High quality molecular beam epitaxy growth and characterization of lead titanate zirconate based complex-oxides

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High quality Molecular Beam Epitaxy growth and
colorization of Lead zirconate titanate based complex-oxides

A dissertation submitted in partial satisfaction of the
preliminary examination requirements for the degree of Doctor of Philosophy
in Electrical and Computer Engineering

by

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ABSTRACT

High quality Molecular Beam Epitaxy growth, characterization, and analysis of Lead zirconate titanate based complex-oxides

by Xing Gu, Ph.D

A dissertation submitted in partial satisfaction of the preliminary examination requirements for the degree of Doctor of Philosophy in Electrical and Computer Engineering at Virginia Commonwealth University

Major Director: Dr. Hadis Morkoc

Research interest in complex oxides has resurfaced owing to progress in modern epitaxial techniques. Among such oxides, lead-titanate-based thin films such as PbTiO₃ (PTO) and Pb(ZrₓTi₁₋ₓ)O₃ (PZT) offer attractive advantages for a wide variety of applications. Moreover, integration between functional oxides with compound semiconductors has the potential to realize multi-functional devices which enjoy the properties from both groups of materials. Ferroelectric materials with a perovskite structure (ABO₃) and semiconductors such as GaN with a hexagonal structure, require a
careful choice of a bridge layer and suitable epitaxial technique. Molecular beam epitaxy (MBE) has been an established technique in providing epitaxial growth with high crystal perfection and precise control over material composition. Single-crystal oxides grown by molecular beam epitaxy (MBE) can in principle avoid grain boundaries and provide a sharp interface as well.

In this dissertation, the MBE growth mechanism of PZT was investigated. In-situ RHEED patterns indicate that the growth of PTO and PZT occur in a two-dimensional, layer by layer mode, as confirmed by a streaky pattern. The crystal quality of PTO, PZO, and PZT thin films prepared by MBE are evaluated by X-ray diffraction (XRD), and have a full width at half maximum (FWHM) value of 4 arcmin for an 80nm thick layer. Optical properties of the PTO thin films have been characterized by variable angle spectroscopic ellipsometry (VASE), and well resolved dielectric functions are extracted. The refractive index is determined as 2.605 at 633 nm, and bandgap energy as 3.778eV. The electrical properties of the PTO and PZT are evaluated by the measurement of polarization-field hysteresis loops, give a remanent polarization of 83 μC/cm² and a coercive field of 77 kV/cm. Lead oxide (PbO), titanium dioxide (TiO₂), and zirconium dioxide (ZrO₂), on GaN templates for potential PZT/GaN integration. The epitaxial growth of TiO₂, PbO, and ZrO₂ is realized on GaN templates for the first time by MBE. The PbO epitaxial layer was also used as a nucleation layer to enable single crystalline, perovskite PTO growth on GaN.
Chapter 1 Introduction

1.1 Motivation

Due to the rapid development of modern epitaxy techniques such as MBE and MOCVD, there has been a resurgence of interest in researching the functional complex oxides. These modern deposition techniques are expected to lead to high-quality materials and attractive, proposed device concepts, in a single mode or using a stack structure (i.e., a combination of functional oxides with semiconductors such as Si or GaN).

Molecular beam epitaxy (MBE) is a growth method that allows precise control of beam fluxes and growth conditions. As a direct consequence, it has been established as a powerful method for realizing the high-quality deposition of most advanced semiconductor materials as well as hetero-structure devices for which high purity and precise control of layer thickness and composition are required. The enormous progress in the control of growth parameters afforded by MBE leads to great success in the growth of conventional semiconductors, particularly as relates to the growth of III-V semiconductors, both from the academic side and the commercial production side. Somehow surprisingly, MBE is much less intensively involved in oxides’ growth, especially lead-containing oxides such as PZT group materials. The low-level activity may in part be due to the perceived view that, in MBE, the sources would be oxidized as
well as lack precise control of Pb and PbO due to their volatility in high vacuum. A study on the growth mechanism and an evaluation on the application of the oxides' MBE are, therefore, imperative.

1.2 Objectives

Complex oxides contain two or more metal elements; this means that stoichiometry control is of great importance in avoiding impurity phases, which hinder the realization of high quality epitaxy. The high volatility of Pb and PbO could play positive roles in realizing single phase, high-quality PZT-based complex oxides when they are used appropriately. In this dissertation, the growth mechanism of PZT-based, complex oxides will be investigated, and the phase control of PTO/PZT MBE growth will be studied using reflection high-energy electron diffraction (RHEED). MBE grown, single phase, single crystalline PZT will be demonstrated as a benefit from this study. The hetero-integration of oxides with GaN will also be discussed.

1.3 Literature review

1.3.1 Introduction to PZT based complex oxides

\( \text{Pb(Zr}_{x}\text{Ti}_{1-x})\text{O}_3 \) (PZT) is a solid solution of antiferroelectric (AFE) PbZrO\(_3\) and ferroelectric (FE) PbTiO\(_3\), and is a well known material that is used in a number of extremely important applications such as integrated piezoelectric devices\(^1\), pyroelectric infrared sensors\(^2\), nonvolatile memory\(^3\), gate material for ion-sensitive field-effect transistors (ISFET)\(^4,5\), ferroelectric field-effect transistors\(^6\), optical waveguide devices,\(^7\) and electro-optic modulators\(^8\). All of these oxides (PZT, PTO, and PZO) have a perovskite structure above their respective Curie temperatures. Perovskite oxides have the formula ABO\(_3\), for which O is oxygen, A represents a cation, and B is a cation with a
smaller ionic radius. Figure 1 is a figure modified from ref.9 that shows a PbTiO3 (PTO) perovskite-type unit cell. A perovskite structure is essentially a three-dimensional network of BO6 octahedra, with A ions filling the octahedral interstitial positions. In PTO case, Ti4+ ions occupy the center of each tetragonally distorted cube, Pb2+ ions occupy the corners, and O2- ions occupy the face centers of the distorted cube. Similar to the case of GaN, ferroelectric (FE) materials lack centrosymmetry, which is the origination of piezoelectric behavior. One remarkable difference between FE materials and GaN is that in FE materials, the ion nearly occupying the center of the unit cell can be displaced in relation to the center of the negative charge, causing large polarization. As shown in figure 1.1, with tetragonal distortion, the cubic system would therefore be stretched in the c-direction and compressed in the a- and b-directions. As a result, the central ion, in PZT’s case the Ti4+, can be moved along the c-direction with external field or strain, which causes the polarization to be either in the c+ or c- direction, and the direction depends on the sign of the external electric field or force. The polarization, even when the external field or force is removed, would be retained for a long time.
Figure 1.1 Schematic of a unit cell of perovskite PbTiO$_3$. In this structure, Pb fits for A, Ti fits for B. The external electric field or force would cause the Ti$^{4+}$ to move up or down, while the O$^{2-}$ plane moves in the reverse direction. Modified from ref.9.
Ferroelectric domains exist in the FE materials, especially those with inferior quality, which are analogous to magnetic domains in magnetic materials. This means that in some regions the polarization vector may be directed up and in others it is directed down. All of these ferroelectric domains, however, line up in the same direction when enough electric field is being applied (usually a few kV/cm). Notice that they can remain aligned even after removal of the field. This kind of polarization can therefore be switched into either up or down directions to meet the need for device applications, by controlling the polarity of the applied field. In the real devices, those oxides are usually thin films (thickness is small), which means that the applied voltage can be very small to produce the same field. While this is positive in terms of energy savings, noise margins must be taken into consideration when finding the threshold voltage, which is determined by the film thickness and the coercive field.

Polarization-field characteristics of ferroelectric materials show hysteresis behavior, in analogy to the magnetization vs. magnetic field in ferromagnetic materials. The electrical field is swung from zero to some positive voltage, then to negative voltage, and back to the positive voltage. As shown in figure 1.2, the electric field at which the polarization is zero is called the coercive field (+Ec and –Ec), which is an important parameter in determining the threshold voltage. A change in the direction of polarization would occur when the change in the electric field passes through this critical point. The remanent polarization (+Pr and –Pr), which is defined as both the positive and negative polarization at zero field, is stable, requires no external field for retention, and usually functions as logic “1” and “0”. This intrinsic property of ferroelectric material is of extreme importance in memory applications since no external field is required to
maintain data in a ferroelectric memory device. Moreover, the retention time could be as long as years. The ferroelectric memory is, therefore, called a non-volatile one, and its data will not be lost even after power failure. Furthermore, in traditional memories, the system falls back to a favorite state upon power failure while the ferroelectric memories are operated in a bistable (two-state) operation mode. Finally, the polarization saturates at an electric field that is high enough, and the difference in value between the saturation polarization and remanent polarization is called the non-remanent polarization.
Figure 1.2 Schematic shown of polarization curve for a typical ferroelectric material.
PZT is a perovskite alloy of PbZrO$_3$ (PZO) and PbTiO$_3$ (PTO). PTO is a ferroelectric material with a simple tetragonal structure at room temperature, while PZO has a complex antiferroelectric ground state and has rhombohedral structure at room temperature. By themselves, neither PZO nor PTO are particularly good piezoelectrics, but mixing these materials in a disordered solid solution gives rise to excellent piezoelectric response. The macroscopic phase of PZT depends on the Zr/Ti ratio and temperature. Six phases have been observed: a Zr-rich (P$_{bam}$) phase (AFE), two rhombohedral (R$_{3m}$ and R$_{3c}$) phases at different temperatures (FE), a tetragonal (p$_{4mm}$) phase (FE), a para-electric, high-temperature cubic phase, and the low-temperature, monoclinic (C$_m$) phase (FE) around the 50/50 Zr/Ti composition. Figure 1.3 is a PZT phase diagram, which was done by Woodward et al.$^{10}$ and corresponds to temperature and Zr/Ti composition. The dashed line suggests that the boundary between the R$_{3m}$ and R$_{3c}$, which separates the tilted and untilted rhombohedral phase, extends to the monoclinic phase (C$_m$) and forms a small phase field of C$_c$, which is a subgroup of both C$_m$ and R$_{3c}$. Similarly, another small phase field is proposed between the AFE (P$_{bam}$) and rhombohedral phase (R$_{3m}$ and R$_{3c}$), which form the phases with Pm and Pc symmetry, respectively.
Figure 1.3 Phase diagram of PZT corresponding to Zr/Ti composition and temperature. After ref.10.
It was demonstrated that the piezoelectric coefficient, relative permittivity, and remanent polarization peaked near the morphotropic phase boundary\textsuperscript{11}. However, most of the studies were done on ceramic samples despite the fact that the properties of single-crystal thin films can differ drastically from those for ceramics\textsuperscript{12} and depend strongly on film orientation\textsuperscript{13}. Therefore, to exploit the unique properties of PZT for device applications, preparation and characterization of high-quality, single-crystal PZT film is of vital importance.

### 1.3.2 Introduction to oxides MBE

The understanding and technological development of perovskite oxide is often complicated by the fact that distortions and imperfections in the perovskite structure can be the source of the desired properties\textsuperscript{14}. Because of the epitaxial compatibility of many of these materials, it is, in theory, possible to engineer unique structures with unique properties at the atomic level. Moreover, the so-called artificial oxide super lattices have also attracted more and more attention recently, since properties of oxides can be engineered using super lattice effects including epitaxial strain, quantum confinement, spin exchange as well as charge transfer. Similar to those in semiconductor super lattices, there have also been reports on the optical\textsuperscript{15} and transport\textsuperscript{16} properties of oxide super lattices. All of these activities require precise control of thin film growth such as that achievable using oxide molecular beam epitaxy, which is less frequently utilized in oxides’ thin-film growth, especially lead-containing oxides. The low-level activity may, in part, be due to the perceived view that, in MBE, the sources would be oxidized as well as lack precise control of Pb and PbO due to their volatility in high vacuum. The large amount of bonding energy of O\textsubscript{2} makes this source less attractive, and, thus, reactive
oxygen species are used for the oxides’ MBE (i.e., plasma enhanced oxygen sources). However, an oxygen plasma source is not ideally suited in that the material surface can potentially be damaged due to the high-energy particles. In addition, substantial degradation of the plasma source in the highly reactive oxygen ambient is an intractable problem. Moreover, there is a limitation of oxygen pressure for the plasma source to be ignited, which hinders the use of large oxygen fluxes needed to overcome potential oxygen vacancies in the lead-containing oxide films. Schlom et al. used a purified ozone source as an alternative oxygen source, which is effective but expensive\textsuperscript{17,18}. Using this ozone-assisted molecular beam epitaxy, the bilayer heterostructures such as YBCO and LCMO have also been demonstrated\textsuperscript{19}.

1.3.3 Introduction to oxides and semiconductor integration

Functional complex-oxide thin films such as PTO and PZT offer attractive advantages for a wide variety of applications such as integrated piezoelectric devices\textsuperscript{20}, pyroelectric infrared sensors\textsuperscript{21}, nonvolatile memory\textsuperscript{22}, optical waveguide devices,\textsuperscript{23} and electro-optic modulators\textsuperscript{24}. The integration of these perovskite oxides with existing semiconductors such as Si or GaN is of particular interest, which makes use of intrinsic characteristics of ferroelectric thin films (e.g., PZT-gated, GaN-based ferroelectric MODFET\textsuperscript{25}). Obviously, due to the very different crystal structure between the PZT and GaN (i.e., perovskite for PZT while hexagonal for GaN), a bridge layer must be inserted for successful integration.

1.4 Organization of the dissertation

This dissertation includes the following seven chapters:

Chapter 1: Introduction
Chapter 2: Growth of oxides by MBE

Chapter 3: Characterization of epitaxial oxides

Chapter 4: Stoichiometry control during complex oxides epitaxy

Chapter 5: Epitaxy, characterization and property analysis of PZT

Chapter 6: Investigation of integration of oxides and GaN

Chapter 7: Summary and future research

The current chapter is an introduction of the dissertation and is followed by a literature review of PZT-based complex oxides, oxides MBE, and integration of functional oxides with compound semiconductors. In Chapter 2, the basics of MBE growth will be introduced, and a detailed description of an oxides MBE system will be given. This is followed by a discussion of characterization methods used in the study, which is covered by Chapter 3. As a power method in analyzing the oxide phase and crystalline quality, different XRD measurements, including polar figure and reciprocal space mapping, will be discussed in detail while other useful technique such as RHEED and AFM are included as well. Chapter 4 will describe the stoichiometry control during complex oxides epitaxy, which is of critical importance in realizing high-quality epitaxy. The different adsorption / desorption behavior of different reactants will be covered and the intrinsic mechanism in achieving a stoic metric epilayer will be introduced. The results will be discussed based on theoretical calculations. Chapter 5 deals with the epitaxy, characterization, and property analysis of PZT-based complex oxides, using the stoichiometry controlled method described in Chapter 4. The effort of exploring oxides’ integration with GaN-based materials will be discussed in Chapter 6. Three candidates,
including PbO, ZrO$_2$ and TiO$_2$ will be discussed and evaluated according to different aspects. Finally, Chapter 7 will summarize the key contributions of this dissertation.
Chapter 2 Growth of oxides by MBE

Molecular Beam Epitaxy (MBE) takes place in high vacuum or ultra high vacuum (usually up to $10^{-10}$ torr). One of the most important features of MBE is the slow deposition rate (0.1 to 300 nm per minute), which facilitates the epitaxial growth of the films. As a consequence, the slow deposition rates require a proportionally better vacuum in order to achieve the same impurity levels as other deposition techniques. In solid-source MBE, ultra-pure elements such as gallium or lead are heated in separate quasi-knudsen effusion cells where they begin to evaporate slowly. The evaporated elements, typically in molecular beam form, condense on the wafer, where they may react with each other. In the case of gallium and ammonia, single crystalline gallium nitride is formed. The term "beam" simply means that evaporated atoms do not interact with each other or any other vacuum chamber gases until they reach the wafer due to the long mean-free paths of the beams. During the MBE growth, the composition of the epilayer and its doping level depend on the arrival rates of the constituent elements and dopants. Therefore, MBE growth is carried out under conditions that are governed primarily by kinetics, rather than mass transfer.

Reflection High Energy Electron Diffraction (RHEED) is commonly used for monitoring the growth of the epitaxial layers in-situ. It needs to be pointed out, however, that in the oxides MBE system such as the one used in this dissertation, a differential pump is highly desirable for the RHEED system to prevent it from oxidation due to the reactive oxygen species. Cell shutters in front of each effusion cell, usually controlled either by computers or manually, allow precise control of the thickness of each layer.
down to a single layer of atoms. Advanced structures of epitaxial layers of different materials and/or thickness may be fabricated this way. Such control has allowed the development of structures where the electrons can be confined in space, giving quantum wells or even quantum dots. Such layers are now a critical part of many modern semiconductor and/or oxides devices, such as laser diodes and light-emitting diodes. Typically, the ultra-high vacuum environment within the growth chamber is maintained by a system of cryopumps and cryopanels, which are chilled to a temperature close to 77 K (−196°C) using liquid nitrogen or cold nitrogen gas. Gas-source MBE is a variated form of traditional MBE, which applies a metal-organic source and resembles chemical vapor deposition.

### 2.1 Customized oxides MBE system used in this dissertation

To address the issues related to lead-based oxide growth efficiently, we employed hydrogen peroxide (H$_2$O$_2$), a highly reactive oxygen-containing compound, which is very affordable, as the oxygen source for the growth of lead-containing oxides.
Figure 2.1 Schematic drawing of our Riber 32 system for oxides growth.
A schematic shown of our Riber 32 MBE system customized for PZT-related materials growth can be found in Figure 2.1. The 50% H₂O₂ was kept in a stainless steel vessel that was heated using water-bath heating. The mixture of H₂O₂ and water entered the chamber through a quartz tube, and the flow rate was controlled by a leak valve. Ti and Pb flux came from Knudsen effusion cells, and the cell temperatures were controlled by Eurotherm controllers. Zirconium tetra (Zr-t) butoxide was chosen as the Zr source. For controlling the precursor vapor pressure, another stainless steel bubbler was used. Argon was used as the carrier gas for the Zr-t-butoxide. The Argon gas passed through the bubbler, and the mixture of N₂ and the metal-organic (MO) source were heated at the tip of the gas injector where the Zr MO source decomposed into Zr and ligands.

2.1.1 H₂O₂ reactive oxygen source

Hydrogen peroxide (H₂O₂) is a very pale blue liquid that appears colorless in a dilute solution, slightly more viscous than water. It has strong oxidizing properties and, therefore, can be used an alternative reactive oxygen source. Oxygen is formed during the natural decomposition of the peroxide, resulting in increased pressure inside the container. Therefore, before each growth run, the bubbler containing H₂O₂ needs to be pumped to maintain reproducible pressure/mixture concentration. Peroxide should be kept cool because peroxide vapor can detonate above 70 °C. In this dissertation, all of the operational temperatures of the H₂O₂ bubbler are equal to or below 35°C. Hydrogen peroxide always decomposes exothermically into water and oxygen gas spontaneously:

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \]
The rate of decomposition is dependent on the temperature and concentration of
the peroxide, as well as the pH and the presence of impurities and stabilizers. Hydrogen
peroxide is incompatible with many substances that catalyse its decomposition such as
most of the transition metals and their compounds. Therefore, a stainless steel bubbler
was chosen as the container for the 50% H$_2$O$_2$ solution used in this dissertation.
Figure 2.2 A detailed description of the H$_2$O$_2$ oxygen source setup
A detailed description of the setup of H$_2$O$_2$ source can be found in figure 2.2. The 50% H$_2$O$_2$ was kept in a stainless steel vessel that was heated using water-bath heating. The mixture of H$_2$O$_2$ and water entered the chamber through a quartz tube, and the flow rate was controlled by a leak valve. Another gas loop was employed as the pre-growth pumping, aiming to keep bubbler pressure and mixture concentration reproducible. The open/close loop action was controlled by both a membrane valve followed by a needle valve, as indicated in figure 2.2.

H$_2$O$_2$ is one of the most powerful oxidizers. Moreover, through catalysis, H$_2$O$_2$ can be converted into hydroxyl radicals (OH) with reactivity second only to fluorine. Table 2.1 is a comparison of the oxidation potential between the most commonly used oxidants. In its stable form, the oxidation potential of H$_2$O$_2$ is 1.8V, comparable to the 2.1 V value of ozone.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>F</th>
<th>OH</th>
<th>O$_3$</th>
<th>H$_2$O$_2$</th>
<th>ClO$_2$</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation potential</td>
<td>3.0V</td>
<td>2.8V</td>
<td>2.1V</td>
<td>1.8V</td>
<td>1.5V</td>
<td>1.4V</td>
</tr>
</tbody>
</table>

Table 2.1 A comparison of the oxidation potential between the most commonly used oxidants

2.1.2 Pb and Ti effusion cells

Effusion cells (or Knudsen Cells) are often used in thin film growth as source evaporators for relatively low partial-pressure elementary sources (e.g., Ga, Al, Pb, Ti, etc.). It is easy to control the temperature of evaporating content and is commonly used in MBE. A typical effusion cell contains a crucible (made of pyrolytic Boron Nitride, quartz,
or Tantulum), heating filaments (often made of metal Tantulum), water cooling system (usually for those with high operating temperatures), heat shields, and an orifice shutter. Inside the effusion cells, equilibrium is established between the gas and the condensed phase for pure substances. Therefore, the equilibrium pressure \( P_{\text{eq}} \) is a function of the crucible temperature \( T \) and can be approximately expressed by the Clapeyron equation:\(^{29}\)  

\[
p_{\text{eq}}(T) = A \exp\left(\frac{-\Delta H}{k_B T}\right) \tag{2.1}
\]

where \( \Delta H \) is the evaporation enthalpy and \( k_B \) is the Boltzmann constant.

When taking the geometry of the cell into consideration, the equilibrium vapor pressure can be described by the Knudsen equation:

\[
p_{\text{eq}}(T) = \frac{dW}{dt} \left(\frac{2 \pi k_B T}{m} \right)^{\frac{1}{2}} \frac{1}{A_0 W} \tag{2.2}
\]

where \( \frac{dW}{dt} \) is the weight loss rate of the substance inside the cell, \( T \) is the temperature of the orifice of the cell (K), \( k_B \) is the Boltzmann constant, \( m \) is the mass of the effusion species, \( A_0 \) is the orifice area, and \( W \) is the Clausing correction factor for the cylindrical orifice.

The equilibrium pressure of metallic Ti and Pb as a function of temperature has been determined and is described in figure 2.3.
Figure 2.3 The equilibrium pressure of metallic Ti and Pb as a function of temperature.
Clearly, the Ti cell needs to be operated at a much high temperature than the Pb cell in order to provide comparable vapor pressure of both elements. Practically, a dual filament, hot-tip effusion cell was used for lead. Compared with the conventional cell, an additional heating system with a separate thermocouple was installed at the top end of the crucible. The purpose of doing so was to prevent material condensation at the crucible orifice. All of the nominal temperature of the Pb cell used in this dissertation was, therefore, tip temperature, which is usually 200°C or higher than the base temperature at which Pb ingots are placed.

2.1.3(Zr–t) butoxide source

Because of a very low equilibrium pressure of metal Zr (making thermal evaporation exceedingly difficult), alternative Zr sources need to be introduced other than the conventional effusion cells. In this dissertation, zirconium tetra (Zr-t) butoxide was chosen as the metal organic (MO) precursor for Zr. (Zr-t) butoxide is in clear colorless liquid form with a formula of Zr(OC4H9)4 and a density of 0.96g/ml.

During growth, the (Zr-t) butoxide was kept in a stainless steel bubbler that was heated by water bath. Ar gas was used as the carrier gas, and the flow rate was controlled by mass flow controller (MFC). Therefore, the flux rate of effective Zr-species was determined mainly by two parameters: bubbler temperature (T) and carrier gas (Ar) flow rate. Practically, manipulating the carrier gas would result in a dramatic change in chamber pressure, which may change the growth mode employed in MBE. A better way is to control the bubbler temperature to get different Zr flux while maintaining the chamber pressure at the same level. Experiments were designed to depict the relationship between the bubbler temperature/ Zr flux rate and substrate temperature/ Zr flux rate. The
Zr flux rate were estimated by measuring the thickness of ZrO$_2$ thin film deposited on Si (100) substrate, and the results are shown in figure 2.4.
Ar carrier gas MF rate 0.25 sccm

PHO2/H2O = 4x10^-5 Torr

TS = 550°C

ZrO2 deposition rate (nm/h)

Bubbler temperature (°C)

520 5 60 6 0 6 4 0 6 8 0 1 0 2 0 3 0 4 0 5 0 6 0

Tbubbler = 52°C

PHO2/H2O = 4x10^-5 Torr

ZrO2 Deposition rate (nm/h)

Substrate temperature (°C)

40 50 60 70 80

Figure 2.4 relationships between the bubbler temperature / Zr flux rate and substrate temperature/ Zr flux rate
Obviously, the ZrO$_2$ growth rate is well-controlled by the bubbler temperature, and it increases from 15nm/hr at a bubbler temperature of 47°C to around 60nm/hr when bubbler temperature increases to 56°C. Moreover, an abrupt decrease in ZrO$_2$ growth rate appears at substrate temperatures over 650°C. The decomposition rate of Zr-t butoxide should be a function of substrate temperature, and higher temperature may facilitate local, hydrocarbon-rich circumstances, which hinder the incorporation of Zr. Therefore, in the PZT growth part of this dissertation for which high Zr incorporation was necessary, the substrate temperature was always kept at a moderate level (i.e., around 600°C).

2.2 Preparation of STO substrate and GaN template for oxide growth

In this dissertation, two kinds of substrates/templates have been used: SrTiO$_3$ (STO) bulk substrate and a GaN template produced by MOCVD. The quality of the epitaxial layer depends not only on the growth conditions, but also on the substrate quality. The defects on the epitaxial layer, which can originate from both the bulk of the substrate and from the substrate preparation, need to be taken care of. While less effort could be done to reduce the defects on the bulk substrate, we can control the substrate preparation to reduce the defects introduced as a result of chemical polishing or cutting.

2.2.1 Preparation of the GaN template

The cleaning procedures for the GaN and Si are well-established and are summarized as follows: GaN template starts with the degreasing procedure. The template is ultrasonically cleaned for 3 minutes each in acetone and methanol, and then rinsed for 3 minutes in deionized (DI) water. The above process is repeated three times to complete the degreasing process. Following degreasing, the substrates undergo a chemical
etching/cleaning process, during which the GaN template is heated in a 3:1 solution of HCl: HNO₃ (aqua regia) in a temperature around 100°C for 10 to 20 minutes. The purpose of this etching is to remove the thin, oxidized layer that formed on the top of GaN template. After etching, the substrate is rinsed in DI water for 3 minutes.

2.2.2 Preparation of STO substrate

As-received STO substrates have surface damage, such as scratches, that must be removed prior to epitaxial growth, as shown in Figure 2.5 (a).
Figure 2.5 AFM image of (a) as received STO substrate and (b) prepared STO substrate
In order to remove the surface scratch, the STO substrate was first dipped into buffered oxide etch (BOE) solution (6 parts 40% NH₄F and 1 part HF) for 5 mins after appropriate cleaning. Then the sample was rinsed carefully in DI water again and dried by Nitrogen purging. This was followed by a 1000°C annealing in the air in order to create a smooth surface with atomic terrace features, which is shown in figure 2.5 (b). After such annealing, the STO wafer was cleaned again in DI water before it was loaded into the MBE chamber.
Chapter 3 Characterization of epitaxial oxides

Several characterization methods were used in this dissertation to investigate the growth mechanism; structural, optical quality; and surface morphology of epitaxial oxides. In-situ reflection high energy electron diffraction (RHEED) was employed to monitor the evolution of the surface during growth. The surface morphology of the grown samples was evaluated ex-situ by SEM and atomic force microscopy (AFM) after growth. The oxides phase, crystalline quality, and strain were measured by x-ray diffraction (XRD) and TEM (conducted at ASU). Optical properties were measured by ellipsometry (conducted in Korea).

3.1 XRD

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength x-rays (hard x-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. XRD usually refers to a group of non-destructive analytical techniques that reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. Moreover, XRD can also be used to evaluate the thickness and fine structure of materials with superlattice structures. These techniques are based on observing the scattered intensity of an x-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Bragg’s Law is the simplest and most useful description of crystal diffraction:

\[ n\lambda = 2dsin\theta \]
where \( n \) represents the order of diffraction, \( \lambda \) is the x-ray wavelength, \( d \) is the inter-planar spacing of the diffracting planes and \( \theta \) is the incidence angle.

### 3.1.1. XRD \( \omega-2\theta \) scans and rocking curve (\( \omega \) scan)

XRD \( \omega-2\theta \) scan is the basic application of Bragg’s law, measuring the diffraction pattern that allows user to deduce the distribution of atoms in a material. Diffracted waves from different atoms can interfere with each other, and the resultant intensity distribution is determined by such interaction. If the atoms are arranged periodically, as in crystals, the diffracted waves will consist of sharp peaks with the same symmetry as in the distribution of atoms. Therefore, XRD \( \omega-2\theta \) scans are generally used to analyze the material composition and crystalline orientations. In this dissertation, examples of XRD \( \omega-2\theta \) scans are widely used in Chapter 4, Chapter 5, and Chapter 6. Moreover, as described by Bragg’s law, precise lattice constant measurements are possible deriving from \( \omega-2\theta \) scans, which provide information about lattice mismatch between the film and the substrate and, therefore, is indicative of strain as well. Therefore, XRD \( \omega-2\theta \) scans are also used in strain calculations, for instance, in Chapter 4 when calculating the lattice constant of PTO and in Chapter 6 when calculating the lattice constant of ZrO\(_2\).

The XRD rocking curve is used to quantify grain size and mosaic spread in crystalline materials. The measurements made by doing a \( \theta \) scan at a fixed \( 2\theta \) angle, the width of which is inversely proportionally to the dislocation density in the film. Therefore, it can be used as a gauge of the quality of the film. In this dissertation, the rocking curve measurements are used in Chapter 4, Chapter 5, and Chapter 6 in evaluating the crystalline quality of PTO, PZT, and ZrO\(_2\), respectively.

### 3.1.2 Phi scan and XRD pole figure
Similar to the XRD $\omega$-2$\theta$ scans, XRD phi scan is also a “single scan”, which means that scans consist of a series of intensity values recorded as one of the coordinate axes, in this case phi. This distinguished it from “area scans” as part of which data consists of a series of single scans made with one axis while the second axis is offset between each scan, such as XRD pole figures and XRD reciprocal scans, which will be introduced later.

The XRD coordinate system is a four-axis system, including 2$\theta$, $\omega$, phi and psi as the variables. $\omega$ (or $\theta$) is the angle between the incident beam and the sample surface. It can be varied independent of 2$\theta$ by setting the offset, and 2$\theta$ is the angle between the incident beam and the diffracted beam. Phi is the rotation angle about the sample normal and Psi is the tilt angle about a horizontal and centered line in the sample surface. Since Phi scan performs a 360\degree scan rotating normal to the sample, it provides the information on the crystalline symmetry when performing on the asymmetrical scans (i.e., Phi scan of hexagonal GaN (102) will generate 6 peaks and Phi scan of tetragonal PTO (101) will give 4 symmetric peaks). Examples of applications of Phi scan in this dissertation work can be found in Chapter 4, where the in-place epitaxial relationship between STO and PTO was determined by the XRD phi scan.

As an enhanced manner of Phi scan, the XRD pole figure program executes a series of Phi scans at regularly spaced Psi positions. Therefore, such measurements are used to determine the orientation distribution of crystalline grains in a polycrystalline sample, or in a heteroepitaxy system where epitaxial relationship is to be determined. As a consequence, it enables one to analyze and determine the distribution of crystalline
orientations within a crystalline thin-film sample. The name, pole figure, is derived from the fact that it is often plotted in polar coordinates consisting of the tilt and rotation angles with respect to a given crystallographic orientation. Practically, XRD pole figures are measured at a fixed scattering angle (constant d spacing) and consist of a series of $\Phi$ (Phi) scans (in-plane rotation around the center of the sample) at different tilt or $\psi$ (Psi, azimuth) angles, as illustrated in figure 3.1.
Figure 3.1 Schematic shown of $\Phi$, $\psi$ and $\theta$ variants in a XRD system
An example of XRD pole figure in analyzing the MBE-grown oxides layer can be found in Chapter 6, where the in-place epitaxial relationship between GaN and ZrO₂ is evaluated.

### 3.1.3 Reciprocal space mapping

XRD reciprocal scan, or Q-scan, is defined as a straight line in reciprocal space and is performed as a relative step scan around the current \( \omega \) and \( 2\theta \) positions. A reciprocal space map recorded by means of a high-resolution diffractometer is a function of two angular variables: \( \omega \) and \( 2\theta \) defined as angular position of the studied crystal and position of an analyzer, respectively.

As mentioned before, XRD rocking curve measurement performs the scan \( \omega: 2\theta \) for fixed value of \( 2\theta_0 \). In comparison, XRD reciprocal space mapping performs the scans \( \omega: 2\theta \) for the complete set of the start orientations \( \omega_0 \). During the scan, the inclination of \( \theta \)-scans with respect to the sample surface normal in reciprocal space is given in degrees. For the mapping mode, we obtain the values of the radiation intensities recorded by a detector for the complete set of combinations of \( \omega_0 \) and \( 2\theta_0 \) values. The example of using XRD reciprocal space mapping in this dissertation work is shown in Chapter 6 in evaluating the PZT/PTO/STO structure.

### 3.2 RHEED

Reflection high energy electron diffraction (RHEED) is an attractive technique for investigating the surface structure, which is usually employed during MBE growth and uses an electron gun and a display or recording device (e.g., a fluorescent screen) for typically obtaining information on the surface symmetry. RHEED uses high electron energy (typically 5-100keV) and low impact angles (<5°). The higher energy sharpens
the picture while the lower angle means electrons penetrate just a few atomic layers into
the crystal. Consequently, RHEED patterns represent the surface symmetry and not the
bulk crystal.

Due to its favorable geometry (grazing angle of incidence and exit), it is possible
to investigate in-situ epitaxial thin film growth in real time. The diffraction pattern
analysis allows for distinguishing between different modes of growth, providing the
chance for the grower to optimize growth condition the first time. The RHEED gives
essential information on the structure, orientation, and morphology of the substrate and
epitaxial layer32.

3.2.1 Application in MBE oxides growth

Static detection mode

The RHEED pattern of a clean epilayer surface reveals information about the
surface quality as well as the growth mode33. For a growing epilayer, the RHEED pattern
exhibits streaky lines or spots with high contrast and low background intensity. A
RHEED pattern with streaky lines represents a flat and smooth surface; however, the
spotty pattern represents a rough surface. A smaller full-width half maximum (FWHM)
value of the lines also indicates a higher quality surface. Random defects in the 2-
dimensional periodicity of the surface will broaden the lines and increase the background
intensity. In contrast, a RHEED pattern consisting of spots represents a rough surface of
epilayer34. Because RHEED is sensitive only to the first few atomic layers, it provides
information about any surface reconstructions. In this dissertation, static RHEED pattern
are widely used in Chapter 4, Chapter 5, and Chapter 6 in determining the growth mode
of PTO, PZO, PZT, ZrO₂, and so on.
Application in studying strain relaxation

In addition, changes in separation between RHEED streaks, which are related to changes in the surface lattice constant, can be used to study strain relaxation or superlattice structure. In order to understand this, a brief introduction on the operation principle of RHEED is necessary. Take a cubic lattice, for example. The incoming electrons with a momentum of $k_0$ have a very small incident angle (typically <2.5°) with respect to the sample surface. As a result of the small incident angle, they can only be scattered from the top layer of atoms of the epilayer. As shown in figure 3.2(a), the reciprocal lattice builds a surface with a quadratic array of atoms. Assuming elastic scattering as part of which no energy transfer is allowed from the electrons to the sample, then the scattered wave vector $k_i$ must lie on the surface of the sphere of constant energy, which is called Ewald sphere. In reciprocal space, the two-dimensional array of the surface atoms turns into a vertical line (reciprocal rods). Wherever these rods cross the Ewald sphere, the condition for constructive interference of the elastically scattered electron beams from the surface is fulfilled, as shown in figure 3.2(b). Therefore, these crossing points in k-space determine the directions of constructive interference for the electrons in real space.

Consequently, the separation between RHEED streaks depends on the real lattice constant of the epitaxial layer. Remember in RHEED screen we see the reciprocal space instead of the real space. As a result, the separation between RHEED rods is inversely proportional to the real lattice constant. The application of RHEED in calculating the strain in the epitaxial oxides layer is demonstrated in Chapter 6 when calculating the in-plane lattice constant of ZrO$_2$ in this dissertation.
Therefore, RHEED is a powerful tool for \textit{in-situ} analysis of thin film deposition. As the RHEED intensity depends on the film roughness, the growth process leads to characteristic \textit{intensity oscillations} of the RHEED spots during the growth process with a single oscillation usually corresponding to the completion of a single monolayer.
Figure 3.2 (a) schematic shown of reciprocal lattice and Ewald sphere (top view) (b) schematic shown of reciprocal lattice and Ewald sphere (side view) After Jürgen Klein, *Epitaktische Heterostrukturen aus dotierten Manganaten*, PhD Thesis, University of Cologne (2001).
3.3 Other characterizations used in this dissertation

3.3.1 AFM

A powerful tool in investigating the surface morphology and properties of materials, the atomic force microscope (AFM) was invented in 1986 by Binnig, Quate, and Gerber\textsuperscript{35}. Like all other scanning probe microscopes, the AFM utilizes a sharp probe moving over the surface of a sample in a raster scan. In AFM, the probe is a tip on the end of a cantilever (usually Si or SiN), which bends in response to the force between the tip and the sample. When the tip is brought into the proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. A schematic description of the AFM can be found in Figure 3.3.
Figure 3.3. schematic description of the AFM system
In the case that the tip was scanned at a constant height, there would be a risk that the tip would collide with the surface, causing damage. Therefore, a feedback mechanism is necessary to adjust the distance between the tip and the surface of the sample to maintain a constant force between them. Traditionally, the sample is mounted on a piezoelectric tube, which can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. The resulting map of the area $s = f(x,y)$ represents the topography of the sample.

Contact mode and tapping mode are the two most used modes for a typical AFM operation. Of these, contact mode is the most common method. As the name suggests, the tip and sample keep in close contact during the scanning. "Contact" means that it is operated in the repulsive regime of the inter-molecular force curve. Tapping mode is the next most common mode used in AFM. When operated in air or other gases, the cantilever is oscillated at its resonant frequency (often hundreds of KHz) and positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. When investigating poorly immobilized or soft samples, tapping mode may be a better choice over contact mode for experimentation.

In this dissertation, all the AFM images are performed under tapping mode. Examples of utilizing AFM images in investigating oxides surface morphology can be found in Chapter 5 and Chapter 6 when evaluating the surface morphology of PZT, ZrO$_2$, and PbO.

3.3.2 SEM

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface, which was pioneered by
Manfred von Ardenne in the 1930s. In a typical SEM, electrons are thermionically emitted from a cathode (usually W or LaB$_6$) and are accelerated towards an anode. In some alternative situations, electrons can also be emitted via field emission. The electron beam, which typically has an energy ranging from 0.1 to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot, which is typically around 1 nm. This finely focused electron beam scanned across the surface of the sample generates secondary electrons, backscattered electrons, and characteristic X-rays. These signals are collected by detectors to form images of the sample displayed on a cathode ray tube screen. Features seen in the SEM image may then be immediately analyzed for elemental composition using energy dispersive spectrometer (EDS).

The topography of SEM images is generated from either secondary electron imaging or backscattered electron imaging. Among them, secondary electron imaging shows the topography of surface features a few nm across. Films and stains as thin as 20 nm produce adequate-contrast images. Materials are viewed at useful magnifications up to 100,000 times without the need for extensive sample preparation and without damaging the sample. On the other hand, backscattered electron imaging shows the spatial distribution of elements or compounds within the top micron of the sample. Features as small as 10 nm are resolved, and composition variations of as little as 0.2% can be determined. EDS identifies the elemental composition of materials imaged in an SEM for all elements with an atomic number greater than boron. Most elements are detected at concentrations on the order of 0.1%.

In this dissertation, SEM has been used in morphology investigation, such as in the case in Chapter 4 when evaluating the surface morphology of PTO and the presence
of PbO second phase. EDS has also been used in estimation of the PZT composition as well.

3.3.3 Other characterization methods

In this dissertation, oxide samples have been sent out for various characterizations. For instance, optical properties of the oxides’ thin film have been characterized by variable angle spectroscopic ellipsometry (VASE), which was performed by Prof. H.S. Lee et al. in Korea; microstructure has been analyzed in TEM and composition of PZT has been analyzed in RBS in Arizona State University by Prof. D. Smith et al. These data are used in some of the following chapters.
Chapter 4 Stoichiometry control during complex oxides epitaxy

In this Chapter, the stoichiometry control of complex oxides will be investigated. First, the general issues related to growth of PZT-based oxides will be discussed in Section 4.1, followed by a discussion about forming and quenching of impurity phases such as TiO$_2$ and PbO in Section 4.2. Section 4.3 will discuss growth mechanism involved in the PTO growth, emphasizing the attempt to achieve the stoichiometric growth of PTO/PZT. A self-adjusting growth mechanism, which leads to realization of single-phase, single-crystalline PTO growth, will be given in Section 4.4. Section 4.5 will be a brief summary of this chapter.

4.1 PTO, PZO, and PZT growth by oxides MBE

4.1.1 Introduction

These studies of PZT growth were carried out in an oxides MBE system equipped with conventional Ti and Pb effusion cells, a Zr-t butoxide MO source and an H$_2$O$_2$ reactive oxygen source. Bulk STO substrates that have smooth surfaces with atomically flat terraces were used in this study. The growth system and the preparation of the STO substrates were discussed in detail in Chapter 2. The PTO, PZO, and PZT epilayer studied here were grown at a nominal substrate temperature between 550°C to 620°C. The Ti cell was manipulated at a temperature between 1550°C to 1650 °C and Pb cell at a tip temperature between 780 to 825°C. An oxygen-rich environment was maintained to
facilitate this growth, and the chamber pressure was kept between $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ torr, depending on the growth condition employed.

### 4.1.2 Pre-growth preparation

The preparation of a clean and atomically smooth substrate surface is of great importance for thin film epitaxial growth. After the STO sample was loaded into the growth chamber, a preliminary heating step to outgas adsorbed gases in the preparation chamber is necessary. The exposure to H$_2$O$_2$ gas is necessary, to prevent STO decomposition and loss of oxygen when the substrate is heated above 500°C. The design of the Riber 32 system enables the pre-balance of conditions before the growth started (i.e., the shutters of effusion cells are open for a few minutes before the epitaxy begins to prevent the “flux pulse” during opening of the cell shutter and to let the flux stabilize). After the growth conditions (metal flux, chamber pressure, etc.) are stabilized, the manipulator is rotated towards those reactants and epitaxial growth begins.

*In-situ* RHEED observation of STO substrate provides a method to monitor the real-time surface preparation processes. A 2X2 reconstruction along STO [110] direction will be observed after the H$_2$O$_2$ treatment at 600°C, as shown in figure 4.1. This reconstruction in the [110] direction is a clear indication of a Sr-rich surface.$^{36}$
Figure 4.1 RHEED pattern of STO substrate along [110] direction (a) as loaded (b) after H₂O₂ exposure at 600°C
4.2 TiO$_2$ and PbO impurity phases

For the epitaxial growth of complex oxides like PTO or PZT, growth in a stoichiometric mode is always important. Take PTO epitaxial growth for example, TiO$_2$ and PbO impurities may form during non-stoichiometric growth. Those impurity phases would give rise to defects such as grain boundary in the epitaxial thin film and, therefore, be responsible for the films with inferior crystalline quality. In order to achieve high-quality epitaxial growth, it is imperative to avoid forming such impurity phases.

4.2.1 Characteristic RHEED pattern of TiO$_2$ and PbO impurity phases

A reliable and prompt way to detect the formation of TiO$_2$ and/or PbO impurity phases is the in-situ RHEED monitoring. Both TiO$_2$ and PbO have their characteristic patterns, which help growth to determine the growth region and make adjustments accordingly.

4.2.1.1 High temperature TiO$_2$ phase

At high growth temperatures (usually 650°C or even higher), the impurity TiO$_2$ phase, if there is any, will form in an anatase form. The characteristic RHEED pattern of such TiO$_2$ is easy to distinguish; as shown in figure 4.2, along the STO [100] direction, a 1X4 reconstruction is clearly observable with a streaky main pattern and along the STO [110] direction, a two-folded tail distinguishes the TiO$_2$ patterns from that of typical PTO. Another major difference between TiO$_2$ and pure PTO pattern is that PTO patterns are always 2X2 reconstructed along the STO [110] direction while the patterns for TiO$_2$ along that direction are never reconstructed.
Figure 4.2 RHEED pattern of TiO$_2$ anatase phase (a) along STO [100] direction (b) along STO [110] direction
4.2.1.2 Low-temperature TiO$_2$ phase

When growth temperature is moderate (600°C or lower), the impurity TiO$_2$ phase appears in the rutile form. The characteristic RHEED pattern of the rutile TiO$_2$ is 3-D dots, and the dots are aligned near each other in a quasi-hexagonal shape, along the STO [110] direction, as shown in figure 4.3.
Figure 4.3 (a) RHEED pattern of TiO$_2$ rutile phase along the STO [110] direction (b) XRD 2theta-omega scan of PTO with TiO$_2$ impurity phase
The impurity TiO$_2$, regardless of which phase it is in, can easily be determined using XRD 2theta-omega scan. Figure 4.3(b) is an example that shows TiO$_2$ (200) reflection in XRD pattern in addition to those of PTO phase.

4.2.1.3 PbO phase on PTO surface

PbO impurity phases usually occur as a result of lower-than-optimized growth temperature. Moreover, it is usually easier to form during an extraordinarily high oxygen pressure (i.e., a jump in pressure due to the form/deform of the liquid droplet within the H$_2$O$_2$ bubbler or gas line). In the early stage, the PbO tends to nucleate on the surface of PTO. The characteristic RHEED pattern of PbO while sitting on the surface of the epilayer, is shown in Figure 4.4 (a). The 2-D long streaks correspond to the PTO epilayer while a series of 3-D spots correspond to the PbO sitting on the surface. These are also confirmed by the SEM image, and PbO appear in two forms: either small islands or long streaks that have a 45° or 90° crossing angle in between. It needs to be emphasized that, at this stage, the PbO are just located on the surface, and while they can be detected by surface-sensitive techniques, such as RHEED and SEM, in XRD, pattern no PbO phase can be found, which distinguishes it from the embedded PbO impurity phase.
Figure 4.4 (a) RHEED pattern of PTO with PbO on the surface along STO [110] direction (b) SEM image of PTO with PbO sitting on the surface
4.2.1.4 PbO phase imbedded in PTO layer

The PbO impurity phase starts to form on the surface, and will accumulate to such an extent that those small islands and/or long streaks grow and for embedded impurity phase within the PTO, similar to the case of TiO$_2$, if no action is taken in the early stage. This will inevitably lead to defects such as grain boundary, and result in inferior crystalline quality.

The characteristic RHEED pattern of PbO, which sits on the surface of the epilayer, is shown in Figure 4.5 (a). The large density of the irregularly arranged 3-D spots is formed along the streaks corresponding to PTO, and the density keeps increasing with the accumulation of PbO. Finally, the epitaxial layer turns into polycrystalline if no actions, such as in-situ annealing and raising of the substrate temperature, are taken. Moreover, at this stage, the PbO are formed not only on the surface, but also “inside” the epilayer. As a result, XRD can determine the existence of such impurity forms, as shown in Figure 4.5 (b).
Figure 4.5 (a) RHEED pattern of PTO with embedded PbO along STO [110] (b) XRD 2theta-omega scan of PTO with PbO embedded impurity phase
4.3 Growth mechanism of PTO using MBE

In general, the composition of the MBE depends on the arrival and departure rates of the constituent elements and dopants\textsuperscript{37}. As a result, MBE growth is carried out under conditions that are governed primarily by kinetics rather than by mass transfer\textsuperscript{38}.

Five steps are mainly involved during the MBE processes: adsorption, surface diffusion, incorporation, desorption, and decomposition.

4.3.1 Self-adjusting of Pb

A section of the equilibrium vaporization curve for elemental lead is shown in Figure 4.6, where the solid line divides the lead gas phase from the liquid phase:
Figure 4.6 Equilibrium vaporization curve for elemental lead. After reference 17
In Chapter 2, we pointed out that the equilibrium vapor pressure can be described by the Knudsen equation:

\[
p_{eq}(T) = \frac{dW}{dt}\left[\frac{2\pi k_B T}{m}\right]^\frac{1}{2} \frac{1}{A_W}
\]

where \(\frac{dW}{dt}\) is the weight loss rate of the substance inside the cell, \(T\) is the temperature of the orifice of the cell (K), \(k_B\) is the Boltzmann constant, \(m\) is the mass of the effusion species, \(A_W\) is the orifice area, \(W\) is the Clausing correction factor for the cylindrical orifice. In a more practical way, Theis et. al. has calculated that the typical incident lead flux during growth can be converted into the lead gas pressure as:

\[
P_{pb}(T) = \frac{\Phi_{pb}}{\cos \theta} \left[\frac{\pi m k_B T}{8}\right]^\frac{1}{2}
\]

where \(P_{pb}(T)\) is lead gas pressure (Pa), \(m\) is lead atomic mass (kg), \(k_B\) is Boltzmann’s constant (J/K), \(T\) is temperature (K), \(\theta\) is the angle of the incident molecular beam and \(\Phi\) is flux (atoms/m\(^2\) s). In both cases, the estimated lead flux equilibrium pressure at the substrate surface is in the range of 10\(^{-6}\) torr at the substrate temperature of 600°C, which is more than two orders below the stability line for the vaporization of elemental lead. That is to say, Pb by itself would not be able to condense on the surface and be included into the epitaxial layer at the growth temperature. The extra Pb will automatically be evaporated during the MBE growth. In other words, we call this automatic evaporation of Pb at proper high temperature “Self-adjusting” because, when armed with such a property, crystal growers do not have to accurately adjust the Pb/Ti ratio. Instead, a Pb/Ti>>1 ratio
is essential for the stoichiometric growth, while the real Pb flux is flexible, which facilitates the epitaxial growth.

4.3.2 Adsorption-controlled PTO growth

PbO is also a highly volatile material. Theoretical calculation pointed out that, at the substrate temperature of 600°C, congruent vaporization of PbO happens at an oxygen vapor pressure as low as $10^{-6}$ torr. All the nominate growth pressure in this dissertation is in the range of $10^{-5}$ torr or higher. Considering the location of the cathode vacuum gauge, the real local pressure of H$_2$O$_2$ close to the substrate should be even higher than the nominate pressure. Therefore, the PbO discussed in the growth dynamic is mainly in gaseous form. While the Pb simply cannot be condensed into the epitaxial layer at the growth temperature, the dominant ambient close to the surface of the substrate would be gaseous PbO, which is formed by the oxidation of Pb by H$_2$O$_2$:

$$ Pb + H_2O_2 \rightarrow PbO(g) + H_2O $$

Unlike Pb, the sticking coefficient of Ti was considerably high, which means the majority of the Ti flux is incorporated into the epitaxial layer, while a small amount of Ti is being scattered by the collision with other reactants such as H$_2$O$_2$ and Pb:

$$ Ti + 2H_2O_2 \rightarrow TiO_2(s) + 2H_2O $$

Therefore, the formation of PTO can be described as follows:

$$ TiO_2(s) + PbO(g) \rightarrow PbTiO_3(s) $$

Figure 4.7 is a phase diagram drawing from experimental data, which depicts this equilibrium, and three different regions are resolved: In region (I), the less-than-optimized substrate temperature or higher-than-necessary H$_2$O$_2$ pressure leads to the unwanted PbO impurity phase in addition to the PTO. This can be solved by optimizing
the growth conditions by tuning the substrate temperature/ \( \text{H}_2\text{O}_2 \) pressure, which makes the growth adsorption-controlled and is defined as region (II). In this growth region, single-phase, single-crystalline PTO can be achieved, while extra PbO simply desorbs into a vacuum chamber and will not be incorporated in the epilayer. While the substrate temperature is increased further, a TiO\(_2\) impurity phase was resolved, in addition to the PTO phase, by XRD. This indicates that, due to the limitations of the available reactive oxygen, simply increasing the Pb flux is not able to form sufficient PbO to maintain the stoichiometry of the thin film.
Figure 4.7 Phase diagram drawing from experimental data showing different growth regions of PTO
4.3.3 Decomposition of PbO

In addition to the growth mechanism discussed above, the decomposition of PbO is also an important process involved. Indeed, excess PbO in lead-based ferroelectric materials should be required to control the precise stoichiometry of the desired ferroelectric materials, but the accurate amount differs from each other when grown on different substrate such as sapphire, Pt or Si, due to the different inter-diffusion between lead and substrates. Early reports pointed out that PbO undergoes an obvious decomposition as early as 550°C when lacking oxygen ambient. Considering the dynamic equilibrium between the condensed PbO and O₂:

\[
2PbO(S) \rightarrow 2Pb(l) + O_2
\]

\[
2H_2O_2 \rightarrow 2H_2O + O_2
\]

It is obvious that the decomposition of PbO will be accelerated with decreased H₂O₂ pressure or increased substrate temperature. Armed with this knowledge, we can make use of this property to modify the epitaxial processes and optimize the growth condition in-situ.

For example, Figure 4.8 (a) is a RHEED pattern of an on-growing PTO. It can be determined, as discussed before, if the growth was under PbO over-rich conditions, and if some PbO islands have started to nucleate on the surface of the PTO. Without necessary actions being taken, those PbO will grow and become embedded into the layer. The correct method is to switch the substrate face off the reactant flux, stop the supply of H₂O₂, and raise the substrate temperature for an in-situ annealing. Figure 4.8 (b) is the RHEED pattern of the same sample, after annealing at 700°C for 5 minutes. All the PbO that sit on the surface are decomposed and pure PTO growth is resumed.
Figure 4.8 RHEED pattern of PTO (a) with PbO on the surface (b) after annealing at 700°C for 5 minutes, all the PbO was driven away.
The decomposition of PbO can also be made use of after the growth is finished. The embedded PbO can also be quenched by annealing at air ambient at 850°C, as shown in Figure 4.9. However, such a high-temperature annealing usually causes severe surface roughening and is not a recommended method.
Figure 4.9 XRD pattern of (a) PTO with PbO-embedded impurity phase (b) after annealing at 850°C for 1hr, PbO peaks have disappeared
Figure 4.10 RHEED pattern of (a) PTO epitaxial layer along [100] direction (b) PTO epitaxial layer along [110] direction
4.4 Epitaxy of single-crystalline, single-phase PTO

Understanding the growth mechanisms involved in PTO MBE growth, single-crystalline, single-phase PTO is achieved as a consequence. Figure 4.10 is the RHEED pattern of PTO grown under optimized condition, where streaky 2-D patterns were observed throughout the growth.

The structural properties of the epitaxial PTO were studied by the XRD. Φ-scan of the asymmetrical (101) reflection was performed for the STO substrate and PTO layer, and four-fold rotation symmetry was observed (figure 4.11 (a)), suggesting a PTO [100]// STO [100] and PTO [001]// STO [001] in-plane and out-of-plane epitaxial relationships, respectively. The crystalline quality of the PTO thin film was evaluated by XRD rocking curves, and the results are shown in Fig. 4.11 (b). The full-width at half-maximum (FWHM) of PTO (001) is 15.9 arcmin for a 25-nm-thick sample and reduces to 8.2 and 6.2 arcmin for 50-nm and a 65-nm-thick films, respectively. The value of 6.2 arcmin is comparable to the best figures reported for PTO films grown by MOCVD and hydrothermal methods with thicknesses over 100nm.

The out-of-plane, c, and in-plane, a, lattice constants of the PTO were deduced from the peak position for symmetrical (001) and asymmetrical (101) reflections, respectively, in 0-2θ XRD patterns. For a 40-nm-thick PTO film, we obtained c=4.11 Å and a=3.92 Å, which represent the strained values. The out-of-plane and in-plane misfit strains were determined to be -1.11% and 0.41%, respectively, using $\varepsilon_{\perp misfit} = \frac{c - c_0}{c}$ and $\varepsilon_{// misfit} = \frac{a - a_0}{a}$, where $c_0=4.156$ Å and $a_0=3.904$ Å are bulk values. This indicates that our PTO thin films are under in-plane tensile strain. Considering the small
lattice mismatch of 0.1% between STO and PTO, we believe that the strain is attributable to, to a larger extent, thermal expansion rather than the lattice mismatch. Moreover, with increasing thickness, the $c$ lattice constant of PTO tends to increase as well. For a 65-nm layer, we found $c$ still smaller than the bulk value, which indicates that the layer is not yet fully relaxed. As demonstrated by Ohno et al.,\textsuperscript{43} the volume change during transformation from the cubic phase to the tetragonal phase affects the residual stress more than the difference in the thermal expansion coefficients between PTO and the substrates.
Figure 4.11 (a) Φ-scan of asymmetrical (101) reflection of STO and PTO (b) Rocking curve of PTO (001)
4.5 Summary

The growth mechanism of PTO using oxides MBE was discussed in this chapter, focusing on realizing the stoichiometric growth of the single-crystalline, single-phase epilayer. The self-adjusting mechanism of Pb was employed, due to the highly volatile nature of this material. An adsorption-controlled growth was maintained in achieving pure PTO phase. The RHEED indicates that 2-D epitaxial growth was achieved under optimized conditions, and high crystalline quality has been confirmed by the XRD analysis.
Chapter 5 Epitaxy, characterization and property analysis of PZT

In this Chapter, the epitaxy, characterization and property analysis of PZT-based complex oxides will be investigated. First, the epitaxy of PZT with different Zr/Ti ratio using a co-deposition method was introduced in Section 5.1, followed by an effort of realizing PTO/PZO super lattice structure in Section 5.2. Section 5.3 will cover the different characterizations of the structural, optical, and electrical properties of the PZT-based complex oxides, and a brief summary will be given in section 5.4.

5.1 Epitaxy of PZT with different composition using co-deposition

In the previous chapter, the high-quality, epitaxial growth of PTO was introduced. While PTO films showed streaky RHEED patterns, indicative of two-dimensional growth, spotty RHEED patterns were observed for PZT films at the beginning of growth on STO due to a three-dimensional (3D) growth mode leading to a rough surface morphology. The spotty RHEED patterns of the PZT films progressively became worse with further deposition, transforming partially into a ring pattern, characteristic of textured polycrystalline films, as shown in figure 5.1 (a) and (b). To overcome this problem, a PTO buffer layer was introduced between the SrTiO₃ substrate and the PZT film. As a result, the PbZr₀.₀₇Ti₀.₉₃O₃ layer grown on the PbTiO₃/SrTiO₃ template showed a streaky RHEED pattern, characteristic of 2-D growth, and a smooth film surface. The RHEED
pattern could be found in figure 5.1 (c) and (d). It should be mentioned that although the PTO buffer works perfectly for PZT layers with low Zr concentration (around 10%), the PZT films with higher Zr content (up to 40% Zr) show more complex behavior. Initially, 2D RHEED patterns that switched to a 3-D mode as the growth progressed, and then returned back to 2-D pattern were observed, as illustrated in Fig. 5.2. The higher the Zr content, the earlier the transition started, which will lead to a more pronounced 3-D pattern.
Figure 5.1 RHEED pattern evolution during MBE growth of PZT film on SrTiO$_3$ substrate (a) (b) without and (c) (d) with PTO buffer layer.
Figure 5.2 RHEED pattern evolution during MBE growth of Pb(Zr0.3T0.7)O3 film on SrTiO3 substrate
Phase composition and structural properties of the films were determined by x-ray diffraction. The PZT films were found to be single-phase and c-axis oriented. Figure 5.3 presents a reciprocal space mapping of a PZT/PbTiO$_3$/SrTiO$_3$ structure. Only the (001) reflections of the substrate and the layers are visible. However, (100) reflections of tetragonal PZT with low Zr content should virtually coincide with (001) reflections from the SrTiO$_3$ substrate, due to the small difference in lattice constant. Therefore, to detect a-axis-oriented regions (a-domains) possibly present in the films, rocking curves ($\omega$-scan) were measured at the 2θ angle corresponding to PbTiO$_3$(100) reflection overlapping with the SrTiO$_3$(001) reflection$^{44,45}$. For a scan with 8-degree span centered at peak of STO substrate, only the diffraction peak corresponding to the substrate was observed, and no evidence of a-domains was found, which should appear within a 4-degree span centered at peak of STO substrate. XRD and RHEED data indicate that the PZT layers exhibit the epitaxial relationship of PZT$(100)\parallel$ SrTiO$_3$(100) and PZT$[001]\parallel$SrTiO$_3$[001]. The measured full width at half maximum (FWHM) of (001) $\omega$-rocking curve for the 80-nm-thick PbZr$_{0.07}$Ti$_{0.93}$O$_3$ film was as low as 4 arcmin, as compared to 2.3 arcmin for the substrate, which is indicative of high crystal quality of the grown layer. However, an increase in Zr content resulted in broadening of the XRD rocking curves to 24 arcmin for the PbZr$_{0.4}$Ti$_{0.6}$O$_3$ film. The out-of-plane and in-plane lattice parameters $a$ and $c$ calculated from 2θ positions of symmetrical (001) and asymmetrical (101) XRD reflections were found to be $a = 3.93$ Å and $c = 4.19$ Å for PbZr$_{0.4}$Ti$_{0.6}$O$_3$ and $a = 3.88$ Å and $c = 4.17$ Å for the PZT layers containing 7% of Zr. It is interesting to note that the $a$
parameter for the \(\text{PbZr}_{0.07}\text{Ti}_{0.93}\text{O}_3\) layers is very close to the bulk \(a\) parameter for \(\text{PbTiO}_3\), indicating that the \(\text{PbZr}_{0.07}\text{Ti}_{0.93}\text{O}_3\) films are pseudomorphic to the \(\text{PbTiO}_3\) buffer layers.
Figure 5.3 XRD reciprocal spaces mapping of a 75-nm-thick Pb(Zr_{0.07}Ti_{0.93})O_3 film grown on a PbTiO_3 buffer layer on a SrTiO_3 substrate
In the case of PTO growth, when Ti flux increased to a certain amount, the availability of gaseous PbO was no longer able to keep the growth in stoichiometric growth. A similar situation happened in PZT as well; when Zr-flux was increased in order to achieving higher Zr composition (>40%), the gaseous PbO could not catch up and impurity ZrO$_2$ phase appeared, as shown in Figure 5.4. Therefore, an alternative solution needs to be used in order to further tune up the composition of PZT.
Figure 5.4 XRD 2theta-theta scan of PZT with ZrO$_2$ impurity phase due to high Zr flux
5.2 Epitaxy of PZT using PTO/PZO superlattice structure

MBE allows the growth of multilayer structures with sharp interfaces and well-controlled layer thicknesses. Therefore, epitaxy of PZT using PTO/PZO superlattice structure would be another plausible method. In this case, the average composition of the structure is determined by the thicknesses of the PTO and PZO layers. Moreover, by using this alternative method, the competition between the Ti and Zr for gaseous PbO was reduced, since, at one time, only one of the Ti/Zr elements was supplied to the surface of the substrate together with gaseous PbO.
Figure 5.5 XRD 2θ-ω scan of PTO/PZO super lattice. There is no evidence of TiO$_2$ or ZrO$_2$ impurity phases. The insertion is the schematic shown of the superlattice structure.
Figure 5.5 is the XRD 2θ-ω scan of PTO/PZO super lattice, where 15 periods of PTO and PZO layer, 1.5 nm each thick, were grown on the STO substrate via a PTO buffer layer. This structure lead to a theatrical Zr/Ti 1:1, or Pb(Zr0.50T0.50)O3 composition. The PTO and PZO peaks were not resolved from the 2θ-ω scan, and alloy peaks appear instead.

Φ-scan of asymmetrical (101) reflection of PTO/PZO superlattice resolved a 4-fold symmetry for PTO and 2 fold-symmetry for PZT. This is in good accordance with the fact that PTO has a tetragonal structure while PZO has an orthorhombic structure at room temperature. The out-of-plane and in-plane lattice parameters $a$ and $c$, which were calculated from 2θ positions of symmetrical (001) and asymmetrical (101) XRD reflections, were found to be $a = 3.98$ Å and $c = 4.185$ Å for PbO/PZO superlattice structure. A summary of the calculated $a$ and $c$ parameters on PZT-based complex oxides with different composition can be found in Table 5.1, which shows a consistent increase in the in-plane lattice constant with the increase of Zr concentration.
Figure 5.6 Φ-scan of asymmetrical (101) reflection of PTO/PZO superlattice. (b) Comparison of 2θ-ω scans of PTO/PZO superlattice with Pb(Zr0.4T0.6)O3.
Moreover, the measured FWHM of (001) $\omega$-rocking curve for the PTO/PZO superlattice was 12 arcmin, which is considerably improved from the 24 arcmin value of the PbZr$_{0.40}$Ti$_{0.60}$O$_3$ layer, despite the fact that the Zr concentration in the superlattice sample should be even higher. Therefore, the application of the PTO/PZO superlattice epitaxy method seems to be a promising alternative to the conventional co-deposition method.

### 5.3 Structural, optical, and electrical properties of the PZT-based complex oxides

The microstructure of the PZT was examined by transmission electron microscopy (TEM). Figure 5.7 shows a cross-sectional electron micrograph of a PbZr$_{0.07}$Ti$_{0.93}$O$_3$/PbTiO$_3$/SrTiO$_3$ structure. Misfit dislocations are visible at the PbTiO$_3$/SrTiO$_3$ interface. Furthermore, there is no pronounced boundary between the PbTiO$_3$ buffer and the PZT layer, confirming that the PbZr$_{0.07}$Ti$_{0.93}$O$_3$/PbTiO$_3$ bilayer structure relaxed as a whole by introduction of the misfit dislocations at the PbTiO$_3$/SrTiO$_3$ interface. It should also be mentioned that no a-domains were visible in the electron micrographs, in agreement with the XRD data. The entire layer shows

<table>
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<th>PTO</th>
<th>PbZr$<em>{0.07}$Ti$</em>{0.93}$O$_3$</th>
<th>PbZr$<em>{0.40}$Ti$</em>{0.60}$O$_3$</th>
<th>PTO/PZO superlattice</th>
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<td>a</td>
<td>3.88</td>
<td>3.88</td>
<td>3.93</td>
<td>3.98</td>
<td>4.10</td>
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<tr>
<td>c</td>
<td>4.11</td>
<td>4.17</td>
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Table 5.1 A summary of the calculated a and c parameters on PZT-based complex oxides with different composition
extended area with defect-free growth, which is a good indication of high crystalline quality.
Figure 5.7 Cross-sectional electron micrograph of Pb(Zr$_{0.07}$T$_{0.93}$)O$_3$ film grown on PbTiO$_3$ buffer layer on SrTiO$_3$ substrate.
The optical properties of the PTO and PZO were studied by variable angle spectroscopic ellipsometry (VASE) at room temperature. Spectroscopic ellipsometry (SE) is capable of measuring the dielectric functions of ferroelectric thin films and, subsequently, can help determine the thickness, microstructure, and electronic band structures. Auto-retarder was used to measure the dielectric function accurately in the transparent region. The angle of incidence varied between 65 and 70 degrees. The pseudodielectric function of PTO/STO is shown in Figure 12. The layer dielectric function of PTO was fitted using the parametric optical constant (POC) model, assuming a 3-phase model of surface roughness, PTO, and STO substrate. The raw and fitted spectra in Fig. 5.8 (a) are not discernible because of the excellent curve-fitting, which reflects the high optical quality of the PTO grown by MBE. The fitted dielectric function of the PTO layer is shown in Figure 5.8 (b). Fig. 5.8 (c) is the fitted complex refractive index of the PTO layer. Note that the dielectric function is the square of the complex refractive index, that is, \( \varepsilon = (n+ik)^2 \). The refractive index, 2.605, at 633 nm (1.96 eV) is consistent with literature, which gives the refractive index value between 2.60 and 2.70. The fitted bandgap energies are \( E_a = 3.778\pm0.005 \), \( E_b = 4.189\pm0.014 \), and \( E_c = 5.25\pm0.24 \) eV. The band gap energies of \( E_a \) and \( E_b \) are similar to those of PZT thin films reported by Lee et al. This suggests that electronic bandgaps of PZTs do not change much with the addition of Zr to PTO. Indeed, the raw and fitted spectra of the second derivative of the PZO dielectric function is shown in Figure 5.8 (e). In \( E_a = 3.885\pm0.005 \) eV has been extracted, indicating only a small change in energy bandgap from pure PTO to pure PZO, the two ending points of PZT.
Figure 5.8 (a) Pseudodielectric function $\langle \varepsilon \rangle$ of PTO grown on (100) STO. (b) Fitted dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) of the PTO layer using POC model. (c) The fitted complex refractive index ($n+ik$) of the PTO layer. (d) The raw (discrete symbol) and fitted spectra (solid line) of the second derivative of the PTO dielectric function using SCP model. (e) The raw (discrete symbol) and fitted spectra (solid line) of the second derivative of the PZO dielectric function using SCP model.
To investigate the ferroelectric properties, additional PZT films were also grown on conductive, Nb-doped SrTiO$_3$ substrates. Au/Pt top electrodes of 30nm/30nm in thickness and 300 $\mu$m in diameter were then fabricated by e-beam evaporation. The polarization vs. applied electric field (P-E) characteristics was measured at room temperature with a Radiant Technologies Precision LC ferroelectric test system. Figure 5.9(a) shows a P-E hysteresis loop for a 70-nm-thick PbZr$_{0.07}$Ti$_{0.93}$O$_3$ film grown on a thin (6 nm) PbTiO$_3$ buffer layer, which extracts a remanent polarization of 83 $\mu$C/cm$^2$, and a coercive field of 77 kV/cm. It should be mentioned, however, that current-voltage characteristics of the PZT films suffered from high leakage current (from $10^{-4}$ to $10^{-2}$ A/cm$^2$ for an applied bias of 2 V), which resulted in the distortion of the hysteresis loop at high fields. High leakage currents have been observed previously for PZT layers with low Zr content (below 30%) by Foster et al.$^{48}$. 

While the origin of such leakage current still remains unclear, conductive atomic force microscopy (C-AFM) studies have been performed in order to shed some light on this issue. Figure 5.9(b) shows a typical C-AFM scan for PbZr$_{0.07}$Ti$_{0.93}$O$_3$. The darker spots of the image correspond to higher current. It can be easily seen that a non-uniform distribution of electrical current over the sample surface. Most of the sample surface exhibits the current values below the detection limit of our apparatus (~1 pA), while some local areas are highly leaky. Such a distribution of current allows for the assumption that some defects are responsible for high leakage in the PZT film.

Several possibilities could be speculated for the leakage current. First, these defects may originate from the SrTiO$_3$:Nb substrates, which are known to be composed of inferior crystal quality compared to undoped SrTiO$_3$ substrates. However, the second
phase inclusions (e.g. lead oxide) also cannot be ruled out. Moreover, in ternary oxides, such as STO, the exact stoichiometry is difficult to be obtained. For example, even a very slight Sr-rich condition may lead to the formation of 2nd phase as Sr₄Ti₃O₁₀. Indeed, if the PTO/PZT grown under self-adjusting mechanism slightly suffered from an imperfection of stoichiometry, some lead-rich or Ti-rich (most likely lead rich) phase can be expected. Therefore, TEM investigation of PZT films grown on conductive substrates is necessary to clarify this issue.
Figure 5.9. (a) P-E hysteresis curve measured for the 70-nm-thick Pb(Zr_{0.07}Ti_{0.93})O_3 film. (b) 3x3 μm C-AFM image for Pb(Zr_{0.07}Ti_{0.93})O_3 layer recorded at a bias voltage of -2 V; Δz = 4 pA, mean: -1 pA.
5.4 Summary

In conclusion, single crystal, single-phase PZT films were successfully grown on (001) SrTiO$_3$ substrates by peroxide molecular beam epitaxy. The use of a PbTiO$_3$ buffer layer between the SrTiO$_3$ substrate and PZT resulted in layer-by-layer growth of PZT films. Good crystalline quality has been confirmed by the XRD study. A nearly square-shaped P-E hysteresis loop was observed for a 70-nm-thick PZT film with a remanent polarization of 83 $\mu$C/cm$^2$. Non-uniform distribution of leakage current across the films was found by conductive AFM. Defects penetrating from the SrTiO$_3$:Nb substrate and/or second-phase inclusion are presumably responsible for the electrical leakage.
Chapter 6: Investigation on integration between oxides and GaN

PbO, ZrO$_2$, and TiO$_2$ are interesting materials by themselves, and each of them has its applications in different fields. In this dissertation, these oxides are of particular interest due to the fact that they are cousin oxides of PZT and, therefore, could be promising in the integration of PZT and GaN, a wide band gap semiconductor that has numerous applications in electrical and optoelectronic devices. The integration of ZrO$_2$, TiO$_2$, and PbO on GaN will be introduced in Section 6.1 and 6.2, respectively. Moreover, the integration of perovskite PTO with GaN will be discussed in Section 6.3. Finally, a summary will be given in Section 6.4.

6.1 Integration of ZrO$_2$ with GaN

Zirconium dioxide (ZrO$_2$) thin films have been used in a wide range of applications such as solid electrolytes$^{49}$, catalysts$^{50}$, and optical coatings$^{51}$. In terms of electronics, ZrO$_2$ has been considered as a gate dielectric in the realm of scaled down metal-oxide-semiconductor (MOS) devices, which requires the reduction of the thickness of the gate dielectric. For instance, it has been pointed out that the equivalent thickness of a gate dielectric should be around 0.8nm for the devices with short gate lengths$^{52}$, which is sufficiently thin for SiO$_2$ to suffer from direct tunneling current. As a material with a wide band gap (~5.8 eV), a dielectric constant higher than 20, high breakdown field (15-20 MV/cm), good thermal stability, and large conduction band offset ($\Delta E_c$~1.4 eV) with
silicon (ref \textsuperscript{53}), ZrO\textsubscript{2} has been studied as a candidate for a gate oxide for scaled MOS devices, and the basic properties of ZrO\textsubscript{2}/Si for metal-oxide-semiconductor field-effect-transistor (MOSFET) applications have been reported\textsuperscript{54}. The epitaxial growth of ZrO\textsubscript{2} on Si by various methods, such as metal organic chemical vapor deposition (MOCVD)\textsuperscript{55} and pulsed laser deposition (PLD)\textsuperscript{56} has been reported. Single-crystal oxides grown by molecular beam epitaxy (MBE) can, in principle, avoid grain boundaries and provide a good interface. However, attempts of ZrO\textsubscript{2} epitaxy on Si (100) by MBE using O\textsubscript{2} gas as the oxidant have also been resulted in polycrystalline ZrO\textsubscript{2}\textsuperscript{57,58}.

ZrO\textsubscript{2} can be considered effective bridge material between complex perovskite oxides and semiconductors, since it helps to accommodate the large discrepancy in crystal structure and lattice constant between the perovskite oxides and hexagonal GaN. To make possible the integration of ferroelectric perovskite oxides and semiconductors such as GaN, suitable bridge layers are required to provide a platform for high-quality oxide growth on GaN. In this vein, crystalline, especially single crystalline, ZrO\textsubscript{2} is required. In addition to being a bridge layer, single-crystal ZrO\textsubscript{2} can also be used as a gate dielectric material if sufficiently high-quality ZrO\textsubscript{2} can be attained. In a somewhat related application, amorphous ZrO\textsubscript{2} has also been explored as a gate dielectric for GaN-based devices by using ultraviolet ozone oxidation of Zr metal\textsuperscript{59} or electron beam evaporation\textsuperscript{60}. However, to the best of our knowledge, epitaxial growth of ZrO\textsubscript{2} on GaN has not been reported to date.

\textbf{6.1.1 Epitaxial growth of ZrO\textsubscript{2} on GaN}

In Chapter 5, it has been mentioned that, due to the very low equilibrium pressure of metal Zr (making thermal evaporation exceedingly difficult), zirconium tetra (Zr-t)
butoxide was chosen as the metal organic (MO) precursor for Zr. GaN (0001) templates fabricated by metal-organic chemical vapor deposition on $c$-plane sapphire served as substrates. During the growth, the temperature of the bubbler for the Zr MO source was kept at 56°C. The flow rate of the Ar carrier gas was controlled by a mass flow controller (MFC), and the flow rate values used in this work ranged between 0.25 to 2 sccm for the different growth conditions. The ZrO$_2$ films were grown under oxygen-rich conditions, and the pressure of H$_2$O$_2$ was kept between 1.5 to 3.0 x 10$^{-5}$ Torr. The evolution of growth of ZrO$_2$ by MBE was monitored \textit{in situ} by a RHEED system. Figure 6.1 displays a set of RHEED patterns of the GaN template before the growth was initiated and ZrO$_2$ patterns taken at different stages of the ZrO$_2$ growth.
Figure 6.1 RHEED pattern of (a) GaN (11\(\bar{2}\) 0) (b) GaN (1 \(\bar{1}\)00) and (c) ZrO\(_2\) (011) low temperature buffer layer (d) high temperature growth ZrO\(_2\) (011)
The diffraction pattern of ZrO$_2$ (011) is rotated about 15 degrees from both the GaN (11$ar{2}$0) and GaN (1$ar{1}$00) directions. At the initial stages of the growth, a few monolayers of ZrO$_2$ were deposited on the GaN template at a low temperature of 300°C to minimize the potential oxidation of GaN, which has a strong tendency to occur at higher temperatures. Without such a low temperature buffer layer, the RHEED pattern of high-temperature (700°C)-grown ZrO$_2$ showed a highly $a$-textured (100) structure, which is speculated to be caused by the above-mentioned oxidation of GaN at high temperature. Since the reactive species cannot acquire enough thermal energy to achieve the 2-D growth at low growth temperatures, the low temperature grown ZrO$_2$ exhibits a 3-dimensional RHEED pattern, as shown in Fig.6.1 (c). The low temperature ZrO$_2$ thin buffer was then annealed in situ at 750°C with H$_2$O$_2$ flow. A noticeable surface flattening was observed at annealing temperatures above 700°C, as indicated by the transition from a 3-D spotty RHEED pattern to a 2-D streaky one (Fig. 6.1 (d)). The high-temperature growth of ZrO$_2$ was then performed at 700°C, and the streaky RHEED pattern was maintained.

6.1.2 Characterization and analysis

The surface morphology of the epitaxially grown, 10-nm-thick ZrO$_2$ was examined by AFM (see Fig.6.2). The AFM image indicates a smooth and uniform oxide thin film with an rms value of ~4 Å for the 5 μm by 5 μm image. The ZrO$_2$ layer is contiguous, and some features of the atomic steps from the MOCVD GaN template remain observable. The continuous feature of the film is a hallmark of good epitaxy, and
must be reached for both of the discussed applications of ZrO$_2$, “bridge layers”, for the potential ferroelectric/semiconductor integration and gate dielectric.
Figure 6.2 AFM image pattern of ZrO$_2$ on GaN. The image size is 5 μm by 5 μm and rms is 4.1 Å
Figure 6.3(a) shows the XRD 0-2θ pattern of a 30-nm-thick ZrO$_2$ grown on GaN (0001)/c-Al$_2$O$_3$. The peak position of ZrO$_2$ reflection is consistent with (100) reflection of monoclinic ZrO$_2$. In other words, the out-of-plane epitaxial relationship for the growth of ZrO$_2$ on GaN (0001) is ZrO$_2$ (100)//GaN (0001). The out-of-plane a-lattice constant of the ZrO$_2$ was deduced from the peak position using the sapphire (0006) reflection as a reference. We obtained $a=5.203 \, \text{Å}$ for the 30-nm-thick ZrO$_2$ thin film. A comparison with the bulk value of $a_0=5.169 \, \text{Å}$ indicates that the ZrO$_2$ thin film is under an in-plane compressive strain and is not fully relaxed yet. The rocking curve of the ZrO$_2$ (100) reflection is plotted in Fig 6.3 (b), and the full width at half-maximum (FWHM) of the peak is 0.4 arc degree. This value is considerably small for such a thin film, and is indicative of decent crystalline quality of the epitaxially grown ZrO$_2$. 
Figure 6.3 (a) XRD theta-2theta pattern of ZrO$_2$/GaN (b) rocking curve of ZrO$_2$(100) (c) XRD Pole figure scan of ZrO$_2$ (101) and GaN (10-11)
The residual (or biaxial compressive/tensile) strain in ZrO$_2$ layers on GaN templates could be due to either lattice constant or thermal mismatch between these two materials. In order to clarify the dominant source of the strain, we have compared the strain calculated from XRD patterns, which reflects the strain condition in the layer after it was cooled. The strain during the growth (at 700°C) can be extracted from RHEED patterns, as determined by the distance between the reflections is dependent on the lattice constant. It should be noticed that, at the growth temperature, the epitaxial ZrO$_2$ does not suffer from strain caused by the thermal expansion mismatch and, therefore, the strain calculated the RHEED pattern recorded at the growth temperature is a pure reflection of the lattice mismatch. The thermal expansion coefficient for monoclinic ZrO$_2$ along the $b$ and $c$ directions (monoclinic ZrO$_2$ has a $b=5.24\text{Å}$ and $c=5.37\text{Å}$ while $\beta=99.1^\circ$) is $1.35 \times 10^{-6} \text{K}^{-1}$ and $14.68 \times 10^{-6} \text{K}^{-1}$, while that for wurtzitic GaN along the $a$ direction is $5.59 \times 10^{-6} \text{K}^{-1}$. Therefore, the $a$ lattice constant of GaN at 650°C (the growth temperature) can be estimated as $a=a_0*(1+a_a*\Delta T)=3.203\text{Å}$, where $a_0=3.191\text{Å}$ was calculated from the XRD pattern measured at room temperature. Since $\alpha=90^\circ$ in monoclinic ZrO$_2$, the inter-plane distance of ZrO$_2$ can be estimated as:

$$d = \frac{b*c}{\sqrt{b^2+c^2}},$$

while the distance between the GaN $(11\overline{2}0)$ reflection plane is $\frac{\sqrt{3}a}{2}$. Therefore, we can establish the relationship as:

$$d*S_{ZrO_2} = \frac{\sqrt{3}a}{2} * S_{GaN(11\overline{2}0)},$$

where $S_{ZrO_2}$ and $S_{GaN(11\overline{2}0)}$ are the separations of streaks in the RHEED patterns shown in Fig 6.1. The in-plane distance for ZrO$_2$ was found to be equal 3.71 Å. On the other hand, the $d$ value for the bulk ZrO$_2$ at 650°C, $d_{bulk(HT)}$, can be
estimated as

\[ d_{\text{bulk}(HT)} = \frac{b_{\text{bulk}(HT)} \cdot c_{\text{bulk}(HT)}}{\sqrt{b_{\text{bulk}(HT)}^2 + c_{\text{bulk}(HT)}^2}} \]

where

\[ b_{\text{bulk}(HT)} = b_0(1 + \alpha_b \Delta T) = 5.25 \, \text{Å} \]

and

\[ c_{\text{bulk}(HT)} = c_0(1 + \alpha_c \Delta T) = 5.43 \, \text{Å}, \]

and \( b_0 \) and \( c_0 \) are the lattice parameters of ZrO\(_2\) at room temperature. As a result, the \( d \) value for bulk ZrO\(_2\) was calculated as 3.83 Å, which confirms the in-plane compressive strain when compared with the value of 3.71 Å found from the RHEED pattern. This result is in good agreement with the XRD data, which also reveal in-plane compressive strain in the ZrO\(_2\) film at room temperature. Moreover, the difference in the distance between the RHEED reflections of ZrO\(_2\) at 700°C and 300°C was below the accuracy of our measurements, which suggests that the strain in ZrO\(_2\) grown by MBE is primarily due to lattice mismatch.

It is well known that the ZrO\(_2\) has three different crystal structures; the monoclinic structure (baddeleyite) is stable at low temperatures. As temperature rises to around 1400 K, ZrO\(_2\) undergoes a first-order martensitic phase transition into the tetragonal structure. Further increases in temperature to 2570 K will render the ZrO\(_2\) into the cubic structure (fluorite) stable at very high temperatures. Compared to monoclinic ZrO\(_2\), which commonly has a dielectric constant around 20–24, the tetragonal ZrO\(_2\) possesses a dielectric constant of up to 35–50 (Ref.\(^61\)), despite the fact that polarization at the atomic level is reduced. Dopants such as Yttria can stabilize high-temperature forms of zirconium dioxide partially or fully at room temperature, making the Yttria-stabilized zirconia (YSZ) tetragonal or cubic (when fully stabilized) and, thus, raising the dielectric constant effectively. Such YSZ thin films have already been realized by different epitaxy methods including MOCVD\(^62\), e-beam evaporation\(^63,64\) and pulsed organometallic beam epitaxy (POMBE)\(^65\). While in this dissertation monoclinic ZrO\(_2\) was achieved, further
efforts on the stabilized ZrO\textsubscript{2} will be required to follow up the study of the crystal structure and electrical properties of the epitaxial ZrO\textsubscript{2}.

An X-ray pole figure analysis was performed in order to confirm the structure of the ZrO\textsubscript{2}. The X-ray pole figures were recorded with 0.5 degree scan steps for phi (\(\varphi\)) and 1 degree steps for psi (\(\psi\)) angles; the scan ranges were 0 to 360 degree and 0 to 90 degree for phi and psi, respectively. The results are shown in Fig. 6.3 (c). The peaks with the six-fold symmetry correspond to the GaN (10\(\bar{1}\)1) reflections. Compared with the reflections of GaN, the peaks corresponding to ZrO\textsubscript{2} were relatively weak and broad, in part due to the small thickness of the film. However, it can still be confirmed that the reflection of ZrO\textsubscript{2} (101) is of two-fold symmetry, which is consistent with the monoclinic structure; however, if ZrO\textsubscript{2} has the tetragonal structure, it should be 4-fold symmetry.

The \(\theta-2\theta\) XRD patterns discussed above indicate that the out-of-plane epitaxial relationship is ZrO\textsubscript{2} (100)//GaN (0001). From our observations of RHEED, the symmetric pattern corresponding to ZrO\textsubscript{2} [011] azimuth always appeared around 15 degrees rotated regards to GaN [11\(\bar{2}\)0]. From the pole figures, the angle between the GaN and ZrO\textsubscript{2} reflections is also close to 15 degrees. Based on these findings, we can propose the in-plane epitaxial relationship for ZrO\textsubscript{2}/GaN heterostructures. Figure 6.4 illustrates the possible in-plane alignment of ZrO\textsubscript{2} and GaN lattices. The reflection plane (011) of ZrO\textsubscript{2} has 14.3 degree and 15.7 degree rotation from GaN(11\(\bar{2}\)0) and GaN(1\(\bar{1}\)00), respectively (arctan\((c/b)=45.7^\circ\), see Fig 6.4), and the in-plane epitaxial relationship of ZrO\textsubscript{2}[010]/GaN [11\(\bar{2}\)0] and ZrO\textsubscript{2}[001]/GaN[11\(\bar{1}\)00] is suggested.
Figure 6.4 proposed in-plane epitaxial relationship between ZrO$_2$ and GaN
In summary, epitaxial ZrO$_2$ has been grown on GaN(0001)/c-Al$_2$O$_3$ by oxide MBE using H$_2$O$_2$ as a source of reactive oxygen and Zr-t butoxide as a Zr precursor. To achieve 2-D growth mode, a 2-step process was adopted: low-temperature deposition of the thin buffer layer at 300°C followed by in situ annealing at 750°C and high-temperature growth at 700°C. AFM studies reveal the smooth surface with rms value for 5 x 5 µm scans of about 4 Å. The FWHM of the ZrO$_2$ (100) rocking curve is 0.4 arc degree for a 30-nm layer. The structural studies indicate that monoclinic, (100)-oriented ZrO$_2$ grows on GaN (0001). Based on the RHEED and XRD patterns, the in-plane epitaxial relationship is found to be ZrO$_2$ [010]//GaN [112 0] and ZrO$_2$ [001]//GaN [1 100] according to our observations.

6.2 Integration of TiO$_2$ and PbO with GaN

6.2.1 Epitaxial growth of TiO$_2$ and PbO on GaN

Due to the different nature of the materials, the epitaxial growth of PbO and TiO$_2$ were performed using different approaches, though both of them using traditional effusion cells as the metal source. The epitaxy TiO$_2$ was performed at 600°C and the H$_2$O$_2$ pressure was controlled between 1.5 to 3.0 x 10$^{-5}$ Torr. It is well known that Ti is easy to be oxidize and, in most cases, molecular O$_2$ is enough for the TiO$_2$ growth. Indeed, the growth conditions throughout these experiments result in an oxygen-rich one. The situation is different in the growth of PbO, in which Pb is more volatile than both TiO$_2$ and ZrO$_2$, and is notoriously difficult to oxidized. Therefore, a reduced substrate temperature (550°C) and high H$_2$O$_2$ pressure (~5.0 x 10$^{-5}$ Torr) was adopted. The deposition rate is a function of oxygen (or H$_2$O$_2$) pressure, and extra Pb just evaporates.
The epitaxial growth of both PbO and TiO$_2$ were achieved on GaN templates. In the PbO case, a 2-D growth mode was revealed by RHEED pattern. Figure 6.5 is the RHEED pattern of the PbO grown on GaN at 12 minutes, from which a streaky pattern of PbO is clearly visible in the direction parallel to GaN (11\overline{2}0) and rotated 15 degrees from (11\overline{2}0). The thickness of the PbO buffer was estimated to be ~ 20nm, according to the growth rate at that growth condition. The RHEED pattern clearly indicated that PbO was epitaxially grown on GaN as part of a layer-by-layer growth mode.
Figure 6.5 RHEED pattern of PbO grown on GaN (a) parallel to GaN (11\overline{2}0) direction (b) 15 degrees rotated from GaN (11\overline{2}0) direction
The evolution of TiO$_2$ epitaxy on GaN is somewhat different. Figure 6.6 is a set of RHEED patterns of GaN and TiO$_2$/GaN along the $(11\overline{2}0)$ direction taken at different time points. After 5 minutes of growth, the pattern of GaN gave way to the pattern of TiO$_2$. Notice that the spacing between the patterns is roughly half of that of GaN. It is noticeable that the TiO$_2$ epitaxy on GaN started in a 2-Dimensional mode. With the increase in thickness, the growth mode switched to 3-Dimensional, reflecting stress most likely coming from the lattice mismatch and thermal expansion mismatch.
Figure 6.6 RHEED pattern of (a) GaN along (11 \bar{2} 0) (b) 10 nm TiO$_2$ parallel to GaN (11 \bar{2} 0)) and (c) 120nm TiO$_2$ parallel to GaN(11 \bar{2} 0)
6.2.2 Characterization and analysis

In order to address the surface and crystalline properties of the PbO and TiO$_2$ buffer layer, AFM and X-ray diffraction studies were performed. In the PbO case, the growth was interrupted and the thin PbO buffer was taken out. AFM was performed to study the surface morphology of the epitaxially grown, 20nm-thick PbO since the growth was maintained at a 2-D mode; the images are shown in Figure 6.7. The AFM image indicates a smooth and uniform oxide film. The continuous feature of the film is a hallmark of a good epitaxy period, and must be reached in order to be applied as a “bridge layer” for the potential ferroelectric/semiconductor integration.
Figure 6.7 AFM images of PbO on GaN. The image size is 2μm by 2μm and vertical scale is 5nm.
In order to address the structure and crystal properties of the epitaxially grown TiO$_2$ and PbO, XRD phase measurement was also performed, and the spectrum is shown in Figure 6.8(a). For the 20nm PbO, the spectra-only orthorhombic PbO in the (111) direction can be detected along with the GaN the sapphire substrate. The phase of TiO$_2$ grown on GaN is clarified as orthorhombic (200), as shown in the XRD spectrum in figure 6.8(b).
Figure 6.8 XRD theta-2theta pattern of (a) PbO(111)/GaN(0002) (b) TiO$_2$ (200)/GaN(0002)
In summary, epitaxially grown PbO and TiO$_2$ has been prepared on an MOCVD grown GaN template using oxides MBE with a reactive H$_2$O$_2$ oxygen source. In situ RHEED was used to monitor the growth in-situ, which shows 2-D growth for PbO and ZrO$_2$, and a 2-D to 3-D transition for TiO$_2$. AFM was used to characterize the surface morphology of the thin PbO and ZrO$_2$, and indicates a contiguous feature. XRD pattern indicates that the epitaxial relationship between these oxides and GaN are PbO [111]/GaN [0002] and TiO$_2$ [200]/GaN[0002].

6.3 Integration of perovskite PTO with GaN

The emergence of the concept of integrating semiconductor materials such as Si or GaN, with perovskite ferroelectric materials such as PTO and PZT, is due to the anticipation that realizes new devices that enjoy the properties from both groups of materials. While considerable achievements have been attained on STO/Si, little work has been done on GaN, which do possess some intrinsic properties such as high thermal and mechanical stability, breakdown voltage, and electron saturation velocity. Therefore, the combination of attractive properties of perovskite with GaN could potentially form the basis for novel or new generation devices including ferroelectric field effect transistors, ferroelectric gate on AlGaN/GaN two-dimensional gas, RF devices and electro-optic devices. One major challenge related to the integration of perovskite with GaN, however, is the low quality of oxide films on GaN, coming from the different crystalline structures forming the aforementioned composite (perovskite PTO/PZT vs. wurtzite GaN) including a large lattice mismatch. Although post-deposition annealing is commonly used to facilitate the formation of perovskite PZT films, which is possible by the high thermal and chemical stability of GaN, diffusion of Pb and Ti into
GaN\textsuperscript{72} and cracking of PZT films because of the large lattice mismatch acts adversely and restricts the parameters of high-temperature annealing. Therefore, it is imperative to incorporate a so-called bridge layer between perovskite and GaN, which can promote the crystallization of the perovskite-phase PZT films. In this dissertation, the epitaxial growth of PTO on GaN using PbO as a bridge layer was introduced.

The epitaxial growth of PbO has been discussed in Section 6.2, and, in this situation, a 2-3nm of PbO was adopted, followed by the PbTiO\textsubscript{3} deposition. The PbTiO\textsubscript{3} layers were grown under an H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O vapor pressure of 5\times10\textsuperscript{-5} Torr, and in a substrate temperature range of 600 °C. RHEED was used to monitor the growth of PbO and PbTiO\textsubscript{3} \textit{in situ}, which clearly indicated the RHEED pattern evolution from GaN to PbO and PbTiO\textsubscript{3}. Prior to the PTO growth, the RHEED illustrated in Fig. 6.9 (c) and (d), the streaky patterns along the [1\bar{1}00] and [1\bar{1}2\bar{0}] azimuths of GaN signify the two-dimensional growth mode of the PbO film. For the following PbTiO\textsubscript{3} growth, the RHEED patterns partially transformed into three-dimensional ones and showed 2-fold surface reconstructions along both azimuths of GaN [see Fig 6.9 (e) and (f)]. The RHEED patterns of both PbO and PbTiO\textsubscript{3} repeated every 60° of substrate rotation. This behavior is inconsistent with the symmetries of bulk PbO and PbTiO\textsubscript{3} (cubic and tetragonal, respectively) and may suggest the formation of 60° domains or the pseudomorphous growth in the hexagonal structure.
Figure 6.9 RHEED patterns of PbO and PbTiO$_3$ grown on GaN: (a) GaN [1 1 0 0], (b) GaN [1 1 2 0], (c) PbO parallel to GaN [1 1 0 0], (d) PbO parallel to GaN [1 1 2 0], (e) PbTiO$_3$ parallel to GaN [1 1 0 0] and (f) PbTiO$_3$ parallel to GaN [1 1 2 0]
The crystalline structure and orientation of the as-deposited PbTiO$_3$/PbO film was determined by high resolution XRD. A pure perovskite phase was observed in the PbTiO$_3$/PbO bridge layer as shown in Fig. 6.10, corresponding to the PbTiO$_3$ (111) orientation. It needs to be emphasized, however, that the PbO seeding layer played an important role in the successful integration of the perovskite PTO and hexagonal GaN. As a contrast, the direct growth of PTO on GaN without any seeding layer results in polycrystalline materials as confirmed from RHEED patterns.
Figure 6.10 X-ray diffraction patterns of (a) PbTiO$_3$/PbO/GaN, (b) PZT/PbTiO$_3$/PbO/GaN and (c) PZT/GaN structures. Figure 6.10 (b) and figure 6.10(c) are after Reference 73.
This epitaxially grown PTO/PbO/GaN structure has been evaluated in a comparison experiment, in which PZT layers have been grown on PTO/PbO/GaN template and on GaN in the same run by sputtering. The details of the experiments are not done by the author of this dissertation, and can be found in the References. The XRD data 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. An XRD pole figure analysis was performed and the in-plane epitaxial relationships can be established as follows: PTO [112]/GaN [1100] and PTO [110]/GaN [1120]. The similar epitaxial relationships, which are for the PZT growth on GaN (0001) by MOCVD, have been reported by S. Key et al.

**6.4 Summary**

In this chapter, pioneered work on integration of epitaxial oxides including ZrO$_2$, PbO, TiO$_2$, and PTO with GaN has been demonstrated for the first time. The structural studies indicate that monoclinic, (100)-oriented ZrO$_2$ grows on GaN (0001), and the in-plane epitaxial relationship has been found to be ZrO$_2$ [010]/GaN [1120] and ZrO$_2$ [001]/GaN [1100] according to the observations documented herein. Moreover, the XRD pattern indicates that the epitaxial relationship between these oxides and GaN are PbO [111]/GaN [0002] and TiO$_2$ [200]/GaN [0002]. The PbO epitaxial layer was also used as a nucleation layer to enable the single crystalline, perovskite PTO growth on GaN. The in-plane epitaxial relationships can be established as follows: PTO [112]/GaN [1100] and PTO [110]/GaN [1120] and out-of-plane as PTO[111]/GaN(0001). Such a
PbTiO$_3$/PbO seed layer was found to influence the orientation and crystal structure of PZT films and promotes heterogeneous PZT nucleation on GaN.
Chapter 7 Summary and future research

The functional complex oxides have been investigated extensively as a result of the rapid development in the modern epitaxy techniques that lead to high-quality materials. Due to their attractive properties, such as large piezoelectric coefficient, electrical polarization, and electromechanical coupling factor, ferroelectric PTO and PZT thin films are currently of considerable interest for a wide range of applications, including the gate material for field effect, transistor-based ultrasonic and motion sensors, infrared detectors, surface acoustic wave devices, microactuators, ferroelectric field effect transistors, and nonvolatile ferroelectric random access memory devices, as well as a plethora of applications in non-linear optics.

To exploit the unique properties of PTO and PZT for device applications, high-quality, single-crystal films are required. Epitaxial PZT thin films have been prepared by various methods such as sol-gel, hydrothermal, metal-organic chemical vapor deposition, rf magnetron sputtering, and pulsed laser deposition. On the other hand, the growth of single-crystal PZT films by MBE, a modern technique providing high crystal perfection and precise control over material composition, has not yet been reported. In this research, the growth of high-quality, single-crystal PZT layers by peroxide MBE, as well as their structural and ferroelectric characteristics have been investigated. First, the growth mechanism of the lead-containing, complex oxides using oxides MBE was discussed, focusing on realizing the stoichiometric growth of single-crystal, single-phase epilayer. A self-adjusting mechanism of Pb was employed, due to the highly volatile nature of this material. An adsorption-controlled growth was maintained in achieving the pure PTO
phase. The RHEED indicates that 2-D epitaxial growth was achieved under optimized conditions, and high crystalline quality has been confirmed by the XRD analysis. Using this self-adjusting growth method, single-crystal, single-phase PZT films were successfully grown on (001) SrTiO₃ substrates by peroxide molecular beam epitaxy. The use of a PbTiO₃ buffer layer between the SrTiO₃ substrate and PZT resulted in layer-by-layer growth of PZT films. The small value of FWHM of PZT (100) rocking curve indicates the high crystalline quality of the material. A nearly square-shaped P-E hysteresis loop was observed for a 70-nm-thick PZT film with a remanent polarization of 83 μC/cm².

On the other hand, the integration of various oxides with hexagonal semiconductor GaN, has been investigated. Epitaxially grown PbO, TiO₂, ZrO₂, as well as PTO have been demonstrated. The PbO epitaxial layer was also used as a nucleation layer to enable the single-crystal, perovskite PTO growth on GaN. The in-plane and out-of-plane epitaxial relationships of these oxides with GaN have been determined by XRD technique supplemented by RHEED as well. The PbTiO₃/PbO seed layer was found to influence the orientation and crystal structure of PZT films and to promote heterogeneous PZT nucleation on GaN.

**Future research**

Ferroelectric PZT material has a wide range of applications in devices such as surface acoustic wave devices, microactuators, and ferroelectric field effect transistors. Moreover, due to its ideal piezoelectric properties, it has also been highlighted in the application as a stressor in the electro-magnetic coupling system. However, in order to make MBE-grown PZT compatible with such applications, some further works are
definitely necessary. For example, in memory applications, a low leakage density in the PZT layer is crucial. In Chapter 6, it has been mentioned that non-uniform distribution of leakage current across the films was found by conductive AFM. Defects penetrating from the SrTiO$_3$:Nb substrate and/or second-phase inclusion are presumably responsible for the electrical leakage. Therefore, several alternative methods are plausible. SrRuO$_3$ layer could be a suitable candidate to replace the expensive SrTiO$_3$:Nb, which is also inferior in crystalline quality. It needs to be pointed out that traditional effusion cells will not work well with Ru due to its low equilibrium vapor pressure, as in the case of Zr. To eliminate the 2nd phase, on the other hand, should be a direct and effective method. This requires near-perfect control over stoichiometry during the growth. Take SrTiO$_3$ for example; the 2nd phase know as Sr$_4$Ti$_3$O$_{10}$, is a product grown with slightly Sr-rich conditions. The method to accurately control the stoichiometry would be attained by RHEED patterns. Again, take STO for example; the streaky pattern should be achievable when approximate stoichiometric conditions are attained. However, when a slightly Sr-rich condition appears (even within 1%), a 2X2 reconstruction in the STO [110] direction would occur, which means a fine adjust on the Sr/Ti ratio is necessary. Similarly, when a slightly Ti-rich condition appears, a 2X2 reconstruction in the STO [210] direction would occur (which is difficult to be observed in a small sample like 1cm by 1cm), which means the Ti flux needs to be reduced. When the Ti continue to accumulate on the surface, it will turn out to be a 2X2 reconstruction in the STO [100] direction, which is representative of a very Ti-rich surface. In analogue, a similar trend should be seen / investigated in the case of PTO growth, which is expected to help reduce / eliminate the
2nd phase, which may cause leakage current. Besides that, a compensation of leakage current with doped material, such as La, should be another effective method.

On the other hand, in order to use PZT as a surface acoustic wave device or even as a “stressor”, a certain thickness of the layer is needed, which can range from several hundred nm to several hundred µm, depending on the application. This, however, is not affordable by the current growth rate of the MBE work that is documented in this dissertation. In Chapter 4, it has been mentioned that the growth rate of PTO/PZT, is limited by the rate of Ti instead of the other elements. Due to the low equilibrium vapor pressure of Ti, and the purpose of preventing alloying between the Ti material and Ta crucible, the growth rate has almost no room for increase when using the effusion cell. Therefore, an alternative Ti source is desirable in terms of increasing the growth rate. The Ti-ball system or even the Ti MO sources are available candidates. Nevertheless, even with the alternative source, it may not be a smart approach to use MBE to produce PZT thin film, hundreds of µm in thickness. In order to obtain a relative thickness while benefiting from the high crystalline quality provided by MBE, it would come to the hybrid method that employs MBE to produce the nucleation layer and use other technique such as LPE or sputtering to produce the thick layer. Some of the groundwork has been demonstrated in Reference 25 in Chapter 6.

Finally, most ferroelectric materials exhibit degradation of switched polarization during the voltage cycling, known as polarization fatigue. Fatigue is regarded as an important reliability issue for PZT films and was studied intensively over the last decade in the context of nonvolatile memory applications. It would be interesting to review these special properties of the MBE grown PZT, especially considering that most of the
speculation on the origin of the fatigue, up to now, is still on the pinning of the domain wall motion,75 or due to the inhibition of the centers of opposite domain nucleation76, which is caused either by oxygen vacancy migration during the repeated cycling77, or electron/hole injection from the electrodes due to the high electric field appearing during the polarization reversal near the interfacial region78. Therefore, it may be speculated that an improvement in the stoichiometry, including eliminating the 2nd phase, which introduces the domains and leakage current, and eliminating the oxygen vacancy, could be a plausible approach to material with improved fatigue properties. The detailed study should be performed, after the prerequisite of the low-leakage current level is achieved.
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