can be simply expressed as:

\[
G = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 - EP
\]

where \(a, b\) and \(c\) are the free-energy expansion coefficients. In Figure 1.3, the free energy is plotted as a function of polarization in ferroelectric and paraelectric phases.

![Figure 1.3](image)

**Figure 1.3** Free energy as a function of polarization: (a) paraelectric phase and (b) ferroelectric phase
In the equilibrium state of ferroelectrics, the minima of the free energy can be determined from

\[ \frac{\partial G}{\partial P} = aP + bP^3 + cP^4 - E = 0 \quad \text{or} \quad E = aP + bP^3 + cP^4 \]  \hspace{1cm} (1.3)

Above the transition temperature, there is only one minimum of the polarization which can be set as zero. Thus the dielectric susceptibility can be obtained by differentiating the equation: \( \chi = \frac{1}{a} \) where \( \chi \) is the dielectric susceptibility. Using the Curie-Weiss law

\[ \chi = \frac{1}{a_0(T - T_c)} \]

the coefficient \( a \) can be obtained as \( a = a_0(T - T_c) \). In general, the parameters of \( a_0 \) and \( c \) are both positive and the transition of paraelectric-ferroelectric phase is determined by the coefficient \( b \). At the transition point, the polarization transition can be continuous or discontinuous depending on the sign of the coefficient \( b \). More detailed discussion of the Landau-Devonshire theory can be found elsewhere.\(^5\)

1.2 Perovskite oxides: \( \text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 \) and \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \)

The most important ferroelectric materials are perovskite oxides which generally have a chemical formula: \( \text{ABO}_3 \) consisting of two cation atoms and three oxygen atoms, where \( A \) and \( B \) represent two different cation elements. The ideal perovskite structure has the space group \( \text{Pm\overline{3}m} \), with a simple cubic lattice and a basis of five atoms (Figure 1.4).

Some of perovskite oxides can be mixed in all proportions from one endpoint compound to the other to form specific solid solution. The miscibility of these ferroelectric oxides such as \( \text{PbZr}_{1-x}\text{Ti}_x\text{O}_3 \) and \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) with the isoelectronic substitutions of Ti/Zr
and Ba/Sr, provides a special flexibility to modify or adjust their properties since the change of the cation can lead to form specific phases which are desired for particular applications. The change of the chemical composition in ferroelectric oxides is always associated with the shift of transition temperature which is also a nontrivial subject of experimental and theoretical investigation.

**Figure 1.4** Perovskite structure in cubic phase

1.2.1 Lead Zirconate Titanate (PZT)

Lead zirconate titanate, Pb(ZrxTi1-x)O3 (0<x<1) is a well-known ferroelectric material with a perovskite structure, which is a combination of two perovskite materials: lead zirconate (PbZrO3) and lead titanate (PbTiO3). In the unit cell structure shown in **Figure 1.4**, eight divalent Pb^{2+} ions locate at the A sites and one tetravalent Zr^{4+} or Ti^{4+} ion does at the B site; and the oxygen ions sit at the face-center of the unit cell. As a solid
solution of two compounds, PZT has a complicate phase structure that not only depends on temperature but also the ratio of Ti and Zr.

The phase diagram is presented in Figure 1. 5 with respect to the temperature and the ratio of PbZrO3 and PbTiO3, first reported by Jaffe et al.6 PbTiO3 is a ferroelectric material with a Curie temperature of 490 ºC, whereas PbZrO3 is an antiferroelectric with a low Curie temperature of 230 ºC. Above the Curie temperature, PZT has a paraelectric cubic perovskite phase over the whole range of composition. The phase diagram at the Zr rich region is considerably complex below the Curie temperature, where even small amount (1%) of Ti can turn the antiferroelectric structure of PbZrO3 to a rhombohedral ferroelectric phase, which also is reversible to antiferroelectric orthorhombic (AFO) phase at the low temperature. With increasing the Ti concentration (7%), this transformation between antiferroelectric and ferroelectric can be significantly depressed and eventually disappears. Above the concentration, Zr-rich PZT contains high- and low-temperature phases Fd(HT) and Fd(LT), which is a more complex rhombohedral ferroelectric structure with rotated oxygen octahedral.7 The vertical phase boundary, well-known as morphotropic phase boundary occurs at about x ≈ 0.5, associated with favorable piezoelectric and ferroelectric properties due to the coexistence of tetragonal and rhombohedral phases.
1.2.2 Barium Strontium Titanate (BST)

Barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$) is another important ferroelectric material, as a solid solution of BaTiO$_3$ and SrTiO$_3$. Eyeing its promising application in agile tunable microwave application, Ba$_x$Sr$_{1-x}$TiO$_3$ has attracted much attention in recent decades. Similar with Pb(ZrxTi$_{1-x}$)O$_3$, the composition of BaTiO$_3$ and SrTiO$_3$ can be changed to adjust the structural and electrical properties in Ba$_x$Sr$_{1-x}$TiO$_3$. Referring to the unit cell in Figure 1.4, eight divalent Ba$^{2+}$ or Sr$^{2+}$ ions locate at the A sites and one tetravalent Ti$^{4+}$ ion does at the B site instead of the tetravalent Zr$^{4+}$ or Ti$^{4+}$ ions at B site of Pb(ZrxTi$_{1-x}$)O$_3$.

BST also has a complicate phase structure depending on temperature and the ratio of Ba and Sr. The phase structures and phase transitions have been discussed in detail by

![Figure 1.5 PbZrO$_3$-PbTiO$_3$ phase diagram](image-url)
C. Ménoret et al.\textsuperscript{8} Illustrated in Figure 1.6, a critical concentration $x_c$ was found to separate the phase diagram in two main regions. BST with Sr concentration below $x_c$ has a unique SrTiO$_3$-type antiferrodistortive phase. As Ba concentration increases, it causes a decrease and eventually disappearing of the oxygen octahedral tilting. A succession of three ferroelectric phase transitions appears above the critical concentration of $x_c \approx 0.0094$, which agrees well with the values of $x_c \approx 0.01$ proposed by L. Benguigui\textsuperscript{9} and D.Barb\textsuperscript{10}. Small value of $x_c \approx 0.035$ was proposed by Lemanov et al\textsuperscript{11}, and which is believed, has been underestimated due to indirect measurement methods.

The temperature-dependence of phase transition is another important characteristic of ferroelectrics called the Curie point $\Theta_c$. Especially for BST, the ratio of Ba and Sr commonly used is 50/50 or Ba-rich, which is much larger than the critical concentration. As seen in Figure 1.6, it can be noted that the phase transition temperature approaches to the room temperature. At the Curie point, it is generally believed that the ferroelectric phase of BST transits to paraelectric phase with $Pm\overline{3}m$ symmetric crystal structure. The Curie point here only specifies the temperature at which a paraelectric-ferroelectric phase transition occurs. The point of phase transition between different ferroelectric phases is simply referred as a transition temperature.
1.3 Organization of the dissertation

In this study, a series of PZT and BST thin films have been studied and discussed, which were deposited on various substrates. The discussion of structural and electrical properties extends to their corresponding ferroelectric, pyroelectric and dielectric properties. The integration of ferroelectric and semiconductor materials has been exploited for the potential device applications. The coverage of the topics is inherently interdisciplinary, and the main purpose is to present a sound experimental and theoretical basis for further advances in numerous emerging ferroelectric applications. The intention is that the description of experimental methods, results and theoretical analysis is included as an integral part. Theoretical analysis and experimental results are presented and combined together in order to build this integral basis.
Chapter 2 introduces the sputtering technology with emphasis on rf magnetron sputtering which is employed for all growth of ferroelectric thin films discussed in this thesis. Aspects applicable to thin film growth of complex oxides are described with the following of specific discussion of several growth parameters: temperature, pressure, Ar/O₂ ratio and power.

Chapter 3 describes high quality PZT thin films growth on STO substrates. The structural and electrical properties are discussed with focus on their ferroelectric properties. Pyroelectric properties of PZT thin films of the morphotropic boundary composition are studied in this chapter, and the pyroelectric coefficient is included. Large pyroelectric coefficient was found in PZT films on STO: Nb substrate and the measurement technique is discussed in detail.

Chapter 4 shifts the focus on high quality BST thin films on STO substrates and its dielectric properties. The dependence of strain and temperature in BST thin films is investigated. The related strain-induced dielectric properties are discussed experimentally and theoretically.

Chapter 5 is devoted largely to study epitaxial growth of ferroelectric thin films on semiconductor materials. The integration of PZT with GaN and BST with sapphire is proposed and studied. By introducing a bridge layer, high oriented PZT and BST thin films are obtained. Structural properties especially epitaxial relationships are characterized by high resolution X-ray diffraction analysis.

Chapter 6 is intended to describe the realization of ferroelectric field effect transistors (FeFET) based on AlGaN/GaN heterostructures. To achieve smaller size and
nondestructive readout, two different gate structures of ferroelectric transistors are proposed and successfully fabricated. Their transfer characteristic (source-drain current \textit{versus} gate voltage) shows a notable counterclockwise hysteresis loop indicating a significant ferroelectric source-drain current modulation.

Chapter 7 gives a summary of this dissertation and ideas for future work.
Chapter 2 Sputtering growth of ferroelectric thin films

Great efforts have been exerted on the synthesis of ferroelectric perovskite oxides with the advancing of thin film deposition techniques. To produce high quality films with the desired composition, the deposition techniques for ferroelectric oxides must allow precisely controlling the fluxes of elements or stoichiometrically transferring source materials to the substrate. It is primarily because the microstructures and properties of ferroelectric materials strongly depend on the composition, and unlike in the growth of compound semiconductors where an excess of one element can be introduced without resulting an excess of that element in the film. There are several deposition techniques, which have been prove that can obtain precisely composition control and also been widely utilized for the deposition of high quality ferroelectric thin films, such as molecular beam epitaxy (MBE), pulsed leaser deposition (PLD), metal-organic chemical vapor deposition (MOCVD) and sputtering. Among them, sputtering would be the most popular one for ferroelectric deposition due to its relatively simple operation and good composition control as well as low cost. In this work, one advanced sputtering technique, rf magnetron sputtering has been mainly employed to deposit high quality ferroelectric thin films.

2.1 RF magnetron sputtering

In general, two types of sputtering methods are available for the deposition of ferroelectric oxides: dc and rf sputtering. DC sputtering involves the chemical reactions to
form the ferroelectric oxides, using metal sources (targets) to grow ferroelectrics in the presence of oxygen. Complexity and difficulty of composition control makes it very unpractical for the growth of ferroelectric materials, although it has the advantage of composition flexibility in ferroelectric oxides. In contrast, rf sputtering is a physical vapor deposition method which transfer atoms from the surface of a target to the substrate by bombarding the target with an incoming flux of highly energetic particles. The basic method of generating the incident flux of particles in sputtering process is through the creation of a plasma or glow discharge in an inert gas environment. The source target is attached to the sputtering gun coupled as the cathode. Correspondingly, the substrate holder is connected as the anode. An electric field with sufficient strength is applied between the anode and cathode to accelerate the ionized inert gas to produce highly energetic incident particles.

In rf sputtering, an alternating electric field is applied at a typical frequency of 13.56 MHz for generating plasma. Typically the gas in the plasma is Ar, which is ionized to Ar$^+$ ions. These Ar$^+$ ions are accelerated by the electric field towards the target, while electrons are attracted to the anode. The heavy Ar$^+$ ions bombard the target, transferring their kinetic energy to the target, causing the atoms at or near the surface of the target to be ejected. The ejected atoms then travel onto a heated substrate. A schematic diagram illustrating the basic features of one rf sputtering system is shown in Figure 2.1.
In order to yield high deposition rate, one advanced rf sputtering system is developed and called as rf magnetron sputtering, in which a magnet array is placed underneath the target to confine the ions in a torus-shaped region, thus increasing the ionization probability near the surface of the target. The configuration of rf magnetron sputtering is demonstrated in Figure 2. 2.
2.2 Epitaxial growth of ferroelectrics

The success of sputtering growth complex oxides is attributed to the fundamental of the growth processes and nucleation in thin film formation which is basically related to the thermodynamics of adsorption and the kinetics of crystal growth. A numerous parameters involves in the whole process. But among these parameters, temperature, pressure and sputtering power are three most critical ones that substantially affect thin film nucleation.
2.2.1 Epitaxial growth of PZT thin films

The substrate temperature should be taken a prior consideration for the complex oxide growth. In spite of the quality of the thin films, temperature can determine the formation of specific crystal structures. For instance, it is well known that PZT has perovskite phase and pyrochlore phase, and PZT in the pyrochlore phase does not show ferroelectric properties. Commonly PZT thin films form the pyrochlore phase at low growth temperatures (500 - 550°C) whereas the films deposited at relative high temperatures (550 - 600°C) turn out to be a perovskite dominated structure. Okada et al. have demonstrated that composition and crystalline properties of PZT films depend strongly on the substrate temperature as shown in Figure 2.3. Although high temperature (more than 600°C) may cause some reaction between PZT and Pt substrates as Okada et al. reported, there is no evidence that implies the degradation of crystal quality with further increasing the temperature.

![Figure 2.3](image)

**Figure 2.3** Dependence of crystalline structure of PZT thin films
The limitation of temperature in the growth mainly comes from the consideration of the substrate structure (some device structures may not survive in the high temperature), interface reaction and equipment capacity. In our PZT growth on STO substrates, the substrates have good thermal stability. And PZT thin films can be grown at a higher substrate temperature of \(~700\,^\circ\text{C}\) (the heater temperature set at 750 \(^\circ\text{C}\), which is maximum attainable temperature for our system). However, a significant problem appears in PZT growth that the nonstoichiometric growth occurs at such a high growth temperature due to the volatility of Pb. Evaporation loss of Pb increases rapidly with raising the substrate temperature, and causes the defects and Pb deficiency. Therefore, it is imperative to adjust the composition of sputtering target to obtain stoichiometric films. Here Pb\(_{1.1}\)Zr\(_{0.58}\)Ti\(_{0.42}\)O\(_3\) target with 10\% excess of PbO powder was used in the PZT growth to compensate for the Pb loss.

Process gas pressure is another substantial parameter in sputtering deposition, impacting the composition and growth rate. The pressure is controlled by adjusting a background gas, generally inert gas: Ar. In fact, this gas also serves as a plasma source and a particle source which is utilized to generate incident particle flux for bombarding target. For ferroelectric oxide sputtering deposition, some amount of oxygen is generally introduced to enhance the oxidation. The introduction of oxygen decreases the partial pressure of Ar and lowers the growth rate. The reason of low growth rate with the introduction of oxygen gas is not the fact that the mass of oxygen is less than that of Ar. It is because that ionized oxygen does not involve the bombardment of the target since there is a DC bias in the rf sputtering, which drives the negative O\(^{2-}\) ions towards the anode.
These oxygen ions also produce a resputtering process on the surface of the substrate causing rough surface morphology and leading to nonstoichiometric films. In the rf magnetron sputtering system, using off-axis sputtering gun can deviate the transmission path of oxygen ions from bombarding the substrate to suppress the resputtering. Moreover, the magnetron array below the target provides additional reduction of the resputtering, which traps the ionized ions near the target surface so that the energy and density of oxygen ion traveling to the substrates are significantly reduced by scattering. All these configurations, however, can not totally eliminate the resputtering. Thus, the oxygen introduced in the sputtering is usually kept at the order of 10 % - 50 %. In our growth, the ratio of Ar : O₂ is calibrated at 6 : 1.

In addition, rf power is a direct factor which determines growth rate in rf sputtering. ¹³,¹⁴ If the film quality is guaranteed, rf power would be simply set as high as possible to gain the high growth rate. However, high sputtering power may cause some serious problems such as rough surface morphology, deviation in composition and target cracking. ¹³ The effect of rf power on PZT film composition has been studied by S. Kalpat and K. Uchino, ¹⁵ who found that the lead content in the film was higher at high sputtering powers with using a metallic target due to preferential removal of the volatile PbO from the target compared to the stable ZrOₓ and TiOₓ. Such problems are also related to the heat generated on the target during the sputtering. Therefore the target gun in a sputtering system requires a good cooling to dissipate built-up heat.
2.2.2 Epitaxial growth of BST thin films

Sputtering deposition is also commonly used for the production of high quality BST thin films. As aforementioned in PZT growth, target composition and growth temperature need to be considered carefully because of the Pb volatility and the related Pb deficiency in thin films. Unlike PZT sputtering growth, stoichiometric targets and relative high substrate temperature can be employed in BST sputtering deposition without concern of any deficiency. Although using multi-target of BaTiO$_3$ and SrTiO$_3$ provides flexibility in control of Ba and Sr composition, single ceramic target of (Ba, Sr)TiO$_3$ with fixed ratio of Ba and Sr is most popular in BST thin film sputtering owing to its simplicity of growth control and uniformity of composition in sputtered thin films. Similar with PZT growth, high growth temperature is in favor of good crystallinity and electrical properties of BST thin films.$^{16}$ In general, the growth temperature ranges from 500 °C to 800 °C in BST sputtering. There is no evidence that indicates the crystalline degradation in BST thin films with further increasing growth temperature. However, high growth temperature raises the bar of requirement for deposition systems such as cooling efficiency, heater capacity and material stability which applies constrains to high growth temperature.

Oxygen partial pressure or Ar/O$_2$ ratio is a widely discussed issue related to BST sputtering growth. It is believed that the oxygen partial pressure imposes direct influence on structural properties of sputtered BST thin films.$^{17}$ The related tetragonal distortion in BST thin films on MgO substrate was discussed in detailed associated with the dielectric properties.$^{18}$ Although lattice mismatch, thermal expansion mismatch, defects and oxygen vacancies can be attributed to this structure distortion, oxygen vacancies are considered as
the main factor. Additionally, the oxygen vacancies preferentially increase the out-of-plane $c$ lattice parameter and cause the tetragonal distortion as $c > a$. It is suggested that the in-plane $a$ parameter is more confined by the substrate.\textsuperscript{18,19} Similar distortion has been found in the BST films grown by PLD on MgO and LAO.\textsuperscript{19,20} However, the oxygen partial pressure affects the growth rate and high oxygen ratio can dramatically decrease the growth rate as aforementioned that sputtering technique uses Ar as the source to supply ions to bombard the target and increased oxygen partial pressure means the reduction of the effective bombardment Ar ions. Therefore, the oxygen partial pressure needs to be calibrated corresponding to rf power, total pressure and growth temperature. In addition, U. C. Oh \textit{et al.} reported the distortion of BST grown on MgO by rf magnetron sputtering and found that the low rf power yielded less distorted BST films.\textsuperscript{21} It is plausible to suggest that the lattice mismatch and the difference of thermal expansion attribute to the distortion in the BST heterostructures. One would note that high oxygen pressure and low rf power, which resulted the less distortion, have the same influence on the growth condition: both of them lower the growth rate. As the growth rate is reduced, the growth time elongates that would help releasing the strain of the distorted BST films partially at high growth temperature.
Chapter 3 PZT thin films on STO substrates

PZT has many fascinating properties which have been intensively studies in bulk form, PZT ceramic. In industry, piezoelectric PZT ceramics have been widely used for applications in actuators, transducers and sensors. But the driving force in current PZT studies is its ferroelectric properties for ferroelectric memory application. This application need to combine PZT with electronic devices that are difficult and costly to be realized in bulk form regarding to the complexity and integration. Thus the focus has been largely shifted to PZT thin films which can offer such degrees of freedom for the development of novel applications. To exploit the applications of PZT thin films, it is very important to understand the properties of PZT films, and high quality thin films are required. The advanced growth technology has provided the ability to prepare high quality PZT thin films. Epitaxial growth of PZT thin films have been performed by molecular beam epitaxy (MBE),\textsuperscript{22} pulsed laser deposition (PLD) and sputtering methods. In PZT context, it was found that PZT with the morphotropic boundary phase (MPB), consisting of the composition ration of Zr: Ti: 52: 48, exhibits high ferroelectric properties and suitable for the related applications. In this section, the growth of PZT thin films is studied for its MPB phase on SrTiO\textsubscript{3} substrates.
3.1 Preparation of SrTiO$_3$ substrates

Strontium titanate, SrTiO$_3$ (STO) is a perovskite material, which has been widely used as the substrate in oxide heteroepitaxy. Similar crystal structure of PZT and STO makes STO an important substrate material for high quality PZT thin film growth. Additionally the almost identical thermal expansion of PZT and STO allows the fabrication of PZT thick films and the high growth temperature. The lattice constants of Pb(Zr$_{0.58}$Ti$_{0.42}$)O$_3$ and SrTiO$_3$ are listed in Table 3.1. The lattice mismatch of PZT and STO can be obtained by using the equations:

\[
\varepsilon_\perp = \frac{c_{\text{PZT}} - c_{\text{STO}}}{c_{\text{PZT}}} \quad 3.1
\]

\[
\varepsilon_\parallel = \frac{a_{\text{PZT}} - a_{\text{STO}}}{a_{\text{PZT}}} \quad 3.2
\]

where $c$ is the out-of-plane lattice constant and $a$ is the in-plane one. The lattice mismatches of $\varepsilon_\perp$ and $\varepsilon_\parallel$ are 5.8 % and 3.3 %, respectively.

Table 3.1 Lattice constants of PZT and STO

<table>
<thead>
<tr>
<th>Materials</th>
<th>Crystal structure</th>
<th>Crystal system (at 300 K)</th>
<th>Lattice constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>Perovskite</td>
<td>Cubic</td>
<td>3.904 Å</td>
</tr>
<tr>
<td>Pb(Zr$<em>{0.52}$Ti$</em>{0.48}$)O$_3$</td>
<td>Perovskite</td>
<td>Tetragonal23</td>
<td>$c=4.1464$ Å, $a=4.036$ Å</td>
</tr>
</tbody>
</table>

Substrate preparation is an important step for epitaxial growth. To achieve two-dimensional epitaxial growth, it is essential to obtain a step and terrace substrate surface.
STO is a cubic crystal with the chemical formula ABO$_3$. Such perovskite oxides could be terminated by either AO or BO$_2$ surface terminations. To provide single terminated surfaces, different preparation methods have been employed for STO.$^{24,25}$ Generally the preparation includes two procedures: etching and annealing. In general, HF or NH$_4$F-HF (buffered HF, BOE) is used as etchant which can remove Sr more efficiently than Ti to form a Ti-terminated surface. After etching, surface smoothness of STO substrates can be further improved by annealing in O$_2$ ambient. The annealing conditions and consequent surface reconstruction have been studied.$^{24,26,27,28}$ The annealing temperature is around 800 °C – 1200 °C. However oxygen pressure control raises complexity of the preparation and high temperature may cause the contamination and unwanted rough surface morphology depending on the quality of the substrates. Thus the STO substrates were only treated by chemical etching in our preparation. It was found that the step and terrace STO surface can be obtained only by BOE etching. As shown in Figure 3.1, the step and terrace surface appeared after BOE etching, indicating a remarkable transformation of the surface morphology. The surface roughness decreased from 0.5 nm to 0.2 nm measured by atomic force microscope (AFM).
3.2 RF sputtering growth of PZT thin films

As aforementioned in Chapter 2.2, evaporation loss of Pb increases rapidly with the rising substrate temperature and causes the defects and Pb deficiency. Thus the sputtering target comprises of 10% extra PbO to avoid this deficiency. The target has the size of 3” diameter with the composition of morphotropic boundary phase, Zr : Ti = 52 : 48. The sputtering conditions adopted in the experiments are summarized in Table 3.2.

<table>
<thead>
<tr>
<th>Table 3.3 RF magnetron sputtering conditions of PZT thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target material</td>
</tr>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Ar</td>
</tr>
<tr>
<td>O_{2}</td>
</tr>
<tr>
<td>RF power</td>
</tr>
</tbody>
</table>
### 3.3 Characteristics of PZT thin films

#### 3.3.1 Structural properties of PZT thin films

The crystal structure and orientation of the as-deposited PZT films on STO substrates were examined by high resolution X-ray diffraction (XRD) using Cu $K\alpha$ radiation. Single-crystal perovskite (001) reflection was observed in the epitaxial PZT film from XRD 2θ scan as seen in Figure 3.2. The 2θ angle of PZT (001) reflection locates at 21.46 °, which is near the Bragg angle of the PZT angle 21.414 ° from the international center for diffraction data. The corresponding $d$ spacing is 4.136 Å, which is consistent with the (001) reflection of a perovskite PZT with the MPB composition. The asymmetric (101) 2θ scan were performed to determine the out-of-plane lattice parameter, which located the 2θ position of (101) reflection at 30.95 °. The lattice constant of $a$ then was calculated and it is equal to 4.031 Å. The obtained lattice parameters of $c = 4.136$ Å and $a = 4.031$ Å are very close to bulk crystal ones of $c$ and $a$, which are 4.146 Å and 4.036 Å, respectively. Thus it suggests that the 300nm-thick PZT thin film on STO has the stoichiometric growth and is strain relieved. The crystalline quality of the PZT thin film was evaluated by XRD ω-rocking curve scan. The full width at half maximum (FWHM) is 4.2 arc min for symmetric (001) reflection and 30 arc min for asymmetric (101) reflection, indicating high crystal quality of the epitaxial PZT layer. To further determine the epitaxial

<table>
<thead>
<tr>
<th>Temperature</th>
<th>650 °C - 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition rate</td>
<td>2 - 3 nm/min</td>
</tr>
</tbody>
</table>
relationship of PZT/STO heterostructure, Φ scan of asymmetrical (101) reflection was performed separately for PZT and STO at the same setup. The fourfold rotation symmetry was observed in Figure 3.3 which clearly implies the epitaxial relationship of in-plane PZT[100]//STO[100] and out-of-plane PZT(001)//STO(001).

![HRXRD ω rocking curve of the (001) PZT reflection. Inset is a 2θ- ω pattern](image)

**Figure 3.2** HRXRD ω rocking curve of the (001) PZT reflection. Inset is a 2θ- ω pattern of epitaxial PZT film on STO substrate
Figure 3. 3 \( \Phi \) scan pattern of asymmetrical (101) reflection of epitaxial PZT film and STO substrate

3.3.2 Dielectric and ferroelectric properties of PZT thin films

PZT thin films grown on conductive 0.5 wt % Nb-doped STO substrates were used to characterize the electrical behaviors. PZT capacitor structures were fabricated by successive use of photolithography, e-beam evaporation, and lift-off procedures, which has Au/Cr circular top electrodes of 50/30 nm in thickness and 200 um in diameter. The
bottom electrodes of PZT capacitors were placed on the top of the STO substrate as seen in Figure 3.4.

![Diagram of a PZT/STO capacitor structure](image)

**Figure 3.4** Diagram of a PZT/STO capacitor structure

Current-voltage measurements of the PZT films showed leakage current densities of $1 \times 10^{-8} \text{ A/cm}^2$ at 500 kV of electric field. Capacitance-Voltage (C-V) measurements were performed to examine the dielectric properties of PZT thin films using an HP4284 precision LCR (inductor, capacitor, resistor) meter. The butterfly shape of the C-V curves (Figure 3.5) is a typical behavior of ferroelectric capacitors, which indicates the presence of permanent polarization.
The dielectric constant of PZT thin films is much smaller than that of its bulk counterpart, and also it has been reported that the dielectric constants were quite different for PZT thin films, which would depend on thin film thickness, buffer layer, bottom electrode, orientation, substrate, etc. Listed in Table 3.4 are the dielectric constants of PZT thin films on a variety of substrates. The thickness dependence of the dielectric constant was reported that the dielectric constant increases with increasing the thickness. Small dielectric constants were found on STO substrates or SRO buffer layers. It suggests that strain caused by lattice mismatch would play an important role in the dielectric constant. Effect of strain in ferroelectric films has been investigated for BST films on STO.
substrates. That can be applied to explain the dielectric properties of PZT films. The detailed discussion of this issue will be presented in Chapter 4.

**Table 3. 4** Dielectric constant of PZT thin films on different substrates

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness (nm)</th>
<th>Preferential orientation</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(Zr0.3Ti0.7)O3 /Pt/Si</td>
<td>300 nm</td>
<td>(111)</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>500 nm</td>
<td>(111)</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>700 nm</td>
<td>(111)</td>
<td>372</td>
</tr>
<tr>
<td>Pb(Zr0.53Ti0.47)O3/Ti-Al/Si</td>
<td>150 nm</td>
<td>(111)</td>
<td>~425 (500 K)</td>
</tr>
<tr>
<td>Pb(Zr0.53Ti0.47)O3/MgO/Si</td>
<td>2 – 4 μm</td>
<td>(001)</td>
<td>650</td>
</tr>
<tr>
<td>Pb(Zr0.53Ti0.47)O3/MgO/glass</td>
<td>2 – 4 μm</td>
<td>(001)</td>
<td>360</td>
</tr>
<tr>
<td>Pb(Zr0.52Ti0.48)O3/SrRuO3/SrTiO3/MgO/TiN/Si</td>
<td>(001)</td>
<td>400 - 450</td>
<td></td>
</tr>
<tr>
<td>PZT/YBCO/SrTiO3/MgO/TiN/Si (100)</td>
<td>(001)</td>
<td>380 - 400</td>
<td></td>
</tr>
<tr>
<td>PbZr0.5Ti0.5O3/SrRuO3/SrTiO3</td>
<td>200 – 300 nm</td>
<td>(001)</td>
<td>300 – 380</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(110)</td>
<td>500 - 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(111)</td>
<td>600 - 780</td>
</tr>
<tr>
<td>Pb(Zr0.53Ti0.47)O3/YBCO/SrTiO</td>
<td>120 nm</td>
<td>(001)</td>
<td>~260 (300 K)</td>
</tr>
<tr>
<td>PbZr0.52Ti0.48O3/SrTiO3 (our sample)</td>
<td>300 nm</td>
<td>(001)</td>
<td>310</td>
</tr>
</tbody>
</table>

The ferroelectric properties of the PZT films were examined by polarization-electric field (P-E) measurements. **Figure 3. 6** shows P-E curves of one PZT/STO: Nb heterostructure measured at 1kHz. The remanent polarization is around 45 - 58 μC/cm² and the coercive electric field is about 240 kV/cm. One may note that the hysteresis loops are
asymmetric, which are commonly found in the heterostructure ferroelectric-semiconductor structures as reported for PZT/SiO₂/Si, PZT/GaN, PLZT/GaN, and PZT/STO. Using the simple metal-insulator-semiconductor (MIS) model, it can be explained that the depletion layer is formed in the conductive Nb-doped STO, which has n-type conductivity. In addition, charge traps which exist in the interface of PZT and STO or PZT layer are partly attributed to the asymmetric hysteresis loop. The asymmetry of the hysteresis loops is discussed further in Chapter 5.

![Graph showing P-E hysteresis loops of PZT thin film on Nb doped STO substrate](image)

**Figure 3.6** P-E hysteresis loops of PZT thin film on Nb doped STO substrate

### 3.4 Pyroelectric properties of PZT thin films

Uncooled single pyroelectric infrared detectors are ideally suited to the intruder and flame detection application. By virtue of large pyroelectric coefficient of PZT, efforts
have been extended to develop pyroelectric devices,\textsuperscript{41,42} which are capable of operating over a wide range of temperatures without a cooling system.

### 3.4.1 Introduction of pyroelectric coefficient

Pyroelectricity is a coupled effect that relates the change in the electric displacement, $dD$, under the change of temperature or mechanical stress:

$$dD = d(dT) + \varepsilon dE + pd\theta \quad \text{3.3}$$

where $d\theta$ is the temperature change. $p$ is the pyroelectric coefficient which can be expressed by $p = (\partial D / \partial \theta)_{T,E}$. The pyroelectric effect has two contributions, primary and secondary effect. Their relation associated with the mechanism is simply indicated in \textbf{Figure 3.7}.\textsuperscript{43} The so-called primary pyroelectric effect is due to the change in electrical displacement caused by the change in temperature, while the crystal is rigidly clamped under constant stress, to prevent expansion or contraction. The secondary pyroelectric effect is a result of the strain caused by thermal expansion that changes the electric displacement via piezoelectricity. It is extremely difficult to measure directly the primary effect, although the secondary effect can be readily calculated. For most of the ferroelectric materials, the primary pyroelectric coefficient is negative and its magnitude is significantly larger than that of the secondary one resulting in a negative net pyroelectric coefficient, which is usually the one measured in experiments.\textsuperscript{43}
Figure 3.7 Relationship of electrical, mechanical and thermal properties in ferroelectric materials

PZT thin films processes high pyroelectric coefficient and are potential for applications in uncooled infrared sensing. Pyroelectric properties of PZT thin films of the MPB composition are studied here, and the pyroelectric coefficient, which is the key parameter in realizing uncooled pyroelectric infrared sensors, is determined.

Table 3.5 lists the primary, secondary and total pyroelectric coefficients of some materials.
Table 3.5 Primary, secondary and total pyroelectric coefficients of various materials.
(Units are nC/cm²·K)\(^{43}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Primary coefficient</th>
<th>Secondary coefficient</th>
<th>Total coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ferroelectrics (Poled ceramic)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>-26</td>
<td>+6</td>
<td>-20</td>
</tr>
<tr>
<td>PbZr₀.₉₅Ti₀.₀₅O₃</td>
<td>-30.5</td>
<td>+3.7</td>
<td>-26.8</td>
</tr>
<tr>
<td><strong>Ferroelectrics (Crystal)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>-9.5</td>
<td>+1.2</td>
<td>-8.3</td>
</tr>
<tr>
<td>LiTaO₃</td>
<td>-17.5</td>
<td>-0.1</td>
<td>-17.6</td>
</tr>
<tr>
<td><strong>Nonferroelectrics (Crystal)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>-0.69</td>
<td>-0.25</td>
<td>-0.94</td>
</tr>
<tr>
<td>CdS</td>
<td>-0.30</td>
<td>-0.10</td>
<td>-0.40</td>
</tr>
</tbody>
</table>

3.4.2 Experimental setup for pyroelectric coefficient measurement

To study and exploit the properties of PZT thin films for pyroelectric device applications, high-quality PZT thin films have been grown epitaxially on conductive STO substrates doped with Nb to 0.5 wt % (resistivity ~0.01 Ω·cm) by radio-frequency (rf) magnetron sputtering. Capacitor structures composed of 50/30-nm-thick Au/Cr circular electrodes of 200 µm in diameter were fabricated on top of PZT films by successive use of photolithography, e-beam evaporation, and lift-off procedures. The bottom electrodes of PZT capacitors were placed on top of the STO substrate (schematic sketch of the capacitor structure is shown in Figure 3. 4). Using the fabricated capacitor structures, pyroelectric
properties of PZT thin films were studied by the Byer-Roundy method. The pyroelectric coefficient $p$ can be calculated as

$$p = \frac{I}{A \frac{dT}{dt}}$$

where $I$ is the current, $A$ is the capacitor area, and $dT/dt$ is the temperature changing rate. This technique is based on measuring a displacement current associated with the spontaneous polarization change with temperature. A computer-controlled measurement setup consisting of an HP 4142B modular dc source/monitor and a Lakeshore 331 temperature controller was assembled for measuring the pyroelectric response of the PZT films, which is illustrated in Figure 3.8.

![Schematic diagram of the pyroelectric coefficient measurement system](image)

**Figure 3.8** Schematic diagram of the pyroelectric coefficient measurement system

The electrically poled sample under test was placed on a copper plate in a heating chamber equipped with an electrical heater and a liquid-nitrogen cooler. During the
pyroelectric response measurements, the chamber pressure was kept around $10^{-2}$ Torr, and the temperature was ramped up from 160 K to 420 K with a rate of $\sim 0.6$ K/sec. The current induced by temperature change was measured every 200 ms. As demonstrated in, this current gradually increases in region I, at the beginning of the temperature ramping, and then reaches a steady-state value in region II. The gradual current increase cannot be considered as the actual pyroelectric response; because it is mainly caused by the parasitic capacitances in the measurement circuit reflecting their charging time and likely by delayed heat propagation from the heater to the PZT layer. This is the major limitation of this measurement technique which, if disregarded, may lead to observation of a pyroelectric coefficient which does not represent the intrinsic properties of the material. For instance, the magnitude of pyroelectric coefficient as high as 80 nC/cm$^2$K has been reported recently based on measurements performed in a narrow temperature range. In our case, in order to obtain the accurate pyroelectric coefficient at around room temperature, a wide temperature range was chosen where the starting point was far below 300 K.
Figure 3.9 Pyroelectric current response with changing temperature as a function of time. The inset shows current variation for the whole cooling-heating cycle.

Seen in Figure 3.9, as the heating rate was reduced in region III, the induced current decreased accordingly. To some extent, this reduction includes the discharging current from the parasitic capacitances. Hence, the pyroelectric coefficient was calculated only for region II using $p(T) = I (A dT/dt)^{-1}$, where $I$ is the current induced by the pyroelectric effect, $A$ is the capacitor area, and $dT/dt$ is the temperature ramping rate. The magnitude of $p$ was also extracted from the cooling (the inset of Figure 3.9 presents a full heating-cooling cycle). To eliminate the possible contribution from other thermally
stimulated currents, especially those associated with charging/discharging electron traps present in the material, the samples should be measured on both heating and cooling, and the pyroelectric current taken as an average of the two values obtained at any one temperature. This is because thermally stimulated currents (e.g. from trapped charge) tend to be unidirectional in sign, whereas the pyroelectric current changes sign with the sign of \(dT/dt\). However, it is extremely hard to keep the identical heating and cooling rates (limitation of the experimental setup). Thus instead of using average currents to calculate the coefficient, we took the average pyroelectric coefficient of cooling and heating at the same temperature. Below it is demonstrated that this approach is equivalent to averaging measured currents. For the heating and cooling, the pyroelectric coefficient can be expressed as the following equations:

\[
p_H = \frac{I + I_H}{A dT/dt} \tag{3.5}
\]

\[
p_C = \frac{-I + I_C}{A dT/dt} \tag{3.6}
\]

where \(p_H\) and \(p_C\) refer to pyroelectric coefficients measured during heating and cooling, respectively. \(I\) is the displacement current associated with the pyroelectric effect, \(A\) is the capacitor area, and \(I_H\) and \(I_C\) are thermally induced current for heating and cooling cycles, respectively. The coefficient associated only with the pyroelectric effect is expressed as:

\[
p = \frac{I}{A dT/dt} \tag{3.7}
\]
We assume that the thermally induced current is unidirectional, while the pyroelectric current changes the direction with changing sign of temperature ramping. We can obtain two equations as

\[ p_H = p + \frac{I_H}{A \frac{dT}{dt}} \]  

\[ p_C = p + \frac{I_C}{A \frac{dT}{dt}} \]  

( the sign of $\frac{dT}{dt}$ during cooling is negative )

Then these equations are re-written as

\[ p_H \frac{dT}{dt} = p AdT / dt + I_H \]  

\[ p_C \frac{dT}{dt} = p AdT / dt + I_C \]

Take a time integral of the equation (3.10 and 3.11) for the heating and cooling at a temperature range of $T_1$ and $T_2$ ($T_2>T_1$):

\[ \int_{t_H}^{t_C} [p_H(T) AdT / dt]dt = \int_0^{t_H} [p(T) AdT / dt]dt + \int_0^{t_C} I_H dt \]  

\[ \int_{t_H}^{t_C} [p_C(T) AdT / dt]dt = \int_0^{t_C} [p(T) AdT / dt]dt + \int_0^{t_H} I_C dt \]

Then change the variables of the integration of the equation 3.12 and 3.13:

\[ \int_{t_1}^{t_2} p_H(T) dT = \int_{t_1}^{t_2} p(T) dT + \int_0^{t_H} I_H dt \]  

\[ \int_{t_2}^{t_1} p_C(T) dT = \int_{t_2}^{t_1} p(T) dT + \int_0^{t_C} I_C dt \]

where $t_H$ is the heating time from $T_1$ to $T_2$, and $t_C$ is the cooling from $T_2$ to $T_1$.  

40
Subtract the equation (3.15) from the equation (3.14), and set \( Q_H = \int_0^{T_2} I_H dt \) and
\[
Q_C = \int_0^{T_2} I_C dt :
\]
\[
\int_0^{T_2} p_H(T) dT - \int_0^{T_2} p_C(T) dT = \int_0^{T_2} p(T) dT - \int_0^{T_2} p(T) dT + Q_H - Q_C
\]
3.16
\[
\int_0^{T_2} (p_H(T) + p_C(T)) dT = \int_0^{T_2} 2p(T) dT + Q_H - Q_C
\]
Assuming \( Q_H = Q_C \),
\[
\int_0^{T_2} \left[ \frac{p_H(T) + p_C(T)}{2} - p(T) \right] dT = 0
\]
3.17
\[
p(T) = \frac{p_H(T) + p_C(T)}{2}
\]
is one solution of the equation (3.17). If the interval between \( T_1 \) and \( T_2 \) is small enough, it can be considered as \( p(T) = \frac{p_H(T) + p_L(T)}{2} \). We assume that, for the given temperature interval, thermally induced currents will be independent of heating/cooling rate (i.e. amount of charge carriers captured by traps during cooling and released by traps during heating are identical at the same time interval). Therefore, the intrinsic pyroelectric coefficient is \( p = \frac{p_H + p_L}{2} \), the averaged value of the heating and cooling cycles.

3.4.3 Pyroelectric coefficient and figure of merit

Figure 3. 10 shows the magnitude of \( p \), taken as the average of the heating and cooling, in the temperature range from 280 K to 370 K (as was mentioned above, the pyroelectric coefficient is negative for ferroelectrics). At room temperature, the measured
magnitude of $p$ for PZT thin films grown on STO: Nb was 48 nC/cm$^2$K, which are larger than those reported for highly oriented PZT$^{46}$ (26 nC/cm$^2$K) and comparable to Sm-doped$^{47}$ (45 nC/cm$^2$K), Mn-doped (35 nC/cm$^2$K), and Mn- and Sb-co-doped PZT$^{48}$ (45 nC/cm$^2$K) thin films and PZT-based pyroelectric ceramics$^{49}$ (35-40 nC/cm$^2$K). The pyroelectric coefficient observed in our samples is likely due to high crystal quality of the PZT films on closely lattice-matched STO substrates. The weak temperature dependence in the range from 280 - 370 K, implies that the pyroelectricity of the PZT/STO: Nb structure is dominated by the transient, temperature-induced polarization change.

**Figure 3.** Temperature dependence of pyroelectric coefficient of the PZT/STO: Nb heterostructure
In addition, $F_D$, the figure of merit derived from specific detectivity was evaluated:

$$F_D = \frac{p}{[c'(\varepsilon_{\varepsilon} \tan \delta)]^{1/2}}$$

where $c'$ is the volume specific heat ($c'=2.7\times10^6 \text{ Jm}^{-3}\text{K}^{-1}$ for PZT thin films), $\varepsilon$ is the relative permittivity, $\varepsilon_0$ is the vacuum permittivity, $\tan \delta$ is the dielectric loss and $p$ is the pyroelectric coefficient.$^{29,50}$ The values of $F_D$ were found to be $1.89 - 2.60\times10^{-5} \text{ Pa}^{-0.5}$ at 30 Hz, where $\varepsilon$ is 310 and $\tan \delta$ is 0.017 extracted from capacitance-voltage measurements at room temperature.

At different temperatures, the ferroelectric properties of the PZT films were examined by polarization-electric field ($P-E$) measurements. Considering the possibility of $dc$ current leakage at high temperatures, current-voltage measurements have been performed on the PZT thin films at different temperatures. At an applied electric field of 500 kV/cm, leakage current densities as low as $1\times10^{-8} \text{ A/cm}^2$ and $5\times10^{-8} \text{ A/cm}^2$ were observed at 300 K and 400 K, respectively, indicating high dielectric property. At room temperature, the values of remanent polarization were around 45 - 58 $\mu\text{C/cm}^2$, slightly varying among the devices measured. The P-E curves of a PZT/STO: Nb capacitor measured at 260 K and 360 K are shown in Figure 3.11, where the change of temperature dependence is clearly observed in the remanent polarization.
Figure 3. P-E hysteresis loops of a PZT thin film on Nb-doped STO substrate measured at 260 K (dashed) and 360 K (solid). Inset (1) shows the temperature dependence of remanent polarization in the PZT films and inset (2) is a close up of the +P_r region.

The relationship of the ferroelectric polarization and temperature can be expressed by the Landau-Devonshire theory as:\textsuperscript{51}

$$P_s = \sqrt{\frac{a_0(T_0 - T)}{b}}$$

3.19
where \( a_0 \) and \( b \) are the coefficients of the free energy polynomial expansion, \( P_S \) is the spontaneous polarization, and \( T_0 \) is the phase transition temperature (\( T_0 \approx T_C \), \( T_C \) is the Curie temperature). For \( T < T_0 \) (ferroelectric phase), the polarization decreases with increasing temperature in relation to the pyroelectric effect. At a constant external electric field, the pyroelectric coefficient can be expressed simply as the derivative of the spontaneous polarization with respect to the temperature (the primary pyroelectric coefficient, in case the elastic stress is also constant), \( p = dP_S / dT \). The same trend can be obtained by measuring the temperature dependence of the remanent polarization \( P_r \), which corresponds to polarization at zero external electric field. In principle, the temperature dependence of \( P_r \) can be used for estimating the pyroelectric coefficient. For our PZT films, the magnitudes of pyroelectric coefficient estimated from temperature-dependent \( P-E \) measurements range from 10 to 60 nC/cm\(^2\)K from device to device. It should be noted, however, that this approach has some limitations and results in relatively large experimental error. In fact, the value of spontaneous polarization in PZT is about a thousand times larger than that caused by the pyroelectric effect. To obtain a more accurate value of the pyroelectric coefficient, experimental setup-related measurement errors should be minimized. A more significant limitation is related to the asymmetry of the hysteresis loops, as seen in **Figure 3.11**. The difference of \( +P_r \) and \( -P_r \) is up to \( \sim 10 \) μC/cm\(^2\). This asymmetry could be a manifestation of the built-in field in a heterostructure, which may also be temperature dependent, and introduces a large uncertainty into the value of pyroelectric coefficient extracted from the \( P-E \) measurements as the zero applied external
field no longer corresponds to zero net field anymore. In such a case, the pyroelectric coefficients obtained from temperature dependent P-E measurements are not reliable. In our samples, the direction of the built-in field corresponds to the presence of a negative charge on the surface. This asymmetry phenomenon was reported for various heterostructures, such as PZT/SiO$_2$/Si (Ref. 52), PZT/GaN (Ref. 53), and PZT/STO (Ref. 54). In addition to the internal field, dissimilar electrodes, mobile charges, and interface charge traps are also considered as possible sources of the observed asymmetry. The lack of detailed experimental results, however, makes it difficult to quantify their individual contributions to the asymmetry.
Chapter 4 BST Thin Films

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), barium strontium titanate has been the subject of major ferroelectric materials, particularly with the focus on the potential application of tunable microwave devices such as phase shifters, varactors, etc. As a solid solution of BaTiO$_3$ and SrTiO$_3$, BST possesses high dielectric constant and exhibits an ability of tuning dielectric constant with an applied electric field.

In the thin film form, BST is much different with the corresponding bulk material due to the strong coupling between the polarization and the strain of the film. Strain in BST thin films is found to be a significant factor to affect the Curie temperature and dielectric properties. Tailoring strain provides an alternative approach to adjust those properties instead of changing its barium-to-strontium ratio. Introduction of strain in thin films have been developed in semiconductor industry to enhance device performance, as generally referred to strain engineering. It has already been extended to alter some particular properties in ferroelectric materials. Large change of the Curie temperature ($T_c$) and enhancement of ferroelectric properties were found in strained strontium titanate (SrTiO$_3$) and barium titanate (BaTiO$_3$) thin films, which showed much improved ferroelectric and dielectric properties compared to the intrinsic properties of their unstrained bulk materials. \textsuperscript{55,56}
In order to understand strain induced properties of BST thin films, it requires high structural perfection of BST thin films with uniform strain. As a perovskite material, strontium titanate, SrTiO$_3$ (STO) has been widely used as the substrate in oxide epitaxial growth. BST and STO have the similar structure and close thermal expansion coefficient. Thus using STO substrates provides good nucleation basis for high quality BST thin film growth. In this chapter, we firstly describe BST growth by rf sputtering and the structural properties briefly. Then the discussion will be focused on the strain-induced dielectric property, which covers estimation of strain, Curie temperature shift, temperature dependence of dielectric constant and enhanced ferroelectric properties.

4.1 BST epitaxial growth on STO substrates

BST thin films were grown epitaxially by off-axis rf magnetron sputtering using a 3-inch-diamater Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ stoichiometric target. Ar and O$_2$ gases were introduced into the growth chamber through mass flow controllers to keep the growth chamber pressure at 2 mTorr. The use of oxygen for oxide deposition in rf sputtering enhances material oxidation. However, resputtering caused by oxygen ions can deteriorate the crystal quality and lead to off-stoichiometric films. Thus the oxygen flow rate was calibrated carefully to promote high crystal quality and set at a relatively low level of 5 sccm as compared to 30 sccm of Ar to minimize resputtering process. During thin film growth, the substrate temperature was maintained at 750 °C, and the rf sputtering power was set at 120 W. Such
growth condition yielded a deposition rate of BST thin films at around 450 Å/hr. The growth condition is listed in Table 4.1.

Table 4.1 RF magnetron sputtering deposition conditions

<table>
<thead>
<tr>
<th>Target material</th>
<th>Ba$<em>{0.5}$Sr$</em>{0.5}$TiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>2.0 Torr</td>
</tr>
<tr>
<td>Ar</td>
<td>30 sccm</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5 sccm</td>
</tr>
<tr>
<td>RF power</td>
<td>120 W</td>
</tr>
<tr>
<td>Temperature</td>
<td>750 °C</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>45 nm/hr</td>
</tr>
</tbody>
</table>

4.2 Strain induced structural properties of BST thin films

The crystal structure and lattice parameters of the as-deposited BST films were determined by high resolution X-ray diffraction (HRXRD). High quality BST thin films were revealed through $2\theta$-$\omega$ and $\omega$-rocking curve scans of X-ray diffraction. All BST thin films exhibited exclusively (00l) reflections and very high structural perfection. Typical rocking curve full-width at half-maximum (FWHM) is 0.04° (2.4 arcmin) for (001) BST films with a thickness of 500nm or less. Although the increase of thickness reduces the structural perfection of the films due to the generation of misfit and threading dislocations, relatively narrow FWHM was also achieved even for 1000 nm-thick BST films as low as 0.06° (3.6 arcmin). The lattice parameters of the BST thin films were calculated from the symmetric (001) and asymmetric (011) X-ray diffraction patterns. Peak positions of BST films were calibrated as regard to peak positions of STO substrates. Figure 4.1 shows the
symmetric and asymmetric X-ray scans of 150, 300 and 1000 nm-thick BST thin films, which clearly indicates a shift of BST peak as the thickness changes. Both (001) and (011) reflections from BST thin films are shifted to a lower angle than those of the reported bulk BST: (001) 22.493° and (011) 32.031°. As the thickness increases, one can note that the BST peak positions become close to the bulk values.

**Figure 4.1** X-ray diffraction spectrum of BST thin films: (a) symmetric (001) 20-ω scans and (b) asymmetric (011) 20-ω scans

Out-of-plane lattice parameters $c$ of BST films can be calculated directly from the (001) reflections. In-plane lattice parameters $a$ of BST films were derived from the combination of the (011) asymmetric and (001) symmetric reflections, **Figure 4.2** shows lattice parameters $a$ and $c$ as well as $c/a$ ratio as functions of film thickness. As obtained
from the XRD measurement, BST films on STO substrates showed a tetragonal distortion with a large lattice constant $c$ as compared to the bulk ceramics of the same composition. Lattice parameter $c$ shows a remarkable variation (from 4.1390 to 4.0552 Å) with film thickness in the range from 150 nm to 500 nm. Noticeably, the lattice parameter $c$ of 1000 nm-thick film is almost the same as that of 500 nm-thick film. On the contrary, $a$ lattice parameters show a relatively small constant change associated with the thickness. It is suggested that the in-plane lattice parameter $a$ is more confined by the substrate. Similar tetragonal distortion has been reported in the BST films grown on MgO substrates, and it was correlated with the oxygen pressure in the growth due to oxygen vacancies. Oh and et al. reported the distortion of BST grown on MgO by rf magnetron sputtering and found that the low rf power yielded less distorted BST films. In deposition experiments by sputtering, either high oxygen pressure or low rf power can lower the growth rate dramatically. A low growth rate can help to relieve strain in growing film at a relatively high growth temperature. Thus, several factors may act in unison to cause such tetragonal distortion. These factors are generally believed to be the lattice mismatch, the difference of the thermal expansion coefficients, and oxygen vacancies. Most likely, the distortion in our films is associated with lattice mismatch, since the thermal mismatch is believed to be negligible and distortion decreases with increasing film thickness due to strain relaxation.
4.3 Theoretical calculation of strain in BST thin films

The strain state of BST thin films was calculated using the following equations:

\[ x_{12} = (a - a_0) / a_0 \] \hspace{1cm} (4.1)

\[ x_{33} = (c - a_0) / a_0 \] \hspace{1cm} (4.2)

where \( c \) and \( a \) are lattice constants, \( a_0 \) is the freestanding cubic lattice constant of the BST film, \( x_{12} \) is in-plane strain and \( x_3 \) is out-of-plane strain. The freestanding cubic lattice constant \( a_0 \) of the BST film is estimated from

\( \frac{c}{a} \) ratio of epitaxial BST thin films with different thickness.

**Figure 4.2** Lattice parameters \((c, a)\) and \(c/a\) ratio of epitaxial BST thin films with different thickness.
\[ a_0 = \frac{c + 2(c_{12} / c_{11})a}{1 + 2(c_{12} / c_{11})} \]

where \( c_{11} \) and \( c_{12} \) are the averaged elastic constants of bulk BaTiO3 and SrTiO3.\textsuperscript{62} As shown in Figure 4.3, the in-plane strain of BST thin films on STO is highly compressive, which decreases with increasing thickness of the film. Large strain remains in the BST films even as the film thickness is up to 1000 nm, where in-plane and out-of-plane strain are -1.26% and 1.14% respectively.

**Figure 4.3** strain \((x_{12}, x_{33})\) of epitaxial BST thin films with various thickness

### 4.4 Strain enhanced ferroelectric properties

The ferroelectric properties of the BST films were examined by polarization-electric field (P-E) measurements at \( T = 300 \text{ K} \). As seen in Figure 4.4, the 160 nm-thick
BST film, which has the largest tetragonal distortion and strain among the films measured, displays pronounced ferroelectric hysteresis loop with the remanent polarization $P_r = 15 \mu\text{C/cm}^2$. The hysteresis loop for 1000 nm-thick at 300 K is barely detected with a small remanent polarization ($P_r = 1\text{-}2 \mu\text{C/cm}^2$). The results of P-E measurements indicate the strain imposes a large influence on the ferroelectric properties in epitaxial BST thin films.

![Figure 4. 4 P-E hysteresis loops of BST thin films measured at 300 K](image)

**4.5 Temperature dependence of dielectric properties in strained BST**

Measurements of the dielectric permittivity were performed using an HP4284 LCR meter for BST films grown on conductive STO: Nb 0.5% substrates (resistivity $\sim 0.05 \Omega \text{cm}$). The use of conductive STO substrate as a bottom electrode provides a simple and accurate way to examine electrical properties and extract their parameters directly. Au/Cr
(50-nm/30-nm in thickness) circular electrodes were patterned as top electrodes on the top of BST films by using conventional photolithography and lift-off process. The diameter of the top electrode is 200 μm.

In Figure 4.5, C-V measurements show the room-temperature dielectric constant versus electric field for BST thin films at a frequency of 1 MHz with the top electrode connected to the driving voltage and conductive STO to the ground. The applied voltage was swept from -40 V to 40V and then back to -40 V to measure the capacitance which was then used to calculate the dielectric constant. The values of the electric field were converted from the applied voltage and the corresponding thickness of the films. As illustrated in Figure 4.5, except for the curve of 1000 nm-thick film with a slight hysteresis, all curves exhibit pronounced hysteresis behaviors and the shapes of the curves are asymmetric with respect to the position and magnitude of the peaks. The shift of the peak position indicates the enhanced ferroelectric properties which agree well with the founding of P-E measurement. Those properties are resulted from the tetragonal distortion of the strained BST films. However, the difference of the magnitude of the peaks has nothing related to the tetragonal distortion or ferroelectric properties but the dissimilar electrodes. The same influence of the dissimilar electrodes has been discussed in previous chapter for PZT films on conductive STO substrates.
The relative dielectric constant was measured as a function of temperature for a variety of BST thin films with thickness ranging from 160 nm to 1 μm. Figure 4.6 shows the temperature dependence of out-of-plane dielectric constants, $\varepsilon_r$, of BST thin films with the thickness of 160, 250, 500 and 1000 nm measured at 1 MHz. As discussed earlier, the lattice parameters are very sensitive to the thickness due to the relaxation of the thin films. The thinner films (160 and 250 nm), which have a much large tetragonal distortion (large c/a ratio or large strain), show much dissimilar temperature dependence of $\varepsilon_r$ as compared to 500 and 1000 nm-thick films. As seen in Figure 4.6, the values of the dielectric
constant with the thickness of 160 and 250 nm increase steadily with the temperature up to 500 K indicating no sign of any phase transition. The results imply that the Curie temperature ($T_c$) of those strained BST films is much higher than those of bulk BST ($T_c = 250$ K).

\textbf{Figure 4. 6} Out-of-plane dielectric constant in strain BST films as a function of temperature and film thickness.

Theoretical analysis has been proposed based on thermodynamic theory to estimate the Curie temperature of BST thin films under strain.\textsuperscript{63} The in-plane ($x_{\parallel}$) and out-of-plane ($x_{\perp}$) transition strain can be expressed from the equations:
where $T_c$ is the Curie temperature, $C$ is the Curie coefficient, $G_{11}$ and $G_{22}$ are the stress-polarization electrostriction coefficients, $c_{11}$ and $c_{12}$ are the elastic constants. All those parameters are based on the bulk BST, SrTiO$_3$ and BaTiO$_3$. $C$, $G_{11}$, $G_{22}$, $c_{11}$ and $c_{22}$ are the averaged values calculated from BaTiO$_3$ and SrTiO$_3$. The parameters used in the above equations are listed in Table 4.2.

**Table 4.2 Parameters in the transition strain calculation**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (Ba$<em>{0.5}$Sr$</em>{0.5}$TiO$_3$)</td>
<td>250 K</td>
</tr>
<tr>
<td>$G_{11}$</td>
<td>$-0.21658 \times 10^{11}$ N·m$^2$/C$^2$</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>$0.01369 \times 10^{11}$ N·m$^2$/C$^2$</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>$3.11645 \times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>$1.39805 \times 10^{11}$ N/m$^2$</td>
</tr>
<tr>
<td>$C$</td>
<td>$1.15 \times 10^5$ K</td>
</tr>
</tbody>
</table>

Using Equation 4.1 and 4.2, the in-plane and out-of-plane transition strain was plotted as a function of temperature in Figure 4.7. The Curie temperature of strained BST thin films can be predicted accordingly from their strain. For 160 and 250 nm-thick BST films, the out-of-plane strain $x_3$ is 2.54% and 2.09%, respectively. The predicted Curie temperature ($T_c$) is around 1300 - 1500 K, which is far above the measured temperature. On the other hand, for 500 and 1000 nm-thick films, their dielectric properties appear
moderate temperature dependence by comparison. Such weak temperature dependence of dielectric constant is believed to be attributed to the inhomogeneous strain\textsuperscript{64} and occurs normally when the thickness is less than “strain depth” of approximately 300 nm at which the film is generally thought to be fully relaxed. However, the BST thin films on STO substrates appear much large strain even when the thickness up to 1000 nm. Considering this large strain and high crystal perfection, the influence of inhomogeneous strain would be more significant for thicker strained films.

**Figure 4.7** Theoretical in-plane and out-of-plane transition strain of BST films as a function of temperature
4.6 Dielectric constant in strained BST thin films

4.6.1 Dielectric constant as a function of $c/a$ ratio

The values of dielectric constant in our single crystalline thin films are much lower than that in bulk $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and polycrystalline $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films. Small dielectric constant of the BST films agrees well with the theoretical analysis showing that the dielectric constant $\varepsilon_r$ decreases under in-plane compressive strain. It is well-known that increasing film thickness may induce the formation of misfit dislocation which leads a relaxation of the strain. As seen from Figure 4.2, the thicker BST thin film is, the smaller that $c/a$ ratio becomes. The dielectric constant at room temperature is plot as a function of $c/a$ ratio in Figure 4.8. It clearly indicates the trend that the dielectric constant $\varepsilon_r$ decreases with increasing strain under in-plane compressive strain.
4.6.2 Thermodynamic calculation of strained BST thin film

The ferroelectric behavior and phase transition has been investigated and a phenomenological description was developed using the Landau-Devonshire theory. The spontaneous polarization $P=(P_1,P_2,P_3)$ is chosen as the order parameter. According to the theory, the Gibbs free energy ($G$) of a stress-free ferroelectric is written as

$$G(T,P) = F(T,P) - E_i P_i$$

where $F$ and $P_i$ are the Helmholtz free energy and polarization, respectively. When the ferroelectric thin film on a thick substrate is subjected to stresses ($\sigma$), the general expression for the thermodynamic free energy is given by the following Legendre transformation of $G$:66
\[ G^2 = G + u_1 \sigma_1 + u_2 \sigma_2 + u_6 \sigma_6 \]  

where \( u_1, u_2, \) and \( u_6 \) is the in-plane strain. Here, considering the case of (001) ferroelectric thin film on a cubic (001) substrate, we have the in-plane strain of \( u_1 = u_2 \) and \( u_6 = 0 \) where the strain \( u_1 \) and \( u_2 \) can be calculated using Equation 4.4. Using the well-known expression for the elastic Gibbs function of a cubic ferroelectric, the final form of the Gibbs free energy is given by.\(^67\)
\[ G = a_i(P_i^2 + P_i^4 + P_i^6) + a_{ij}(P_i^2 P_j + P_i^4 P_j + P_i^6 P_j) + a_{ijk}(P_i^2 P_j P_k + P_i^4 P_j P_k + P_i^6 P_j P_k) + a_{iij}(P_i^2 + P_i^4 + P_i^6) + a_{iij}(P_i^2 + P_i^4 + P_i^6) + a_{iij}(P_i^2 + P_i^4 + P_i^6) \]

\[ + a_{iij}(P_i^2 + P_i^4 + P_i^6) + a_{iij}(P_i^2 + P_i^4 + P_i^6) + a_{iij}(P_i^2 + P_i^4 + P_i^6) \]

\[ + a_{iij}(P_i^2 + P_i^4 + P_i^6) - \frac{1}{2}s_{ij}(\sigma_i^2 + \sigma_j^2 + \sigma_k^2) - s_{ij}(\sigma_i \sigma_j + \sigma_j \sigma_k + \sigma_k \sigma_i) \]

4. 8

where all of the coefficients \((a_i, a_{ij} \text{ and } a_{ijk})\) except \(a_i\) are assumed to be temperature-independent, \(Q_{ij}\) is the electrostrictive coefficient, \(S_{ij}\) is elastic compliance, and the stress components are eliminated due to the mechanical conditions in the film:

\[ \frac{\partial G}{\partial \sigma_1} = \frac{\partial G}{\partial \sigma_2} = -u_m, \frac{\partial G}{\partial \sigma_3} = 0 \text{ and } \sigma_4 = \sigma_5 = \sigma_6 = 0. \]

Using the aforementioned conditions and assuming the polarization occurs only along the out-of-plane direction \(P=(0,0,P_3)\), Equation 4.8 can be simplified as

\[ G = (a_i - u_m \frac{2Q_{12}}{s_{11} + s_{12}})P_3^2 + (a_{ij} + \frac{Q_{12}^2}{s_{11} + s_{12}})P_i^4 + \frac{u_m}{s_{11} + s_{12}} \]

4. 9

Here, we consider the first-order transition. The transition temperature have to satisfy with \(a_i - u_m \frac{2Q_{12}}{s_{11} + s_{12}} = 0\). Therefore the Curie temperature can be obtained as:

\[ T_C = \theta + u_m \frac{2Q_{12}}{a_0(s_{11} + s_{12})} \]

4. 10

where \(a_0\) is the coefficient of free standing ferroelectric \((a_0 = \frac{1}{\varepsilon_0C}, C\) is the Curie coefficient), and \(\theta\) is the Curie temperature of free standing ferroelectric. Therefore we can
calculate the Curie temperature of the strained BST thin films. Table 4.3 lists the relevant coefficients used in the calculation.

Table 4.3 Relevant coefficients used in the theoretical calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_c (\text{Ba}<em>{0.5}\text{Sr}</em>{0.5}\text{TiO}_3) )</td>
<td>250 K</td>
</tr>
<tr>
<td>( C (\text{STO}) )</td>
<td>0.8 \times 10^5 K</td>
</tr>
<tr>
<td>( C (\text{BTO}) )</td>
<td>1.5 \times 10^5 K</td>
</tr>
<tr>
<td>( s_{11} (\text{STO}) )</td>
<td>3.3 \times 10^{-12} \text{ m}^2/\text{N}</td>
</tr>
<tr>
<td>( s_{12} (\text{STO}) )</td>
<td>-0.74 \times 10^{-12} \text{ m}^2/\text{N}</td>
</tr>
<tr>
<td>( s_{11} (\text{BTO}) )</td>
<td>9.1 \times 10^{-12} \text{ m}^2/\text{N}</td>
</tr>
<tr>
<td>( s_{12} (\text{BTO}) )</td>
<td>-3.2 \times 10^{-12} \text{ m}^2/\text{N}</td>
</tr>
<tr>
<td>( Q_{11} )</td>
<td>-0.1 \text{ m}^4/\text{C}^2</td>
</tr>
<tr>
<td>( Q_{12} )</td>
<td>0.034 \text{ m}^4/\text{C}^2</td>
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The theoretical Curie temperature is shown in Figure 4.9. Compared to the previous prediction using the equation developed by W. Chang et al.,\textsuperscript{63} where the predicted Curie temperature (\( T_c \)) is around 1300 - 1500 K, the Curie temperature here is about 1200 – 1300 K for 2.54% and 2.09% strain of 160 and 250 nm-thick BST films. Both predictions indicate large shift of the Curie temperature. Our predicted values are smaller than the previous ones due to the discrepancy of the reported coefficients used in the calculation.
Figure 4.9 Theoretical Curie temperature as a function of strain
Chapter 5 Integration of ferroelectric & semiconductor materials

5.1 Introduction

Studies of ferroelectrics can be traced back to the early twentieth century. Nowadays ceramic ferroelectric materials have established their technical importance in industry. In thin film form, ferroelectric materials have gradually drawn more attention in recent decades thanks to the advancing of thin film growth techniques making it possible to grow high quality ferroelectric films. Additionally as semiconductor technology has literally penetrated almost all the industries and our everyday life, the majority of applications of ferroelectric thin films are related to semiconductor materials, and the integration of ferroelectric and semiconductor materials is widely studied for developing novel and new generation semiconductor devices. In a sense, ferroelectric applications need to be based on their material properties which in general depend on the crystal quality. However, different crystal structures and lattice mismatch commonly existed in ferroelectric and semiconductor materials raise the challenge to growth high quality ferroelectric thin films. To overcome the barrier in the integration, bridge layers can be employed to promote the growth of ferroelectric thin films. In this chapter, we discuss the employment of bridge layers for PZT and BST thin films growth.
5.2 Integration of PZT and GaN

In recent years, a renewed interest arose in the context of integration of PZT with gallium nitride for the development of the devices. The emergence of this concept is in part due to the properties possessed by GaN such as high thermal and mechanical stability, breakdown voltage, and electron saturation velocity. Therefore, the combination of attractive properties of these two material systems prospects for potentially novel or new generation devices. Studies on the PZT/GaN system have been explored with respect to ferroelectric field effect transistors, ferroelectric gate on AlGaN/GaN two-dimensional gas, microwave devices and electro-optic devices.

Despite the above reports, the integration of PZT with GaN has not yet established much recognition for these potential applications of PZT due in part to the low quality of PZT films on GaN. In other words, the integration concept has so far been limited mainly by the lack of high quality PZT films on GaN. Different crystal structures (perovskite PZT vs. wurtzite GaN) and large lattice mismatch of PZT and GaN materials apparently hampered the pace of this heterostructural growth. Although post-deposition annealing is commonly used to facilitate the formation of perovskite PZT films, which is allowed by high thermal and chemical stability of GaN, diffusion of Pb and Ti into GaN and cracking of PZT films because of the large lattice mismatch act adversely to restrict the high-temperature annealing process. Therefore, it is necessary to incorporate a bridge layer (nucleation or seed layer) between PZT and GaN, which can promote the crystallization of
the perovskite-phase PZT films. Fuflygin et al.\textsuperscript{75} reported the growth of highly (110)-oriented films by employing indium tin oxide (ITO) for (Pb,La)(Ti,Zr)O\textsubscript{3} (PLZT) films on n-GaN/c-sapphire structures, and Masuda et al.\textsuperscript{73} used MgO for Pb(Zr, Ti)O\textsubscript{3} on cubic GaN/GaAs structures to grow preferentially (100)-oriented PZT films. Here, we study on the growth of highly (111)-oriented PZT films on GaN (0001)/c-sapphire by employing of a double PbTiO\textsubscript{3}/PbO bridge layer.

5.2.1 Bridge layer deposition by oxide molecular beam epitaxy

2-µm-thick Si-doped GaN (0001) templates were prepared for PZT growth by metal organic chemical vapor deposition (MOCVD) on c-plane sapphire substrates. These conductive n-type GaN layers also served as the bottom electrode for the electrical characterization of PZT films. The carrier concentration and sheet resistance of the GaN templates were 2×10\textsuperscript{18} cm\textsuperscript{-3} and 30 Ω cm, respectively.

As the first step, the PbTiO\textsubscript{3}/PbO bi-layer buffers were grown by peroxide molecular beam epitaxy (MBE) in the modified Riber 3200 system using a 50% aqueous solution of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) as a source of reactive oxygen. More details of our MBE system as well as the growth technique of PbTiO\textsubscript{3} have been reported elsewhere.\textsuperscript{76} Lead oxide (PbO) was epitaxially grown on GaN as the first layer\textsuperscript{77} followed by PbTiO\textsubscript{3} deposition. Both PbO and PbTiO\textsubscript{3} layers were grown under an H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O vapor pressure of 5×10\textsuperscript{-5} Torr and at a substrate temperature of 580 - 600 ºC. The thickness of PbO and PbTiO\textsubscript{3} thin films were approximate 2 - 3 nm and 10 nm, respectively. Reflection high-
energy electron diffraction (RHEED) monitored the growth of PbO and PbTiO₃ \textit{in situ}, which clearly indicated the RHEED pattern evolution from GaN to PbO and PbTiO₃. As illustrated in Figure 5.1 (a) and (b), the streaky patterns along the \([1\bar{1}00]\) and \([11\bar{2}0]\) azimuths of GaN indicated the two-dimensional growth mode of the PbO film. For the following PbTiO₃ growth, the RHEED patterns partially transformed into three-dimensional one and showed 2-fold surface reconstructions along both the azimuths of GaN [see Figure 5.1 (e) and (f)]. The RHEED patterns of both PbO and PbTiO₃ repeated every 60° during the substrate rotation. This behavior is inconsistent with the symmetries of bulk PbO and PbTiO₃ (cubic and tetragonal, respectively) and may suggest the formation of 60° domains or the pseudomorphic growth in the hexagonal structure.
Figure 5.1 RHEED patterns of PbO and PbTiO$_3$ grown on GaN: (a) GaN [1 1̅00], (b) GaN [1 1̅2 0], (c) PbO parallel to GaN [1 1̅00], (d) PbO parallel to GaN [1 1̅2 0], (e) PbTiO$_3$ parallel to GaN [1 1̅00] and (f) PbTiO$_3$ parallel to GaN [1 1̅2 0]

5.2.2 PZT deposition on GaN with a double bridge layer of PbTiO$_3$/PbO

The GaN templates with PbTiO$_3$/PbO bridge layers were then transferred into the sputtering growth chamber for PZT deposition. PZT films with composition at the morphotropic phase boundary (MPB), Zr : Ti = 52 : 48, were deposited on the MBE grown PbTiO$_3$/PbO bridge layers by radio-frequency (RF) magnetron sputtering at about 600 °C.
using a 3-inch-diameter PZT target comprised 10 mol. % excess PbO to avoid Pb deficiency. In order to avoid possible PbTiO$_3$ decomposition, the substrates with the MBE-grown bi-layer buffer was kept at 6 mTorr during ramping up the temperature in the sputtering chamber. The pressure of 6:1 Ar/O$_2$ gas mixture during the growth of PZT films was 2 mTorr. PZT films (300 - 400 nm) were deposited at 120 W RF power which yielded a growth rate of ~100 nm/hr.

5.2.3 Structural properties of PZT thin films on GaN

The crystal structure and orientation of the as-deposited PbTiO$_3$/PbO and PZT films were determined by high resolution X-ray diffraction (XRD). A pure perovskite phase was observed in the PbTiO$_3$/PbO bridge layer as shown in Figure 5.2(a), corresponding to the PbTiO$_3$ (111) orientation. The 2$\theta$ angle of PbTiO$_3$ (111) reflection located at 39.4º, which was close to the Bragg angle for bulk PbTiO$_3$ (39.17 º) from the international center for diffraction data (JCPDS-ICDD, PDF #780299). The XRD patterns of as-grown PZT films deposited on the PbTiO$_3$/PbO layer are dominated by a peak at 2$\theta$ = 38.2º which is consistent with the (111) reflection of a perovskite PZT with the morphotropic phase boundary composition [see Figure 5.2 (b)]. Three additional weak peaks at 21.7º, 29.5º and 39.4º can be indexed as being associated with PZT (001), pyrochlore, and PbTiO$_3$ (111), respectively. In contrast, PZT films directly grown on GaN without the PbTiO$_3$/PbO bridge layer did not show any perovskite phase reflection. Only a peak at 29.1º corresponding to the reflection of the pyrochlore phase was found in the
XRD patterns (see **Figure 5.2 (c)**). Therefore, the results of XRD measurements strongly suggest that the PbTiO$_3$/PbO seed layer influences the orientation and crystal structure of PZT films and promotes heterogeneous PZT nucleation on GaN. Moreover, the (011) orientation of PZT reported for PZT/GaN structures$^{75,79}$ has not been found in the PZT/PbTiO$_3$/PbO/GaN films. XRD pole figure analysis was performed to investigate the in-plane epitaxial relationship between the PZT and GaN films. The reflection planes were GaN (10$ar{1}$2) and PZT (100) with the center $\Psi$ angles of 43.2° and 54.5°, respectively.
Figure 5.2 X-ray diffraction patterns of (a) PbTiO$_3$/GaN, (b) PZT/PbTiO$_3$/PbO/GaN and (c) PZT/GaN structures
As seen from Figure 5.3, a six-fold symmetric reflection was found for PZT (100) with the same $\Phi$ angles as for GaN (10$\bar{1}$2). It is in agreement with the RHEED data revealing the six-fold symmetry for the nucleation layers. The result suggests the existence of two sets of domains, which are rotated by 60º with respect to each other. Therefore, the in-plane epitaxial relationships can be established as follows: PZT [112]/GaN [1$\bar{1}$00] and PZT [1$\bar{1}$0]/GaN [1120]. The same epitaxial relationships have been reported by S. Key et al.\textsuperscript{80} for PZT films grown on GaN (0001) by MOCVD.

![Figure 5.3 XRD pole figure scan of Pb(Zr$_{0.52}$,Ti$_{0.48}$)O$_3$ on (0001) GaN with a double PbTiO$_3$/PbO bridge layer](image)

Figure 5.3 XRD pole figure scan of Pb(Zr$_{0.52}$,Ti$_{0.48}$)O$_3$ on (0001) GaN with a double PbTiO$_3$/PbO bridge layer
5.2.4 Electrical and ferroelectric properties of PZT thin films on GaN

Capacitor structures of PZT on GaN were fabricated to characterize the electrical properties of the PZT films, the schematic diagram for which is illustrated as an inset in Figure 5.4. Au/Cr circular top electrodes of 30 nm/30 nm in thickness and 150 µm in diameter were defined on the PZT layer by photolithography, e-beam evaporation, and lift-off. Current-voltage measurements of the PZT films showed leakage current densities of 2x10⁻⁷ A/cm² at electric fields of 200 kV/cm and 1x10⁻⁵ A/cm² at 500 kV/cm. The ferroelectric properties of the PZT films were examined by polarization-electric field (P-E) measurements at a frequency of 1 kHz with the top electrode connected to the driving voltage.

Figure 5.4 shows a P-E curve for the PZT/PbTiO₃/PbO/GaN structure that is indicative of a remarkably good ferroelectric behavior. Large values of remanent polarization were obtained with +P_r = ~ 40 µC/cm² and –P_r = ~30 µC/cm². The polarization switched abruptly near the coercive fields and the associated steep slopes further indicate the formation of highly oriented perovskite PZT films on GaN. In addition, it can be seen clearly that the hysteresis loop is asymmetric; and it has an extraordinarily high coercive field of 950 kV/cm under reverse bias, whereas the positive coercive field is only 165 kV/cm. The asymmetry of P-E curves has also been reported previously for PLZT/GaN⁷⁵ and PZT/SiO₂/Si⁸¹ structures. Such an asymmetry can be explained using an approach analogous to a metal-insulator-semiconductor (MIS) structure. Ideally, neglecting any work-function differences, the applied voltage will be shared by the insulator and the semiconductor. When the top electrode is connected to the positive terminal of the driving voltage
voltage, an accumulation of electrons occurs in the n-type GaN layer. As a result, the total voltage appears mostly across the insulator, namely PZT layer. However, for the negative driving voltage, a depletion region is formed in series with the PZT layer near the GaN surface and causes part of the voltage to drop across this depletion region. Consequently, the P-E curve becomes asymmetric which manifests itself as a relatively larger coercive field under the reverse bias as compared to the forward bias.

![P-E hysteresis curve of Pb(Zr0.52,Ti0.48)O3 on Si-doped GaN](image)

**Figure 5.4** P-E hysteresis curve of Pb(Zr0.52,Ti0.48)O3 on Si-doped GaN

### 5.3 Asymmetric hysteresis loop and theoretical analysis

The asymmetry of P-E curves discussed in the previous section is not unique behavior of PZT/GaN structures, which is also found in PZT/STO:Nb structures. Such an
asymmetry is commonly attributed to the dissimilar electrodes and the mechanism is not clearly understood. Here, using the physical model developed by Miller et al.,\textsuperscript{82} the ferroelectric capacitor structure is characterized quantitatively to determine the contributions of the asymmetric behavior. The basic model related to field-dependent ferroelectric polarization was employed, which is capable of modeling the effects of trapped space-charge, nonswitching dielectric layers, and other non-ideal physical properties of the ferroelectric. Associated with a circuit simulation of the Sawyer-Tower circuit (\textbf{Figure 5. 5}),\textsuperscript{82} the model is able to demonstrate the P-E characterization analytically.

\begin{center}
\textbf{Figure 5. 5} Diagram of Sawyer-Tower circuit for P-E measurement
\end{center}

In the ferroelectric capacitor structures of PZT/GaN and PZT/STO:Nb, the bottom electrodes are conductive Nb-doped STO substrate or Si-doped GaN layer which both have
n-type conductivity. A negative bias applied to the top electrode forms more or less a depletion layer in the STO substrate and GaN layer. Hence, the electric field distributed in the depletion region has to be considered accordingly. Although it is difficult to extract the related parameters of STO:Nb and highly doped GaN for accurate modeling, a simple and well-defined ferroelectric capacitor model is able to characterize its ferroelectric behavior. As shown in Figure 5.6, the buffer layer of PTO/PbO in case of PZT grown on GaN manifests itself as a nonswitching dielectric layer, which is also used as a substitute for the depletion layer in PZT/STO:Nb and PZT/GaN under the reverse-bias conditions.

![Figure 5.6 Schematic of a physical model for a ferroelectric capacitor with a dielectric layer and interface charges (σi: interface charge density at the dashed line)](image)

In our analysis, the trapped interface charges were placed between the ferroelectric PZT and the dielectric layer. The thickness and dielectric constant of the ferroelectric layer, respectively, are $d_1$ and $\varepsilon_1$, and those of the dielectric layer are $d_2$ and $\varepsilon_2$. The electric displacement vectors $\mathbf{D}$ in the ferroelectric and dielectric layers are both perpendicular to the plane of the electrode and are defined as
\[ D_1 = \varepsilon_1 \varepsilon_0 E_1 + P_1 \]  
\[ D_2 = \varepsilon_2 \varepsilon_0 E_2 + P_2 \]

where \( P_1 \) is the electric polarization of the ferroelectric material which depends on the electric field, and \( P_2 \) is the polarization of semiconductor, which is zero in the case of the non-polar semiconductor. Assuming that there are trapped interface charges at the interface with a density of \( \sigma_i \), the displacement vectors can be derived from the full set of Maxwell equations as:

\[ D_2 = D_1 + \sigma_i \]

Utilizing charge conservation law, the voltage applied to the whole ferroelectric capacitor structure can be expressed as:

\[ V = E_i (d_1 + \varepsilon_1 d_2) + \frac{1}{\varepsilon_2 \varepsilon_0} (P_1 - P_2 + \sigma_i) d_2 \]

In accordance with the Sawyer-Tower circuit model, the electric field dependence of the ferroelectric polarization \( P_d \) was calculated. In order to obtain the behavior of the polarization, a hyperbolic tangent function is used:

\[ P_d(E) = P_{sat} \tanh \left[ \frac{E - E_c}{2\delta} \right] \]

where \( \delta = \varepsilon_0 [\log \left( \frac{1 + P_r/P_{sat}}{1 - P_r/P_{sat}} \right) ]^{-1} \) and \( P_r, P_s \) and \( E_c \) refer to remanent polarization, saturation polarization, and coercive field, respectively.

The polarization switching in the ferroelectric/semiconductor structure is affected by the semiconductor depletion layer under reverse bias. Thus, the hysteresis behavior is
simulated to characterize the contribution of the trapped interface charges and depletion layer only as the applied voltage sweeps from positive to negative. At first, the affects from trapped interface charges and dielectric layer is considered separately. In the absence of dielectric layer, the affect of the trapped interface charges is totally diminished because in the equation 5.4, $d_2$ is equal to zero and interface charges have no contribution to the applied voltage theoretically. Combining the equation 5.4 and 5.5, the hysteresis behaviors can be predicted as shown in Figure 5. 7 which shows the hysteresis loops in the cases (a) without the dielectric layer and interface charges, (b) with the dielectric layer, and (c) with the dielectric layer and interface charges. It is clear that the dielectric layer alone can lead an asymmetric loop but play minor influence on the coercive fields. A large shift of the coercive field is found under the combined influences of the trapped interface charges and the depletion layer.

![Figure 5.7](image_url)
Figure 5.7 Simulated P-E hysteresis loops of a ferroelectric capacitor: (a) without dielectric layer and interface trapped charge, (b) only with dielectric layer, and (c) with both dielectric layer and interface trapped charges.

The simulated results represent the salient features of the measured data in Figure 5.8. In the case of integration of PZT and GaN, the interface charges in the muti-layer structure incorporating the PTO/PbO buffer would have a much stronger influence on the coercive field, which was observed to increase $E_c$ from 200 kV/cm to 900 kV/cm. The STO:Nb substrates have much lower resistivity that reduces the electric field distribution in STO:Nb substrates and additionally, better crystal structure of PZT films grown on STO give rise to less interface charges as compared to PZT/GaN. Thus, it may explain the reduced asymmetry of $P-E$ curves for the PZT/STO:Nb structure.
Figure 5.8 Measured $P-E$ hysteresis loops of (a) PZT/(001) STO:Nb(001) and PZT/PTO/PbO/GaN/c- sapphire. The insets shows the structures of the ferroelectric capacitors.

5.4 Epitaxial growth of BST thin films on sapphire substrate

Utilizing the unique dielectric property that the dielectric permittivity strongly depends on applied electric field has opened a door for the realization of ferroelectric microwave devices. The desire to achieve miniaturization of microwave components and systems is leading the reemerging ferroelectric microwave application to eye the development of thin film ferroelectric materials. By far, $\text{Ba}_{x}\text{Sr}_{1-x}\text{TiO}_3$ (BST), as one of most studied ferroelectric materials, has attracted an increasing attention towards this application. Besides of large tunable dielectric constant, tunable microwave devices
practically require low loss tangent, which to some extent is affected by the substrate material. BST thin films have been extensively studied to grow on a variety of substrates such as MgO, LaAlO$_3$, SrTiO$_3$ and sapphire. By comparison, sapphire is an excellent candidate with respect to its low cost and chemical stability, especially low loss tangent. However, the integration of BST thin films on sapphire has not yet achieved its potential status in microwave applications of BST due largely to the low quality of BST films on sapphire. Large lattice mismatch and different structures of BST and sapphire apparently are not in favor of epitaxial BST thin film growth. As discussed in the integration of PZT and GaN, a proper bridge layer can be a good solution for the integration of BST and sapphire. Therefore, several bridge layers which have been obtained by MBE have been tested for this purpose, and it was found that an MgO/ZnO bridge layer serves well as a nucleation layer to promote high quality (001)-oriented BST films on $a$-plane sapphire.

### 5.4.1 BST sputtering growth and MgO/ZnO bridge layer prepared by MBE

Double MgO/ZnO bridge (or buffer) layers were grown epitaxially on $a$-plane sapphire by radio-frequency (rf) plasma-assisted molecular beam epitaxy (MBE). The ZnO layers were grown at an oxygen pressure of $2 \times 10^{-5}$ Torr. First, low-temperature ZnO buffer ~10 nm thick was grown at a substrate temperature, $T_S$, of 300 °C followed by annealing at 700 °C, then high-temperature ZnO layer was grown at $T_S =550$ °C. The MgO layer was grown at $T_S = 450$ °C and an oxygen pressure of $9 \times 10^{-6}$ Torr. The thickness of ZnO and MgO thin films were about 50 nm and 10 nm, respectively. The growth progression monitored by in-situ reflection high-energy electron diffraction (RHEED) indicated
clearly the formation of (0001)-oriented ZnO and (001)-oriented MgO. As illustrated in Figure 5.9 (a) and (b), the streaky patterns along the [11 \bar{2} 0] and [\bar{1}100] azimuths of ZnO pointed to the two-dimensional growth mode of the ZnO film. As shown in Figure 5.9 (c) and (d), the MgO film shows the same RHEED pattern along the both azimuthal directions of ZnO; that is, the pattern repeated itself every 30° of substrate rotation. These patterns are consistent with those taken along the [110] azimuthal directions of (001)-oriented MgO films. The pattern characteristic of [100] azimuth of MgO appears to be rotated by 15° from the [110] direction (see Figure 5.9 (e)). The observed behavior is inconsistent with the cubic symmetry of MgO and most likely points to the formation of three sets of 30° domains of (001) MgO. As we will demonstrate below, this assumption is supported by high-resolution X-ray diffraction (HRXRD) measurements.
Figure 5. RHEED patterns of MgO and ZnO grown on a-sapphire: (a) ZnO [11\(\bar{2}\)0], (b) ZnO [1\(\bar{1}\)00], (c) MgO parallel to ZnO [11\(\bar{2}\)0], (d) MgO parallel to ZnO [1\(\bar{1}\)00], (e) MgO rotated by 15° regarding to ZnO [1\(\bar{1}\)00] and [11\(\bar{2}\)0] azimuths.

The ZnO templates with the MgO buffer layer were then transferred into the sputtering growth chamber for BST deposition. BST films with the composition of Ba : Sr = 50 : 50, were deposited on the MBE grown MgO/ZnO layers by radio-frequency (rf) magnetron sputtering at about 700 °C. In order to avoid possible MgO decomposition, the substrates with the MBE-grown layers was kept at 6 mTorr during ramping up the temperature in the sputtering chamber. The pressure of 6:1 Ar/O2 gas mixture during the growth of BST films was 2 mTorr. BST films (350 - 400 nm) were deposited at 120 W rf power which yielded a growth rate of ~80 nm/hr.
5.4.2 Structural properties and epitaxial relationship

High-resolution X-ray diffraction (HRXRD) was employed to evaluate thin film quality and determine the structural properties of the BST thin film. As seen in Figure 5.10, 2θ-ω scan of XRD shows the reflections from the thin films of ZnO, MgO, and BST. The MBE-grown ZnO layer shows the (0002) reflection at 34.47°. Although the MgO layer is thin (10 nm), a weak diffraction peak consistent with the (002) MgO reflection can be seen at 49.32° in Figure 5.10. Only (00l) reflections from BST thin films are observed. The absence of other reflections, such as (111) or (011), indicates that the [001] axes of BST films are well aligned with [0001] ZnO. The full-width at half-maximum (FWHM) of the BST (001) rocking curve is around 0.5° for the 300 nm-thick BST film. The peak positions of HRXRD reflections from the BST films were calibrated using the reflections from the a-plane sapphire substrate as a reference. The out-of-plane lattice parameter c of BST was found to be 3.993 Å. This lattice parameter is larger than that of bulk BST. Similar structural parameters have been reported for BST films grown on MgO substrates, and in those cases, the large lattice parameters that were observed were correlated to the oxygen pressure during growth presumably due to the generation of oxygen vacancies. In addition, there are other factors such as lattice mismatch, difference of the thermal expansion coefficients which would cause such tetragonal distortion.
Figure 5. 10 $\theta$-ω scan of the epitaxial BST/MgO/ZnO film on a-plane sapphire substrate

$\Phi$ scans of XRD reflections were also performed to determine the in-plane epitaxial relationships of BST, MgO, and ZnO layers on a-plane sapphire. As we found from $\Phi$ scans of the (10 12) and (11 22) ZnO reflections and the (10 13) and (11 23) sapphire reflections (see Figure 5. 11 (a) and (b)), the in-plane epitaxial relationships for ZnO on a-plane sapphire are ZnO [11 2 0]//a-sapphire [0001] and ZnO [1 1 0 0]// a-sapphire [1 1 0 0], which is consistent with previous reports.\textsuperscript{87,88} Figure 5. 11 (b) also shows the diffraction profiles of BST (022), ZnO (1 1 2 2), and sapphire (1 1 2 3) reflections along the azimuthal circle $\Phi$. The $\Phi$ scan of BST (022) shows twelve reflected peaks rotated by 30° with respect to each other, which indicates the existence of three sets of BST domains. The results of BST $\Phi$ scans suggest the in-plane relationship of BST and ZnO to be BST
[110]/ZnO [11 2 0] and BST [110]/ZnO [1 1 0 0]. One should note that a thin MgO layer
was grown between BST and ZnO. Although X-ray diffraction is not able to detect the
asymmetric diffraction from MgO thin film due to its low thickness, the above-mentioned
results of RHEED indicate the same in-plane epitaxial relationships for the MgO layer on
ZnO as those found for BST from XRD $\Phi$ scan. Namely, the twelve-fold symmetry is
found for the MgO films, and the [110] directions of MgO are parallel to the [11 2 0] and
[1 1 0 0] directions of ZnO. Thus, it suggests that the BST film follows the in-plane
alignment of the MgO on ZnO template, the in-plane epitaxial relationships for the BST
film and the MgO/ZnO bridge layer are BST [110]/MgO[110]/ZnO [11 2 0] and BST
[110]/MgO[110]/ZnO [1 1 0 0].
Figure 5. Φ scan patterns of asymmetrical reflections of (a) ZnO (1012) and \(a\)-sapphire (10\(\overline{1}3\)), (b) BST (022), ZnO (11\(\overline{2}2\)) and \(a\)-sapphire (11\(\overline{2}3\))
Figure 5.12 displays one possible in-plane alignment of BST and MgO lattices on ZnO. The unit cells of ZnO and BST (or MgO) are represented by hexagonal dash lines and square solid lines, respectively. This alignment shows the [110] directions of BST or MgO are parallel to ZnO [11 \overline{2} 0] that satisfies our founding of 15° rotation of the [100] direction of BST and MgO respecting to the [11 \overline{2} 0] directions of ZnO (or 15° rotation of the reflections of BST/MgO (011) respecting to the reflections of ZnO (11 \overline{2} 2)) as shown in Figure 5.9 and Figure 5.11. In addition, the Φ scans reveal three sets of domains with 30° rotation with respect to each other. Therefore, other two epitaxial alignments can be achieved by 30° and 60° rotation of the BST/MgO alignment of Figure 5.12.

Figure 5.12 In-plane epitaxial relationship between BST/MgO (001) and ZnO (0001)
5.4.3 Electrical properties of BST thin film

The interdigitated capacitor structures (IDCs) were defined on the BST thin films using photolithography and lift-off process in order to investigate their dielectric characteristics. The IDC structures have a total of 10 fingers with a finger width of 5 µm, a gap of 5 µm, and an aperture length of 75 µm. Capacitance–Voltage (C-V) measurements were performed by Hewlett-Packard 4284 LCR meter at 1 MHz. The voltage applied to the fingers was swept from -30 V to 30 V. As seen in Figure 5.13, the BST thin film on a-sapphire exhibits pronounced dielectric tuning. The maximum capacitance is 3.67 pF around zero bias and the minimum one is 0.57 pF at 30 V, which translates into a tunability of about 84 % using the equation: \( T = \frac{C_{\text{max}} - C_{\text{min}}}{C_{\text{max}}} \times \% \). Dissipation factor (loss tangent, \( \tan \delta \)) was also measured as a function of bias (also shown in Figure 5.13). At magnitudes of bias voltages larger than 5 V, loss tangent is around 0.007 - 0.02. However, loss tangent increases to 0.27 at about 4 V and drops to 0.15 gradually as the bias approaches zero. This change in dissipation factor is most likely caused by the contribution of ZnO layer and its large depletion capacitance at low biases. Large bias leads to the depletion of ZnO layer and lower its conductivity. However, those contributions of ZnO may increase dramatically regarding to the total IDC structure as the bias approach to zero. Therefore further investigation is desired to improvement the quality of ZnO buffer layer and lowers its conductivity.
Figure 5.13 C-V measurement of BST/MgO/ZnO/α-sapphire.
Chapter 6 Ferroelectric field effect transistor

Nonvolatile memories using ferroelectric materials have been merited much attention in recent years, which in principle can remain the data intact that occurs even if the power is switched off and also can achieve fast memory access time. Thus a great effort has been done on studying the ferroelectric materials such as Pb(Zr1-xTi_x)O3 (PZT), (Sr, Bi)3Ta2O9 (SBT), (Bi, La)Ti3O7 (BLT), Sr2Nb2O7 (SNO), BaTiO3, KNO3 and so on for the ferroelectric memory application. Among these materials, lead zirconate titanate (PZT), as a ferroelectric material extensively studied, is one of the promising candidates for the ferroelectric memory thanks to its attractive ferroelectric properties given the high remnant polarization. Besides enormous exploration of PZT with Si-based technology, there is an interest arising in the context of integration of PZT with gallium nitride for potentially novel or new generation devices due to the properties possessed by GaN such as high thermal and mechanical stability, breakdown voltage, and electron saturation velocity. These robust properties also make GaN an ideal platform in harsh environment such as radiation where the radiation hardness of a ferroelectric memory depends on the underlying control circuitry. Studies on the PZT/GaN system have been carried out recently.

Amidst the device structures for the ferroelectric random access memory, the 1 transistor/1 capacitor (1T/1C) is the most commonly used one in which each memory cell
is constructed by one transistor and one ferroelectric capacitor. Data in the 1T/1C cell is stored in the polarized ferroelectric capacitor and the data path is controlled by the transistor commonly known as a transmission gate coupled to a bit line and a word line. This conventional 1T/1C cell, however, suffers from the size limitation and destructive readout.\textsuperscript{96} To achieve smaller size and nondestructive readout, one transistor (1T) structure has been proposed and developed, which is in general a metal-oxide-semiconductor field effect transistor (MOSFET) combining with a ferroelectric gate. The polarized ferroelectric gate provides a reversible electric field in the conductive channel to control the source-drain current.

### 6.2 MFS structure ferroelectric field effect transistors

Figure 6.1 shows the cross-section schematic of the ferroelectric field effect transistor (FeFET). PZT thin films were deposited on the AlGaN/GaN 2-dimensional electron gas (2DEG) with an insertion layer Si$_3$N$_4$ preventing the interaction between PZT and GaN. This structure configuration is generally called as metal-ferroelectric-semiconductor (MFS) structure, and metal-ferroelectric-metal-semiconductor (MFMS) structure will be discussed later in this chapter to compare the performance of both structures.
6.1.1 PZT Thin film preparation on AlGaN/GaN HFET

AlGaN/GaN MODFETs were grown on 2-inch (0001) sapphire substrates in a custom designed vertical low-pressure metalorganic chemical vapor deposition (MOCVD) system. Trimethylgallium (TMGa), trimethylaluminum (TMAI), silane (SiH₄) and ammonia (NH₃) were used as sources for Ga, Al, Si and N, respectively. The growth was initiated with a ~200 nm high temperature AlN nucleation layer grown at ~ 1050 ºC, followed by ~ 4 µm GaN buffer layer, and ~ 1 nm AlN interlayer. The barrier consisted of 10 nm undoped Al₀.₂₅Ga₀.₇₅N and 15 nm Si doped Al₀.₂₅Ga₀.₇₅N capped by 2 nm undoped GaN. The doping level in the barrier was ~ 1×10¹⁸ cm³. More details can be found elsewhere. The measured carrier concentration and Hall mobility of the 2-dimensional
electron gas (2DEG) in the AlGaN/GaN MODFET were $1.6 \times 10^{13}$ cm$^{-2}$ and 900 cm$^2$/Vs at room temperature, respectively.

The 50 nm thickness PZT layer was grown on 10 nm thick Si$_3$N$_4$ by rf magnetron sputtering from a 3” diameter Pb$_{1.1}$(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ target. The Si$_3$N$_4$ film was deposited by plasma enhanced chemical vapor deposition technique (PECVD). The Si$_3$N$_4$ layer with bandgap energy $E_g \approx 5$ eV was inserted as a buffer layer between Al$_{0.3}$Ga$_{0.7}$N ($E_g \approx 4.3$ eV) and PZT ($E_g = 3.6 \sim 3.8$ eV) to chemically isolate it from the underlying AlGaN. The substrate temperature, RF power, system pressure, Ar/O$_2$ flow ratio, and substrate-target distance during PZT growth were 650°C, 100W, 3 mTorr, 50/10 sccm, and 10 cm, respectively.

6.1.2 Structure properties of PZT films on AlGaN/GaN

The crystal structure of PZT on AlGaN/GaN was evaluated by X-ray diffraction (XRD) for a PZT thin film with the thickness of 300 nm, which was deposited at the same growth condition as that of the 50 nm gate PZT layer. In Figure 6.2, a highly oriented (111) peak was observed at 38.1°, and two weak peaks were found at about 28.3 ° and 29.5 ° which are due to the pyrochlore phase and the (001) PbO phase. As aforementioned, PZT layers grown at 600 °C were polycrystalline in nature without any preferred orientation. It should be noted that there are efforts to reduce the PZT deposition temperatures in the context of integration with silicon-based technology. However, temperatures as high as 650 °C do not represent any bottleneck for GaN based technology, as GaN is highly stable at high temperatures.
Figure 6.2 X-ray diffraction 2θ−ω scan of the PZT thin film on the AlGaN/GaN/c-plane sapphire substrate

6.1.3 Fabrication of PZT ferroelectric FET

Device fabrication was carried out after the completion of all the growth to avoid degradation of the device performance caused in the growth, especially oxidation in PZT sputtering growth. Firstly, the devices were isolated to each other by reactive ion etching (RIE) using BCl$_3$ to obtain the FET mesa structure. Source and drain electrodes were then patterned and Ti/Al/Ti/Au (300 Å/1000 Å/300 Å/300 Å) ohmic contacts were deposited. To form good ohmic contacts, the devices were treated by rapid thermal annealing (RTA) at 900 °C in nitrogen ambient for 60 s. Finally, Ni/Au (300 Å/800 Å) contacts were
deposited to make the gate electrodes. The details of the flow of the fabrication are demonstrated in Figure 6.3.

![Fabrication flow of the ferroelectric FET](image)

**Figure 6.3** Fabrication flow of the ferroelectric FET

### 6.1.4 Electrical characteristics of PZT/AlGaN/GaN ferroelectric FET

The current-voltage characteristics of the transistors with or without the PZT layer are shown in the Figure 6.4. Both devices have the same structures with 7 µm gate length and 80 µm gate width. A higher \( V_{GS} \) is needed to control the current of the ferroelectric FET compared to the conventional FET due to the voltage drop across the PZT/Si\(_3\)N\(_4\) stack. **Figure 6.4** demonstrates the current saturation phenomenon very well for the two devices at low gate voltages, indicating a typical drain characteristic for an AlGaN/GaN
field effect transistor. The most critical parameters are the thicknesses of PZT, Si$_3$N$_4$ and AlGaN layers (doping levels when applicable) which require further optimization for better performance.
Figure 6. 4 $I_D$-$V_{DS}$ characteristics of the AlGaN/GaN field effect transistors without (a) and with (b) PZT layer

Figure 6. 5 shows the $I_{DS}$ – $V_{GS}$ transfer characteristics for the conventional HFET and FeFET. The gate voltage was increased from the initial -10 V to +10 V, and then back to -10 V. Meanwhile the source-drain current was measured at $V_{DS} = 8$ V. A counter clockwise hysteresis loop was observed as a result of switching effect of the ferroelectric gate. The maximal drain current shift ($\Delta I_D$) is about 10 mV at $V_{GS} = -6$ V, and the channel conductance modulation was estimated to be about 50% which is comparable to the best FeFETs reported.\textsuperscript{100,101} On the other hand, the AlGaN/GaN HFET shows a negligibly small clockwise hysteresis due to trapped interface charges. Clockwise hysteresis has been reported previously for PZT/Al$_2$O$_3$/SiC and SrBi$_2$Ta$_2$O$_9$/Si$_3$N$_4$/Si structures, and it was interpreted as arising from the transfer of free carriers in the channel into the traps at the ferroelectric/semiconductor interface.\textsuperscript{102} In AlGaN/GaN HFETs, the trapping of free
carriers may occur in AlGaN, in GaN buffer and the surface. The negative transconductance \( g_m = \left( \frac{\partial I_D}{\partial V_{GS}} \right) V_{DS} \) when \( V_{GS} > 4 \) V, which is observed in the HFET structure, may arise from the carrier injection from 2DEG into AlGaN for the large gate-to-source voltage, causing a parasitic current conduction path in low mobility AlGaN layer,\(^{103}\) and heating effects as the sapphire substrate is a poor heat conductor. The counter clockwise hysteretic loop presented in the FeFET which is absent in the conventional HFET strongly suggests that the ferroelectric domain switching in PZT controlled the \( g_m \) of 2DEG channel.

Figure 6.5 \( I_D-V_{GS} \) transfer characteristics of the field effect transistors
6.2 MFMS structure ferroelectric FET

Based on the 1T concept of the current modulation through the ferroelectric material, we demonstrate a modified ferroelectric FET structure, metal-ferroelectric–metal-semiconductor (MFMSFET). As shown in the schematic diagram of Figure 6.6, the ferroelectric PZT between two metal electrodes is overlying directly on the AlGaN/GaN 2-dimensional electron gas (2DEG) channel. Through proper electrical connections, the PZT layer would be operated independently as a single ferroelectric capacitor to realize the polarization switch through the top and bottom electrode. Without this bottom electrode, it is a common metal-ferroelectric-semiconductor (MFSFET) structure in which the voltage for switching polarization is not only across the ferroelectric but the semiconductor. Therefore a higher voltage is required for the conventional MFSFET structure especially when a depletion region in the semiconductor is formed along this switching voltage. On the other hand, the bottom electrode can also serve as a barrier to prevent the chemical interaction or the diffusion at the interface between the ferroelectric layer and the semiconductor.

By introducing an insulator layer to eliminate the interface problems, similar structures have been developed such as metal-ferroelectric-insulator-semiconductor (MFIS) and metal-ferroelectric-metal-insulator-semiconductor (MFMIS). Unfortunately both of the structures involve a new obstacle concerning the increasing gate threshold
voltage on account of the formation of two series capacitors. Hence, the using of a Schottky FET overcomes the hurdles ahead of the conventional 1T structure.

![Figure 6.6 Schematic of MFMFET structure AlGaN/GaN ferroelectric MODFET](image)

6.2.1 PZT thin film preparation

Preparation of AlGaN/GaN 2DEG structure is the same as aforementioned for MFS structure FeFET. Hall measurements revealed that the sheet carrier density was $1.2 \times 10^{13}$ cm$^3$ with Hall mobility $\sim 1430$ cm$^2$/Vs at room temperature. Schottky contacts of Ni (30 nm) / Au (30 nm) were fabricated on the AlGaN/GaN heterostructure by e-beam evaporation. Aside from forming a Schottky gate, the Ni/Au multiply metal layer also serves as a bottom electrode and a barrier, which plays a very important role to prevent the interaction between PZT and GaN. Moreover, fatigue behavior of PZT is partially
influenced by the metal of electrodes owing to the interface or metal diffusion. To improve the performance, further investigation is needed to study the metal electrodes.

The gate patterned AlGaN/GaN heterostructure was then transferred into the sputtering growth chamber for PZT deposition. During the growth, the pressure of 6:1 Ar/O₂ gas mixture was kept at 2 mTorr, while the rf power was set at 120 W. Although high growth temperature can facilitate high quality PZT, the substrate temperature remained low at ~350 °C in order to alleviate the degradation of Ni/Au contacts at oxygen plasma ambient. To enhance the crystallinity of the PZT, the samples were subsequently annealed at 600 °C in air. Then top electrodes, source and drain contacts were fabricated using Ti/Au (30 / 100 nm).

6.2.2 Structural properties of PZT thin films

The structural characteristics of the PZT film grown on AlGaN/GaN heterostructure were examined by high resolution X-ray diffraction (XRD). A PZT perovskite phase was observed as illustrated in Figure 6.7, corresponding to the PZT (111) reflection. The 2θ angle of PZT (111) reflection located at 38.4°, which is consistent with the (111) reflection of the perovskite PZT with the morphotropic phase boundary composition. One weak peak at 31.2° was observed as well, which would correspond to the (011) reflection of PZT as reported. A peak at 28° also was observed in some samples grown at the same condition which would correspond to the pyrochlore phase or extra PbO due to the low growth temperature.
6.2.3 Electrical characteristics of MFMS FeFET

The basic current-voltage characteristic of the PZT ferroelectric FET is shown in Figure 6.8, where the source-drain current is plotted versus the source-drain voltage at various gate voltages applied on the top electrode. For the device measured here, the gate length, width and the spacing between source and drain are 2 µm, 140 µm and 5 µm, respectively. The source-drain current shows the pinch-off characteristic at ~ 7 V where the maximum transconductance $g_m$ is ~ 30 mS/mm. As the source-drain voltage is increasing beyond the pinch-off value, it also shows the typical self-heating effect associated with a decreasing of carrier mobility at zero gate bias. This effect would not be found if there is a large leakage path from source and drain formed at the interface between
GaN and PZT. Additionally, the gate leakage current has been measured which remains at a low level of $2 \times 10^{-8}$ A/mm.

**Figure 6.8** $I_D-V_{DS}$ characteristic of AlGaN/GaN ferroelectric MODFET

The modulation of source-drain current through the ferroelectric PZT layer was examined by the transfer characteristics of $I_{DS}$ vs. $V_G$. At a fixed source-drain voltage ($V_{DS} = 7$ V), the gate voltage, which is applied to the top electrode, is swept from -15 V to 15 V and then back to -15 V with a voltage step of 0.1 V. As seen in **Figure 6.9**, the resulting plot of $V_G$ vs. $I_{DS}$ exhibits a hysteresis loop with a counterclockwise trace that clearly indicates the ferroelectric modulation of source-drain current. At zero gate bias, it’s observed that the source-drain current was shifted about 10 mA from 10.5 to 20.2 mA.
6.3 Comparison of MFS and MFMS structures

To analyze the operation of the ferroelectric FET, the critical issue is to obtain the electric field across the ferroelectric layer, which should be large enough to switch the polarization. Approximate calculation of the electric field is discussed here for the ferroelectric AlGaN/GaN HFET which uses a MFISFET structure with a Si$_3$N$_4$ insulator instead of a metal bottom electrode. Considering the MFISFET structure first, the electric field on the PZT ($E_{PZT}$) is given by the expression:

$$E_{PZT} = \frac{V_{GS}}{d_{PZT} + \frac{e_{PZT}}{e_i}d_i}$$  \hspace{1cm} 6.1
where $d$ is the thickness and the subscript $i$ represents the insulator. To simplify the analysis, the electric field distribution in the semiconductor is neglected here. It is not a surprise that $\frac{\varepsilon_{\text{PZT}}}{\varepsilon_i}d_i$ is indispensable even using a thin insulator because the relative permittivity of the PZT ($\varepsilon_{\text{PZT}} = 500 \sim 1300$) is generally larger than that of the insulator such as commonly used Si$_3$N$_4$ ($\varepsilon_{\text{Si$_3$N$_4$}} = 7.5$) and SiO$_2$ ($\varepsilon_{\text{SiO$_2$}} = 3.9$) that provides a large factor $\frac{\varepsilon_{\text{PZT}}}{\varepsilon_i}$. Thus it requires a large voltage to switch the polarization of PZT as mentioned above. In addition, one would note that the electric field across the semiconductor is not negligible in the case of a depletion region formed in the semiconductor. The equation of the electric field in PZT will be modified as:

$$E_{\text{PZT}} = (V_{GS} - V_s) / (d_{\text{PZT}} + \frac{\varepsilon_{\text{PZT}}}{\varepsilon_i}d_i)$$

where $V_s$ is the voltage across the semiconductor. It greatly decreases the voltage used for the polarization switching. In contrast, the demonstrated MFMSFET structure here would not suffer these problems. Because of the existence of the bottom electrode, the electric field in PZT can be expressed as simple as a capacitor:

$$E_{\text{PZT}} = V / d_{\text{PZT}}$$

where $V$ is the polarization voltage of PZT applied between the top and bottom electrode. Hence the MFMSFET would not require a large voltage as MFISFET structure. Furthermore, the MFMSFET structure provides a more efficient modulation of the source-
drain current through the polarized PZT whose induced voltage is applied to the conductive channel without the voltage drop across an insulator.
Chapter 7 Summary

This thesis discussed our investigations of the ferroelectric thin films on their epitaxial growth and a variety of functional properties. The term of “ferroelectric” here refers to one of the major properties commonly shared by those materials but does not confine our exploration into their broad features. All the experimental characterization and theoretical analysis is dedicated to recognizing the technical importance and limitation, and approaching a fundamental understanding of the properties in ferroelectric thin films. To realize the goal, we have established epitaxial growth of BST and PZT thin films on STO substrates and then extended our efforts to integrate those ferroelectric films on several semiconductor materials. Considering the potential applications, the major functional properties of PZT and BST thin films have been carefully examined focusing on their structural and electrical properties where ferroelectric and pyroelectric behaviors of PZT films and dielectric properties of BST films were put much efforts in most of the study. At last, ferroelectric field effect transistors have been fabricated to demonstrate their abilities in potential device applications.

The first priority in our studying is to obtain high quality ferroelectric PZT and BST thin films. Here, the quality mainly refers, all through this thesis, to the structural properties which are determined by X-ray diffraction. It allows us to identify the distinct structural features such as lattice parameters and crystal orientation and links them to the
ferroelectric, pyroelectric or dielectric properties. Depending on X-ray diffraction, the growth conditions of rf magnetron sputtering have been calibrated for BST and PZT thin films. In Chapter 2, several growth parameters (temperature, pressure, mixture gas ratio and power) are discussed to explain their specific influences on the growth of ferroelectric thin films. The importance of growth temperature is emphasized that ferroelectric materials need to be grown at high temperature (~700 °C) to promote a suitable crystal structure. Regardless of the thermal stability of substrates, further improvement of crystallinity in most ferroelectric oxides can turn to higher growth temperature in sputtering. But it raises the requirement of the capacity of the sputtering system such as oxidation resistance of heaters and the efficiency of cooling.

Epitaxial PZT thin films on STO substrates are demonstrated in Chapter 3. Formation of exclusive PZT perovskite phase has been revealed by HRXRD. FWHM of (001) ω-rocking curve is 4.2 arc min for 300-nm-thick layers. Pronounced ferroelectric behavior of PZT thin films appeared in P-E measurement with $P_r = \sim 50 \mu C/cm^2$. The pyroelectric properties of the PZT films have been studied as a function of temperature in the range from 280 K to 370 K. The measurements have yielded a pyroelectric coefficient as high as 48 nC/cm²K at room temperature.

In Chapter 4, we have studied the strained BST thin films grown on STO substrate by rf magnetron sputtering. The structural properties measured by HRXRD reveal large in-plane compressive and out-of-plane tensile strain. The dielectric properties of strained BST thin films were examined as a function of temperature. The results indicate that the existence of large strain can significantly change the dielectric properties and cause a large...
shift of the Curie temperature. The in-plane compressive strain decreases the out-of-plane dielectric constant in BST thin films but enhances the ferroelectric properties.

The combination of attractive properties of PZT/GaN systems prospects for potentially novel or new generation devices. Studies on the integration of those two materials is described in Chapter 5. The use of a double PbTiO₃/PbO bridge layer grown by MBE prior to PZT deposition paved the way to achieve highly (111)-oriented PZT films on GaN (0001). A six-fold symmetry of PZT on GaN (0001) suggesting the presence of 60° rotation domains was observed by XRD pole figure analysis. The (100) reflection planes appeared at with the same Φ angles as the (10 12) reflections for GaN, which indicated an in-plane epitaxial relationship with PZT [11 2]///GaN [1 1 00] and PZT [1 1 0]///GaN [11 2 0]. The leakage current densities were 2x10⁻⁷ A/cm² at electric fields of 200 kV/cm and 1x10⁻⁵ A/cm² at 500 kV/cm. Ferroelectric characterization clearly exhibited the abrupt polarization switch near the coercive fields and large values of remanent polarization with +P_r = ~40 µC/cm² and –P_r = ~30 µC/cm². In this chapter, we also describe the growth of highly (001)-oriented BST on a-plane sapphire substrates using MgO/ZnO bridge layer. The in-plane epitaxial relationships of thin films are determined as follows: ZnO [1 1 2 0]///a-sapphire [0 0 0 1], ZnO [1 1 0 0]///a-sapphire [1 1 0 0], BST[110]///MgO [1 1 0]///ZnO [1 1 2 0] and BST[110]///MgO[1 1 0]///ZnO [1 1 0 0]. However, the dielectric properties of those BST films still remain unexplored for the application of microwave tunable devices. Further investigation is required to minimize the tangent loss
induced from conductive ZnO layer that would be resolved to use thinner ZnO layer or improve its crystal quality.

In addition, we have studied the asymmetry of hysteresis loops in Chapter 5. Using an analytical approach based on a ferroelectric capacitor physical model and Sawyer-Tower circuit model, the asymmetric hysteresis loops in PZT/GaN and PZT/STO:Nb structures have been analyzed. The results point out that the interface trapped charges and nonswitching depletion layer influence the shape of the hysteresis loops. However, the pronounced asymmetry cannot be explained separately by the effects of interface trapped charges or nonswitching depletion layer. Both factors should be considered in order to reach a good agreement between the simulated and measured $P-E$ characteristics.

Based on the 1T concept of the current modulation by the ferroelectric polarization, we demonstrate the development of two different ferroelectric FET based on AlGaN/GaN HFETs. Both devices show a significant ferroelectric source-drain current modulation. One device is based on the traditional 1T design with metal-ferroelectric-semiconductor structure, and the other is fabricated with metal-ferroelectric-metal-semiconductor structures. In the latter design, the introduction of Schottky metal contact between ferroelectric and semiconductor layers provides a barrier layer preventing the chemical interaction at the interface of PZT and GaN, as well as a bottom electrode of PZT which helps decrease the switching voltage for poling the ferroelectric material. The MFMSFET transfer characteristic (source-drain current versus gate voltage) shows a notable counterclockwise hysteresis loop indicating a significant ferroelectric source-drain current
modulation. At zero gate bias, the ferroelectric modulation of the source-drain current is as large as 50%.

Ferroelectric thin films have shown the potential for the applications of novel or new generation devices. On the way to the practical applications, there are still tremendous barriers and challenges which would emerge in the further development. The basis built in this study is expected to provide a part of useful guidance to achieve the multifunctional devices and help the further improvement of the device performance.
REFERENCE

1 J. Valasek, Piezo-electric and allied phenomena in Rochelle Salt, Phys. Rev. 17, 475 (1921)
2 G. Busch and P. Scherer, A new seignette-electric substance, Naturwiss 23, 737 (1935)
3 E. Wainer and N. Salomon, Electrical reports titanium alloys manufacturing division, National Lead Co. Reports No. 8, 9, 10 (1938-1943)
12 A. Okada, Some electrical and optical properties of ferroelectric lead-zirconate-lead-titanate thin films, J. Appl. Phys. 48, 2905 (1977); A. Okada, Electrical properties of lead-


43 S. B. Lang, Phys. Today 58, 31(2005)


57 JCPDS-ICDD Reference code: 00-039-1395


121
84 A. K. Tagantsev, V. O. Sherman, K. F. Astafiev, J. Venkatesh and N. Setter, J.

85 H. Yang, H. Al-Brithen, A. R. Smith, J. A. Borchers, R. L. Cappelletti, M. D. Vaudin,
Appl. Phys. Lett. 78, 3860 (2001)

86 JCPDS-ICDD Reference code: 00-039-1395


202-207


90 M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectric and Related


95 C. Munasinghe, J. Heikenfeld, R. Dorey, R. Whatmore, J. P. Bender, J. F. Wager, and A.
J. Steckl,

Waser, Microelectronic Engineering 80, 296 (2005)