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Artificially Designed Ferroelectromagnetic Superlattices by Laser Molecular Beam Epitaxy

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

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Doctor of Philosophy

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Statement of Originality

Statement of Originality

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

Date _____

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Summary

Summary

Transition metal oxides have attracted great attention for decades because of their interesting physics and various promising properties, such as high temperature superconductivity, ferroelectricity and ferromagnetism. Many commercial electronic devices have been made, for instance, superconducting Josephson junction, ferroelectric random access memory (FeRAM), piezoelectric sensors, actuators and transducers. Thus, recently there has been resurgence for their very interesting physical properties of “multi-ferroicity”, which offers both electric and magnetic parameters to play with. Furthermore, an additional degree of freedom, manipulation of spin by ferroelectric polarization, has been exhibited via magnetoelectric coupling. To conduct magnetoelectric coupling in epitaxial layers, it is required to grow aligned hetero-interfaces at atomic scales. In the present research work, attempts of realizing magnetoelectricity are made for laser molecular beam epitaxial grown single crystalline multiferroic superlattices. To achieve these artificially designed superstructures, alternative layers of ferromagnetic and ferroelectric have been grown in nanometers thickness. Finally, the fully strained multiferroic superlattices are successfully realized by growing mixed valence manganite and barium titanite as layered superstructures.

Atomic smooth surface of substrate is essential to ensure sharp interfaces in epitaxial growth. Before performing growth of thin film, extra efforts have been made to develop a surface processed single crystalline SrTiO_3 substrate. Confirmed by both Reflection High Energy Electron Diffraction (RHEED) and Atomic Force Microscopy (AFM), single phase surface terminated with TiO_2 layer was obtained on SrTiO_3 (001)

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single crystal substrate. This treated substrate provides atomic smooth surface with terrace structure, of step height as one and two unit-cell (0.3905nm) only. The SrTiO₃ thin films have been grown layer-by-layer epitaxially on the pre-treated substrate in an almost perfect 2-dimensional growth mode. This has been demonstrated by intense and clear RHEED oscillations in this thesis. Additionally, the heteroepitaxy of BaTiO₃ single layer was achieved. In ferroelectric property measurements, the typical ferroelectric hysteresis loops were observed and resulted the remnant polarization values of $+P_r=8.47 \mu\text{C}/\text{cm}^2$ and $-P_r=-7.71 \mu\text{C}/\text{cm}^2$ at 35 V applied voltage.

In order to achieve multiferroic superlattices by growing magnetic oxide with ferroelectric BaTiO₃ alternatively, various magnetic transition metal oxides like (i) spinel Co ferrite (CoFe₂O₄), (ii) diluted magnetic oxide of Co doped SrTiO₃, and (iii) mix-valence manganite La_{1-x}Sr_xMnO₃ are used in the present study. Initially, Co ferrite (CoFe₂O₄) was grown on MgO and SrTiO₃ (STO) substrates respectively to investigate the structure and magnetic properties. By varying growth temperature and oxygen pressure, high quality epitaxial Co ferrite thin films were obtained with atomic smooth surface with excellent crystalline nature. The best quality Co ferrite thin films were grown on MgO substrate with the full width at half maximum (FWHM) value of 0.75°, as observed in rocking curve measurement. The strain effect on the magnetic properties was observed on the Co ferrite thin film grown on SrTiO₃ substrate. Although Co ferrite exhibits its attractive ferromagnetic property, the large lattice mismatch makes it unsuitable to form multiferroic superlattices with ferroelectric BaTiO₃ in this study. To overcome the difficulty, Co doped SrTiO₃ has been fabricated as epitaxial single phase thin films with uniform dopants. However, the non-intrinsic magnetism is observed in these thin film

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samples. After examining variety of SrTiO_3 single crystal substrates, some of substrates from certain supplier show magnetism after high vacuum annealing. Eventually, the Co doped SrTiO_3 thin films were proved nonmagnetic when high quality substrates were used. Finally, the mixed valence manganites were then chosen for the two phase multiferroic systems for its attractive magnetic properties as well as lattice mismatch. A variety of Sr doped manganites, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films were grown under different oxygen environment. Excellent performance of epitaxial manganite thin films were evaluated by the FWHM with a value of only 0.02° by the rocking curve measurement using high resolution X-ray diffraction. This result clearly indicates the almost perfect epitaxial growth was realized, and atomic sharp interface also was evidenced by lattice images of transmission electron microscopy. Further characterization by reciprocal space mapping confirmed fully strained epitaxial growth in these manganite films.

To understand the strong coupling between ferroelectric and ferromagnetic ordering in perovskites, a new approach by combination of ferroelectric BaTiO_3 (BTO) and ferromagnetic $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) multiferroic superlattices were adopted. This artificially designed magnetoelectric superlattices were featured with layered superstructure, where both ferroelectric and ferromagnetic layers were alternatively grown in nanometer scale. Using the laser MBE technique, epitaxial growth of these oxide films onto SrTiO_3 (STO) (001) single crystal substrate was controlled. By analyzing the in situ RHEED and strain energy due to the lattice mismatch, the best fit structure to achieve fully strained superlattices was found to be limited by the thickness ratio between compressive and tensile layers. In this light, the layered perovskites superlattices with building blocks of $[\text{LSMO}_{x4n}/\text{BTO}_{x3n}]$, $n = 2, 3$ to 4, were successfully grown up to 16 superlattice

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periods. Evidenced by both in-situ RHEED observations and high resolution XRD characterization, the commensurate epitaxy revealed fully strained superlattices with coherent hetero-interfaces, which coupled ferroelectricity and magnetism. The transmission electron micrographs of the prepared samples showed sharp atomic interfaces in these superlattices. Magnetic properties of multiferroic superlattice samples were measured using a physical properties measurement system (PPMS) in temperature range of 3K-300K. The trend of declining magnetization and Curie temperature from 200K to 150K is observed when n value decreasing. This phenomenon follows with the theory of critical thickness in ultrathin manganite thin films. On the other hand, the ferroelectricity in these magnetoelectric films were evidenced by ferroelectric hysteresis loops measured using a Precision Probe ferroelectric testing system.

In conclusion, this study has concentrated on transition metal oxide materials. Using laser MBE technique, various ferroelectric as well as ferromagnetic epitaxial films have been prepared and investigated on growth mechanism, crystallinity and physical properties. Finally, a new class of multiferroic materials are realized in the form of artificially designed superlattice, with promising both ferroelectric and ferromagnetic behavior simultaneously.

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1. Introduction

1.1 Motivations

Transition metal oxides have been used for centuries from magnet in compass, to current electrical devices with micro and nano scale, but a breakthrough in fundamental understanding is done only in recent years. Dominated by $3d$ outer shell electrons, transition metal oxides offer intriguing physical properties including superconducting, ferroelectricity and magnetism. This has attracted intensive research on device applications as well as fundamental understanding. Among the family of transition metal oxides, perovskite with ABO_3 structure received tremendous attentions because of their crystal structures, in which A site is occupied by the bigger alkaline ions (Sr, Ca, Na, and K) compared with the B site transition metal ions (Ti, Mn, Nb, Co and Ru).

Besides individual ferroics, multiferroics exhibit fantastic material properties for electronic device applications because they offer additional degree of freedoms of electrical induced magnetic ordering and ferroelectric polarization manipulated by magnetism. Although intensive research works have been carried out in past decades, however, the fundamental obstacle to realize strong magnetoelectric coupling in multiferroic materials still remains under the carpet. This issue originates from the conflict between two physical mechanisms of ferroelectricity and ferromagnetism, which are simultaneously exhibited by multiferroics. As we know, metallic phase is generally favored for magnetism, however high conductivity in metals may destroy ferroelectricity due to the large leakage current. In this light, two-phase system, in which both independent

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ferromagnetic and ferroelectric materials are combined, becomes preferable to single phase multiferroic materials. This has revived the strong interest in this research field recently. In this context, many new issues need to be addressed, in which investigation on intimate hetero-interfaces between ferroelectric and ferromagnetic materials at atomic scale has been conducted. This has received large research attention and many efforts have been made. In general, to have electrical or spin polarization in solid state materials, configurations and arrangements of atoms are of fundamental importance.

Recently inspired by the great successes of silicon based semiconductor devices, researchers have implemented transition metal oxides in silicon chips to achieve memory storage. Most interesting one is ferroelectric random access memory (FeRAM), a non-volatile memory offering high-speed writing, low power consumption and long writing endurance in which ferroelectric oxide appears as thin film. But, following the road map of semiconductor devices, the critical dimension of complementary metal oxide semiconductors (CMOS) has scaled into nanometer scale. However, the great challenge lies in the fabrication of high quality thin oxide films. A variety of thin film deposition techniques have been developed in the past decades. Most recently, a technique taking advantage of both pulse laser deposition (PLD) and molecular beam epitaxy (MBE) has been favored by various research groups for deposition of complex oxide thin films. Utilizing excimer laser, and laser MBE is capable for controlling the growth at mono-layer scale with flexibility of changing deposition materials. In this light, the artificially designed functional material is grown as multiple-layer thin films, where different layers are coherent at atomically aligned hetero-interfaces. Super lattices are the representative examples of the periodic structure, which are formed by alternatively growing two or more

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material at nanometers scale. Although the fabrication process of super-lattices is a considerably complicated and greatly challenging growth technique, yet the novel properties of multiferroics superlattices do lure many researchers to work in this research field.

1.2 Objectives

The fabrication of quality transition metal oxides superlattices and the investigation of magnetoelectric property in hetero-interfaces between ferroelectric and ferromagnetic layers are the main objective of the present research work. Laser MBE is the choice of technique for sample preparation in this research because of its great flexibility as well as remarkable quality of film deposition in material research. Firstly, single crystal SrTiO_3 (STO) substrate is used because of minimal lattice mismatch and stable chemical property. Then, a STO substrate showing single phase terminated layer of TiO_2 as well as surface morphology of terrace structure is required in this research, that is further examined by atomic force microscopy (AFM) and reflection high energy electron diffraction (RHEED).

In the growth of single crystal films, only two dimensional layer-by-layer epitaxy promises atomically smooth surface as well as interfaces. By utilizing in-situ RHEED, our laser MBE system is capable of performing mono-layer growth under fully optimized conditions. This shall be demonstrated in later chapters by homoepitaxy of STO using treated substrate. However, before growing multiferroic superlattices, the ferroelectric and magnetic transition metal oxides thin films should be individually prepared and characterized. From the family of ferroelectric perovskites, BaTiO_3 is adopted in the present research because of its exotic ferroelectric properties and environment friendly nature. The crystallinity and ferroelectric property are examined by high resolution X-ray

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diffraction and Precision Pro Ferroelectric Analyzer (Radiant Technologies, Albuquerque, NM, USA) with high voltage interface. On the other hand, the magnetic oxide materials are prepared as single crystal thin films, which shall exhibit excellent crystallinity as well as magnetic properties.

Another challenge in this research is to find the compatible magnetic oxide which could be epitaxially grown together with ferroelectric BaTiO_3 to form atomically sharp hetero-interface. Additionally, this hetero-structure should be periodically repeated in nano scale as a requirement of superlattice. However, there is a great variety of choices for the candidate of magnetic oxides, including diluted magnetic oxides (DMO), ferrite and mixed valence manganites. To identify the best suitable ferromagnetic oxide for growth of magnetoelectric oxide superlattices, a variety of magnetic oxide films have been prepared and characterized on both crystallinity and physical properties.

Finally, an artificially designed superlattice has been fabricated which combines both ferroelectric and magnetic materials via coherent hetero-interfaces. This artificially designed superlattice does not exist in nature because of its complicated structure and novel physical properties. In crystallinity characterization using high resolution XRD, this periodic nano-structure were proved. Using high resolution transition electron microscopy (TEM), the atomic sharp interfaces should be examined. Eventually, diversity of physical properties is revealed on this multiferroic superlattice by offering both ferroelectricity as well as ferromagnetism simultaneously.

1.3 Major Contributions of the Thesis

The present research is triggered by studying the effects of surface treatment on SrTiO_3 single crystal substrate, which is one of the most widely used single crystal

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substrates for epitaxial growth of transition metal oxides. After development of proper surface treatment process for SrTiO₃ single crystal substrate, various magnetic oxides have been grown and investigated, including spinel cobalt ferrite (CoFe₂O₄), diluted magnetic oxide (DMO) of Co-doped SrTiO₃ and mixed-valence manganite La_{1-x}Sr_xMnO₃ (LSMO). Among these ferromagnetic oxides prepared with ferroelectric oxides, a two-phase multiferroic superlattices, LSMO offers much stable ferromagnetic behavior as well as moderate lattice mismatch compared to other magnetic oxides. Consequently, LSMO has received intensive study and impressive high quality epitaxial thin films have been obtained. Eventually, nano-scaled superlattices with atomic coherent heterointerfaces have been successfully grown up to 16 superlattice periods.

To achieve high quality epitaxial thin films with atomic sharp interfaces, a comprehensive study on SrTiO₃ single crystal substrate treatment is performed before growth. Atomically flat SrTiO₃ single crystal substrates, with surfaces terminated by TiO₂, are obtained using wet-etching procedure. A subsequent high temperature annealing in oxygen, surface damage cause by buffered HF solution is repaired. The improved surface morphology is confirmed by atomic force microscopy and reflection high-energy electron diffraction to be terrace structured with unit cell height. On this atomically smooth surface, homoepitaxy of SrTiO₃ film proceeds in a perfect layer-by-layer mode as verified by RHEED oscillations. Furthermore, heteroepitaxy of BaTiO₃ is also carried out under optimized growth conditions. This additional treatment provides a well-defined substrate surface for atomically controlled epitaxial growth of various oxide films.

The first magnetic oxide investigated in this research is cobalt ferrite (CoFe₂O₄), which has high values of magneto-crystalline anisotropy and magnetostriction among the

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family of other ferrite materials. For the epitaxial growth of cobalt ferrite, the issue of lattice parameter mismatch with the substrate is of considerable importance. The growth of thin films of CoFe_2O_4 on MgO and SrTiO_3 single crystal substrates is also studied for comparison. The single crystal thin film growth modes are investigated by changing the key parameters such as oxygen pressure, growth rate and substrate temperature. Results show that the two-dimensional layer-by-layer growth mode only occurs under high oxygen pressure for epitaxy of Co ferrite. The modulation of lattice constant is observed in highly strained thin films by virtue of varying substrate temperature. Thus, to modulate intrinsic magnetic properties it is important to grow high quality Co ferrite thin films. The strong strain effects are observed in the magnetic measurements on the sample grown on different substrate of SrTiO_3 and MgO in this research. Although epitaxial growth of Co ferrite thin film on SrTiO_3 substrate is realized, the large lattice mismatch of 6.9% is the severe obstacle in subsequent research to grow superlattice with ferroelectric BaTiO_3 . The quality Co ferrite thin film grown SrTiO_3 substrate at 700 °C performed best on ferromagnetism as well as crystalline nature.

Comparing with Co ferrite, magnetic ion doped SrTiO_3 shows negligible lattice mismatch with SrTiO_3 single crystal substrate. An alternative approach to ferromagnetic oxide started with growing SrTiO_3 thin films doped with 3% of cobalt as magnetic 3d cation on SrTiO_3 (100) single crystal substrate. Both in-situ RHEED and high-resolution X-ray diffraction (XRD) techniques show high crystalline quality of the epitaxial films with no impurity phase or clusters. Highly uniform dopant distribution and certain ferromagnetic signals are observed in these thin film samples. However, in further magnetic examination on the SrTiO_3 single crystal substrate, the temperature

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ferromagnetism in blank SrTiO_3 substrate is clearly proven after the treatment of high vacuum annealing in epitaxy chamber. This room temperature ferromagnetism in substrate is generated under the growth condition of ultra high vacuum and temperature. In this light, various SrTiO_3 substrates purchased from different suppliers are tested. Then only the material purchased from Shinkosha Co. of Japan is found exhibiting no magnetic signal after vacuum annealing, that is accepted as best SrTiO_3 substrate in the market. Grown on this high grade SrTiO_3 substrates again, the Co-doped SrTiO_3 thin films show weak magnetism. Although magnetic doped SrTiO_3 exhibits almost perfect lattice mismatch with SrTiO_3 substrate, on which growth of Co-doped SrTiO_3 can be regarded as homoepitaxy.

Well known by the double exchange interaction and half-metallic property, mix-valence manganites exhibit much stable ferromagnetism as well as preferred lattice mismatch for epitaxial growth with ferroelectric BaTiO_3 as proposed in the present study. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\sigma}$ (LSMO) thin films, in which Sr concentration varied from 20%, 30% to 45%, are grown on SrTiO_3 (001) single crystal substrates using laser MBE technique. The two-dimensional layer-by-layer growth is monitored by in-situ (RHEED). Kinetic growth with surface relaxation has also been observed. Crystalline nature of the thin films has been investigated by high resolution XRD. Results of 2θ - ω scans revealed a strong correlation between out of plane lattice constant and oxygen content and strontium doping concentration. However, further analysis of spectrum shows the effect of oxygen content on the crystal structure in the (002) plane of thin films grown under different oxygen pressures (P_{O_2}). A considerable value of full-width at half maximum (FWHM) of 0.02° has been obtained from the sample grown at P_{O_2} of 5.0 Pa, that indicates perfect epitaxial

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growth of this LSMO thin film. It assures that further research is needed on growing heterostructure with BaTiO₃ in order to achieve multiferroics superlattice.

Ferromagnetic (FM) La_{0.8}Sr_{0.2}MnO₃ (LSMO) and ferroelectric (FE) BaTiO₃ (BTO) are grown alternatively on SrTiO₃ (001) single crystal substrate layer by layer to form the layered superstructure. Taking advantage of laser MBE technique, epitaxial growth was controlled at unit cell level, monitored by in-situ RHEED. From the analysis of RHEED and strain energy due to large lattice mismatch, the structure for these highly strained superlattices, is found to be best grown. This is with the thickness ratio of 3/4 between compressive and tensile layers to compensate out all stresses in the resultant films. In addition to this, the layered perovskites superlattices, LSMO_{4n}/BTO_{3n}, n = 2, 3 to 4, have been grown experimentally up to 16 periods. The atomic level growth is demonstrated by both in-situ RHEED observations and ex-situ high resolution X-ray diffraction. From the microstructure investigations using high resolution TEM, these superstructures reveal fully strained atomic sharp heterointerfaces. In the further characterization of physical properties, both ferroelectricity and ferromagnetism are identified on these multiferroic superlattices.

1.4 Organization of the Thesis

The work presented in the thesis emphasizes on the growth and characterization of transition metal oxide thin films grown by laser MBE technique. With the objective of achieving magnetoelectricity in transition metal oxide superlattices, a variety of oxide thin films have been fabricated and characterized. In the search for a new class material of multiferroic superlattices, this thesis is organized into five chapters.

Chapter 1 presents the background of the subject, motivations, objectives and

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main contributions of the thesis.

Chapter 2 presents the literature review on the present research work. Starting with, the physics of transition metal oxides followed by the introduction of representative perovskite, SrTiO_3 are presented for the better understanding of the thesis. There are two famous perovskites compounds BaTiO_3 and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ offering ferroelectricity and ferromagnetism respectively. The current status of the field is presented here in brief.

Chapter 3 describes the fundamental knowledge, working principles of experimental techniques and setups used. This includes epitaxial growth using Laser MBE, high resolution X-ray diffraction (XRD), atomic force microscopy (AFM) and transition electron microscopy (TEM) for characterization.

Chapter 4 highlights the major outcomes of the thesis. It contains the results and discussions on the multi-ferroic super-lattices. This chapter starts with investigation of single crystal substrate treatment. Then both homoepitaxy of SrTiO_3 and heteroepitaxy of BaTiO_3 are performed on the atomic smooth surfaces. After examining a variety of magnetic oxides including cobalt ferrite, dilute magnetic oxide of Co-doped SrTiO_3 and mixed-valence manganite of LSMO, multiferroic superlattices are fabricated, which exhibit both ferroelectric and magnetic properties for the grown 16 superlattice periods.

Chapter 5 concludes the major outcome and proposal for future work.

2. Background of Transition Metal Oxides

In this chapter the background knowledge of perovskites transition metal oxides is discussed here, as they offer diverse applications¹⁻⁴. The detailed crystal structure followed by ligand field theory (LFT) and orbital physics are given in detail. Further, three typical ferroics (ferroelectric, ferromagnetic and multiferroic) are introduced. Finally, a brief review of oxide thin film growth is presented.

2.1 Transition Metal Oxides

A class of materials that contains both transition metal and oxygen is known as transition metal oxides. They are studied extensively because they exhibit a variety of physical properties like ferroelectric^{5, 6}, ferromagnetic and superconductivity. These fascinating properties can be attributed to the special electronic structure and multivalent nature of transition metal elements. In the periodic table (Figure 2.1) transition metals occupy the major central parts in three series. Various $3d$ transition metals i.e. Ti, V, Cr, Mn, Fe, Co, Ni and Cu with atomic number from 22 to 29, in band are the most important and representatives. On ionization, the $4s$ electrons are lost first and the $3d$ orbitals are significantly more stabilized (that is, drop to lower energy) than the $4s$ would be. Then the electron configuration of $3d$ cations could be depicted as outer shell electron $3d^n$ with shielded core electrons which show the similar configuration of [Ar] or $(1s^2 2s^2 2p^6 3s^2 3p^6)$. With different valence states of these cations, the metal oxygen bonds could form with overlapping of $3d$ and $2p$ orbital, and the crystal structures will be one of the physical exhibitions in transition metal oxides.

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[illegible]

Figure 2.1 Periodic table with highlighted center zone of transition metal elements

With the different oxidation states, the chemistry of the transition metal oxides is interesting due to the formation of a vast number of complexes. The coordination compounds of ligands, and the number of electron pairs donated by the metal is showing many aspects of chemistry and physics. In order to understand the striking properties of transition metal oxides, it is required to study crystal-field theory, which is discussed in next section.

2.1.1 Common Crystal Structures in Transition Metal Oxides

The complex oxides present great diversity of properties due to specific lattice structure in multi cation oxygen compounds and are complex. It is important to investigate some of the common crystal structures of these materials. The nature of cation – oxygen bond dominates the crystal structure of complex oxides, which results in modified electronic properties. Then at the heart of understanding oxide materials, is recognizing how the chemical structure of the material enables the evolution of the electronic structure.

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2.1.1.1 Binary Oxides

Binary oxides contain a metallic element and oxygen, which is notated such as MO , MO_2 and M_2O_3 (M = metal cation) in stoichiometry. Common structures include rock salt (Figure 2.2 (a)), wurtzite (Figure 2.2 (b)), fluorite (Figure 2.2 (c)), rutile (Figure 2.2 (d)), and corundum (Figure 2.2 (e)). The monoxides (MO) with rock salt structure include such materials as the alkaline earth metal oxides (i.e., MgO) and some transition metal oxides (i.e., TiO , VO , CoO , and MnO) and there are a few examples of monoxides with wurtzite structure (i.e., ZnO and BeO). The properties of these monoxides range from insulators (i.e., MgO and CaO) to semiconductors (i.e., MnO and ZnO) to metals (LaO , NdO , and TiO) to superconductors (i.e., NbO) and even magnets (i.e., EuO). As for the binary dioxides (MO_2), the most common structures are the fluorite (i.e., CeO_2 , ThO_2 and ZrO_2) and rutile (i.e., TiO_2 , IrO_2 , MoO_2 , RuO_2 and WO_2) structures. Materials with the fluorite structure are typically insulators (i.e., CeO_2 , HfO_2 and PrO_2) while materials with the rutile structure are typically metallic or semiconducting in nature (i.e., RuO_2 and TiO_2). Finally, for the binary trivalent oxides (M_2O_3), common structures include bixbyite (i.e., Mn_2O_3 , La_2O_3 , and Dy_2O_3), materials with this structure are typically insulating, and corundum (i.e., Al_2O_3 , V_2O_3 , and Cr_2O_3), materials with this structure are typically insulators at room temperature.

Figure 2.2 Common binary oxide crystal structures including (a) rocksalt, (b) wurtzite, (c) fluorite, (d) rutile, and (e) corundum

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The structure of many binary oxides can be predicted on the basis of the relative sizes of the metal atom, oxide ions and filling of interstices in a close packed oxide lattice. Such predictions of structure are more difficult for ternary phases. The combination of two or more metals in an oxide generates a wealth of structural possibilities. In addition, stoichiometry of the ternary oxides may be changed by varying the proportions of the two component oxides, transition and lanthanide elements, the oxidation state. For example, at least twenty ternary oxide phases are formed between strontium and vanadium including SrV_2O_6 , $\text{Sr}_2\text{V}_2\text{O}_5$, SrVO_3 and Sr_2VO_4 . The structural chemistry of ternary and more complex oxides is, thus, an extensive subject for current research. There are, however, a few structures which are widely adopted by ternary oxides and materials from these structural classes, which have important technological applications. These ternary oxides are used as building unit in more complex compounds, such as high temperature superconductors, CMR and GMR materials. In this research two types of ternary oxides are spinel and perovskite which are widely used for technological applications. Details of these compounds are presented as follows.

2.1.1.2 Spinel

The spinel structures are ternary oxides of the stoichiometry AB_2O_4 . Here the label B applies to cation which is twice as abundant in the structure. The two cations are of similar size in contrast to the perovskites. The spinel structure is rather more complicated than those discussed earlier though one helpful representation shown in Figure 2.3. The structure is based upon a cubic close packed arrangement of anions in which a proportion of tetrahedral and octahedral sites are occupied. For a number 'n' close packed anions, 2n tetrahedral holes and n octahedral holes are generated. In the spinel structure one-eighth of

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the tetrahedral holes and one-half on the octahedral holes are occupied in an ordered manner throughout the structure. The A cations normally occupy the tetrahedral sites and the B cations the octahedral ones giving the stoichiometra $A_{2n}/8B_n/2O_n$, which is equivalent to AB_2O_4 .

Figure 2.3 The unit cell of spinel structure and subunits of the structure

2.1.1.3 Perovskite

Perovskites are named after the mineral $CaTiO_3$ which was identified by the Russian mineralogist L.A. Perovski. There exist several hundred materials with stoichiometry ABO_3 which adopt the perovskite structure or a slighted distorted version. In the notation ABO_3 the A cation is conventionally the larger of two metal ions so, for example, in $SrTiO_3$, [$r(Sr^{2+}) = 1.52 \text{ \AA}$ and $r(Ti^{4+}) = 0.745 \text{ \AA}$] strontium would be denoted as the A cation and titanium as the B cation (shown in Figure 2.4).

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Figure 2.4 The unit cell of perovskite STO and the valence of constitute atoms

Perovskite structures of titanites are one among important family of transition metal oxides, which have attracted great interest of scientific community. The Titanites have the t_{2g} bands at the Fermi level, in contrast with the cuprites and manganites, which show very different properties from these two compounds in comparison of the structural similarity. The perovskite titanite $R_{1-x}A_x\text{TiO}_3$ (where R represents the trivalent rare-earth ions and A the divalent alkaline-earth ions) shows a transition from insulator to metal upon carrier doping by increasing x ^{7, 8}. Thus, this system has been focused on as a typical example of the filling-control metal-insulator transition system⁷. The metallic phase is well described by the Fermi liquid picture⁹ in contrast with the superconducting cuprates^{10, 11} and the magnetoresistive manganites^{6, 12}. As the system approaches the metal-insulator transition via metallic side, strong mass enhancement has been experimentally found in the specific heat and the magnetic susceptibility. This enhancement effect is exhibited by well known heavy fermionic materials. Anomalous filling-dependent behaviors near the transition point have been observed in various experiments and discussed of the nature of

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the Mott transition^{9, 13-15}. The origin of the very different behavior of the titanites from the cuprites and manganites has been a subject of very intensive studies. By virtue of this, titanites have been recognized as an important class of materials in clarifying the strong electron correlation effects.

2.1.2 Crystal Field Theory and Orbital Physics

In transition metal oxides electron with spin $S=1/2$ and charge $-e$ manifests itself in many different ways¹⁶. Since electrons interact strongly not only each other but the crystal potentials [C. Kittel]. These interactions are understood on the basis of the crystal field theory in solid state physics. Thus, crystal field theory is introduced to portray the electron structure of transition metal oxides. Beginning with a description of d orbitals in most common type of oxygen octahedral to understand fascinating properties and theoretical challenges in high-temperature superconductivity and colossal magnetoresistance, orbital physics is presented in this part. A simple brief description of orbital physics that illustrates transition metal oxides as a spin-charge-orbital coupled systems are given in this section.

2.1.2.1 Crystal Field Theory

Crystal field theory is one of several chemical bonding models and is applicable to the transition metal elements. The electron properties of the transition metals as a group are more complex than those of other elements in the periodic table due to electrons being located in incompletely filled $3d$ atomic orbitals having different energy levels. For a transition-metal ion, there are five d orbitals with which oxygen can form the bond are demonstrated in Figure 2.5^{16, 17}, which are designated by d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ and each orbital has four lobes in opposite quadrants. The five d orbitals may be divided into two groups on the basis of their angular distributions. Three of the orbitals, d_{xy} , d_{yz} , and d_{xz} ,

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have lobes projecting between the Cartesian axes. This group is designated t_{2g} : here, t refers to the three-fold degeneracy; subscript 2 indicates that the sign of the wave function does not change on rotation about the axes diagonal to the Cartesian axes; and subscript g again refers to the fact that the wave function does not change sign on inversion. The other two orbitals, $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, have lobes directed along the Cartesian axes. They are designated e_g , where e stands for the two-fold degeneracy. The d_{z^2} orbital appears to have a different shape from the other four. This difference is only apparent, however. In each orbital, two electrons spinning in opposite directions can be accommodated according to the Pauli Exclusion Principle and hence total 10 electrons can be filled in d orbitals.

Figure 2.5 Five orbitals in the cubic crystal field, and this fivefold degeneracy is lifted to two e_g orbitals [$(3z^2-r^2)$ and (x^2-y^2)] and three t_{2g} orbitals [(zx) , (yz) and (xy)].

Electrons in all five 3d orbitals are repelled by the negatively charged anions or dipolar ligands¹⁸. Shown in Figure 2.6, the transition-metal ion is surrounded by six

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oxygen ions to form oxygen octahedral. Since lobes of the e_g orbitals point towards ligands or oxygen anions, electrons in these two orbitals are repelled to a greater extent than others in the three t_{2g} orbitals that project between the ligands¹⁸.

Figure 2.6 Metal-Oxygen 6 octahedron. The position of the i th oxygen ion is labeled by O_i .

Consequently, the e_g orbitals are raised in energy relative to the t_{2g} orbitals, which are represented by an energy level diagram, as in Figure 2.7. The energy separation between the t_{2g} and e_g orbitals is termed as the crystal field splitting designated by Δ_o ($\Delta_o = 10Dq$). An analogous energy separation between t_{2g} and e_g orbital groups exists in the schematic molecular orbital energy level diagram shown in Figure 2.7, shows $10Dq$ (or Δ_o) which is the energy separation between orbitals of the t_{2g} and antibonding e_g groups. The value of Δ_o or $10Dq$ is obtained directly, or may be estimated, from spectral measurements of transition metal-bearing phases in the visible to near-infrared region. In the crystal field model, the split $3d$ orbital energy levels are assumed to obey a 'centre of gravity' rule. As a result, the three t_{2g} orbitals are lowered by $0.4 \Delta_o$ below, and the two e_g

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orbitals raised by $0.6 \Delta_o$ above, the baricentre. This follows from a simple algebraic argument that the energy of six electrons in the three t_{2g} orbitals is compensated by the energy of four electrons in the two e_g orbitals.

Figure 2.7 Schematic diagram (not to scale) of 3d orbital energy lifting into e_g and t_{2g} .

2.1.2.2 Orbital Physics

The quest of understanding the physical properties of transition metal oxides with orbital degeneracy or orbital physics is at the forefront of solid-state physics^{8, 16}. The field started nearly 50 years ago by Wollan and Koehler, reported using neutron scattering to elucidate the lattice and magnetic structures of $\text{La}_{2-x}\text{Ca}_x\text{MnO}_3$ ¹⁹. In this manganese perovskite, the MnO_6 octahedral exhibits subtle distortions which lower the lattice symmetry. Wollan and Koehler noticed that the pattern of octahedral distortions varies systematically with Ca content, and these variations go along with changes in the magnetic ordering pattern of the unpaired 3d electrons on the manganese ions. The basic origin of the lattice superstructure can be understood by inspection of the electron configuration of a single Mn^{3+} ion. The cubic crystal field due to the O^{2-} ligands splits the five 3d levels into a

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lower triply degenerate t_{2g} orbital and a higher doubly degenerate e_g manifold, shown as Figure 2.8 (a). These levels are filled by the four d-electrons of Mn^{3+} according to Hund's rule, which dictates that three of the four electrons with parallel spins occupy the t_{2g} levels. The orbital degeneracy derives from the remaining electron occupying the e_g manifold. The distortion of the MnO_6 octahedral can be ascribed to a John–Teller distortion²⁰ that lifts this degeneracy, shown as Figure 2.8 (b) and (c). Since neighboring octahedral share one oxygen ion, the John–Teller distortion is cooperative and leads to a change in lattice symmetry which favors particular orbitals at neighboring sites (referred to as orbital ordering). In the condition of in plane strain, the energy level of $3z^2-r^2$ is relatively lower and accommodates the only e_g electron of Mn^{3+} ion, illustrated as Figure 2.8 (b). In another way the e_g electron will fill in the x^2-y^2 orbital as shown in Figure 2.8 (c). Different orbital ordering patterns are realized as Ca substitution removes the e_g electron and converts some of the Mn^{3+} ions to orbitally non-degenerate Mn^{4+} .

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Figure 2.8 (a) d energy levels splitting in a cubic octahedral environment, (b) lifting of the degeneracy of the t_{2g} and e_g levels due to the in plane (ab plane) strain of ligands, (c) lifting of the degeneracy of the t_{2g} and e_g levels due to the c -axial strain.

Following Wollan and Koehler, John Goodenough proposed a model describing the interplay between orbital and magnetic superstructures in the manganites²¹. Briefly, the model predicts that relative orientation of e_g orbitals on neighboring Mn sites determines the magnitude and sign of the magnetic exchange interactions, which in turn determine the magnetic ordering pattern. Goodenough's model, together with concurrent work by Kanamori and Anderson, led to a detailed understanding of the magnetic interactions and their dependence on orbital occupation, establishing a framework now known as 'Goodenough–Kanamori–Anderson rules'.

To further explain how orbital physics dominate the electron properties of

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transition metal oxides, the good examples of hole-doped manganese oxides have come up, in which the double-exchange interaction^{4, 16, 22} emerges with the strength being dependent on the doping level, various orbital-ordered and disordered states show up, accompanying the respective spin-ordering features (Figure 2.9, top panel). In the case of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ under ambient pressure²³⁻²⁵, when parent compound NdMnO_3 , is appreciably doped, the compound shows the ferromagnetic-metallic (F) state for $0.3 < x < 0.5$ (Figure 2.9 a). When doped further, the compound shows the 2D metallic state with layered-type antiferromagnetic (A) state for $0.5 < x < 0.7$. Doping above $x=0.7$ further alters the magnetic structure to the chain type (C). Here, the A state is realized as the compromise between the AF superexchange interaction between the t_{2g} spins and the double-exchange interaction through the ferromagnetic (homogeneous) order of $(x^2 - y^2)$ orbital²⁶. In cubic perovskite, the electron transfer is almost prohibited along the c axis because of the $(x^2 - y^2)$ orbital order, which is also the origin for the interplane antiferromagnetic coupling

More effectively, instead of changing the carriers' kinetic energy with doping level, one can use the lattice strain as a biasing field on the orbital state through the Jahn-Teller effect. Figure 2.9 (b) shows a schematic spin-orbital phase diagram in the moderately doped ($0.3 < x < 0.7$) manganese oxides on the plane of the uniaxial strain measured as the ratio of lattice parameter c/a (or almost equivalently the ratio of the apical to equatorial Mn-O bond length) and the doping x . The phase diagram is based on the local density function calculation as well as the experimental results for the epitaxial single-crystalline films of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with coherent lattice strain due to the lattice mismatching with the substrate²⁷. The entanglement of the doping and the strain causes the slanted phase

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boundaries for the F (orbital-disordered), A $[(x^2 - y^2)$ -ordered], and C $[(3x^2 - r^2)$ -ordered] states. As a general trend, the decrease of hole doping enlarges the F region (seeing Figure 2.9), whereas the increase (decrease) in the c/a ratio stabilizes the C (A) state as expected. In fact, thin films of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.5$) epitaxially grown on three different perovskite substrates show the respective ground states (F, A, and C) and similar transport properties to those shown in the case of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ (Figure 2.9 a).

Figure 2.9 Spin-orbital phase diagram in the perovskite manganese oxide. The top panel shows the orbital and spin order realized in the hole-doped manganese oxides. (a) Temperature dependence of resistivity in various magnetic fields $\mu_0 H$ for $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ (NSMO) with the respective magnetic phases (F, A, and C). The numbers in parentheses represent the uniaxial lattice strain, c/a ratio, indicating the coupling of the magnetism to the orbital order as shown in the top panel. (b) The schematic phase diagram in the plane of lattice strain c/a and doping level x . The data labeled LaAlO_3 (LAO),

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(La,Sr)(Al,Ta)O₃ (LSAT), and STO represent the results for the coherently strained epitaxial thin films of La_{1-x}Sr_xMnO₃ (LSMO) grown on the perovskite single-crystal substrates of LaAlO₃, (La,Sr)(Al,Ta)O₃, and SrTiO₃, respectively. LSMO-bulk and NSMO-bulk stand for the results for the bulk single crystals of La_{1-x}Sr_xMnO₃ and Nd_{1-x}Sr_xMnO₃, respectively.

The description of the interplay between spin, orbital and charge degrees of freedom resulting from this pioneering experimental and theoretical work was later refined and extended to several other materials. In the mid-1980s, the discovery of high-temperature superconductivity in cuprates gave a huge boost to research on transition metal oxides. A multitude of new materials have been discovered, including many in which orbital degeneracy plays a central role. Examples include ruthenates and cobaltates, where unconventional superconducting states are realized and compounds in which orbital degeneracy is combined with geometrical frustration. Further on, while most of the work prior to 1986 was carried out on polycrystalline samples, following the discovery of high- T_c superconductivity a meticulous effort has led to the synthesis of high-quality single crystals and thin films of many transition metal oxides.

2.2 Ferroelectricity in Transition Metal Oxides

Ferroelectricity (discovered in 1921), with two stable polarization state $+P$ and $-P$ could be used to encode the 1 and 0 of the Boolean algebra that forms the basis of memory and logic circuitry in all modern computers. Ferroelectric transition metal oxides have offered a great potential for application since the discovery of ferroelectric perovskites in a wide variety of commercial devices, for example of Ferroelectric RAM (random access memory), seen in Figure 2.10. In this section, basic principle of ferroelectricity is introduced based on the prototypical ferroelectric perovskite of Barium Titanate (BaTiO₃). Also, a number of intriguing phenomena on ferroelectric thin films are reviewed.

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Figure 2.10 Cross-sectional SEM image of the Samsung 4 Mbit 1T-1C 2 metal FRAM.

2.2.1 Basic Principle of Ferroelectricity in Perovskite

BaTiO₃ exhibits the perovskite structure above 120 °C and a distorted perovskite structure below 120 °C (Figure 2.11 (a)). Above 120 °C, the crystal structure of BaTiO₃ is cubic; below 120 °C, it is slightly tetragonal ($a = b = 3.98 \text{ \AA}$, $c = 4.03 \text{ \AA}$), which is ferroelectric. The O²⁻ are shifted in the negative c -direction, while the Ti⁴⁺ ion is shifted in the positive c -direction, thus resulting in an electric dipole along the c -axis (Figure 2.11). The dipole moment per unit cell can be calculated from displacement and charge of each ion and summing the contributions from the ions in the unit cell. There are in total five (i) one Ba²⁺, (ii) one Ti⁴⁺ ion and (iii) three O²⁺ ions per unit cell. This shift breaks the cubic symmetry, resulting in six symmetry-equivalent variants with polarization along a , b , and c axes. The polarization of a single variant, regarded within macroscopic electrostatics, produces a bound surface charge on the order of $1.5 \times 10^{14} \text{ electrons/cm}^2$ and an internal electric field that, if unscreened, approaches 300 MV/cm^{28} . Then domain walls separate variants with polarization in different directions.

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Figure 2.11 Crystal structure of the perovskite ferroelectric BaTiO₃. (a) High temperature, paraelectric, cubic phase. (b) and (c) Room temperature, ferroelectric, tetragonal phases, showing up and down polarization variants. The atomic displacements are scaled to be clearly visible.

For ferroelectric materials, domains, consisting of many spontaneously polarized unit cells aligned in the same direction, will start switching directions in response to the electric field and eventually aligned with the electric field as closely as the crystal structure permits, when the externally applied electric field is sufficiently large. The hysteresis of P - E loop (Figure 2.12) is the most important characteristic of a ferroelectric material. In analogy with magnetic hysteresis, when the applied electric field is removed, a remanent polarization P_r (or $-P_r$) appears because of the polarized condition, and the polarization may reach zero when the coercive field E_c is achieved. These properties of ferroelectric materials promise the capability of nonvolatile memory storage. For applications of ferroelectrics, a large spontaneous polarization is one of the most important requirements. A large spontaneous polarization can be achieved in each individual unit cell, which is a motivation of engineering in ferroelectric thin film.

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Figure 2.12 Typical ferroelectric hysteresis loops for BaTiO₃ ceramic ferroelectric material.

2.2.2 Nanoscale Ferroelectric Oxide Thin Film

In epitaxial nanoscale thin film, a number of new physical phenomena are observed, such as the size effect and strain enhanced ferroelectricity. In this section, the developments of such work in thin film ferroelectrics are summarized.

2.2.2.1 Size Effects on Ultrathin Ferroelectric Films

BaTiO₃ (BTO) shows strong ferroelectricity and has great potential to replace another ferroelectric material, lead zirconate titanate (PZT), because of environment and air pollution concerns. To fabricate nano size electron device, thinner ferroelectric films are continually grown, however, the critical thickness in ferroelectric puts limitations, beyond which ferroelectricity would disappear. Recently, depolarization field induced polarization relaxation in ultrathin BTO films has been reported²⁹. The thickness of BTO thin film varied from 5nm to 30nm, and the polarization (P) value significantly responds as cliff curve as shown in Figure 2.13. In Figure 2.13 (b), the P value measured at 2 and 100 kHz are plotted, and the theoretical predictions are carried out by First Principle calculation (FPC) and Landau-Devonshire calculation (LDC), respectively. By taking into account the depolarization field E_d , both theories can fit the experiment result. However,

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the FPC model shows less systematic error when, the polarization value is re-plotted in normalized form, as given in Figure 2.13(c). Through the above observation, the critical thickness can be identified to be 15nm.

Figure 2.13 (a) Upper halves of hysteresis loops for 15 nm thick BTO capacitor at the frequency of 2 and 100 kHz. (b) The experimental value of polarization from pulse measurements is fitted by first principles calculation (FPC), and Landau-Devonshire calculation (LDC), respectively. (c) Normalized behaviors of LDC, FPC, and P_s to the values of BTO capacitors with 30 nm thickness.

Understanding the size effect in ferroelectrics is complicated because there are many properties affected by both intrinsic and extrinsic factors. In the case of a ferroelectric capacitor, the ferroelectric thin film is covered by two metallic layers, then a large depolarization field E_d is built at the BTO film surface. Furthermore, the E_d effect would be critical in a thinner BTO film, and the E_d can be determined by the work function of electrode material. In a further study, by applying an external electrical field, the depolarization field induces polarization relaxation³⁰. Although in this report, the thickness of BTO thin film deposited is as thin as 5 nm, which might not be good enough to have ferroelectric effect. Thus the argument will be: whether an intrinsic critical thickness of ferroelectric thin film exists (or not) to suppress the ferroelectricity. To answer this question, several systematic studies of size effects have been carried out³¹⁻³⁴. However, some other external parameters such as composition, strain and charge complicate the deep

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understanding and explanation, until a great achievement was done by Dillon D. Fong et al.³⁵. In their approach, PbTiO_3 single crystal thin films were grown on STO substrate along the c-axis orientation which induced an in plane compressive strain to constrain polarization direction being perpendicular to the substrate surface. The thickness of PTO thin films was well controlled from 1 to 4 unit cells with only 10% variation. The in-situ synchrotron X-ray diffraction was carried out and the mapping results along the 303 Bragg peak for the various thickness and temperature are shown in Figure 2.14. It is well understood that the 180° domain pattern produces the minimal free energy of this PTO ultra-thin films, which is depicted schematically as the insets in Figure 2.14. The in-plane diffused X-ray scattering profiles of Figure 2.14 can be identified into two different symmetry groups. One is distinguished with the satellite peaks surrounding PTO Bragg peaks that represent the fourfold symmetry of those thin films, and another pattern that only shows the Bragg peaks that manifest the isotropic arrangement of crystallography. Conclusion of intrinsic critical thickness of 3 unit cells on PTO thin film could be made based on the observed results of these samples.

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Figure 2.14 In plane X-ray diffraction around PTO (303) Bragg peak for various thickness and temperature. The inset shows the domains strip orientation of thin film. H and K indicate the in-plane reciprocal space coordinates.

As discussed, the domain strip patterns had been observed in ultra-thin films which showed the ferroelectric phase when the thickness satisfies the critical thickness and above. Although this phenomenon has been well explained by Landau thermodynamic theory, estimation of this impact on the real emerging devices is still not fully understood. In a real device, overall zero polarization could occur in a ferroelectric capacitor because of the 180° switched domain structure when the thickness is smaller than that of critical size. Recently, a good progress was made on this issue whereby the polarization switching dynamics was governed by thermodynamic nucleation process³⁶.

2.2.2.2 Strain Enhanced Ferroelectricity

Epitaxial growth offers a great advantage to researcher, whereby one can manipulate the strain state in thin films. Through selection of the appropriate substrate, the physical properties of thin films can be engineered.

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Reported by Choi et.al³⁷, the remarkably enhanced ferroelectric properties of BTO thin films were achieved by biaxial compressive strain. Using different substrates, the in plane strain was imposed on BTO thin film in coherent epitaxial condition, that results in a ferroelectric transition temperature of nearly 500 °C higher and a remnant polarization at least 250% higher than that of bulk BTO single crystals. Figure 2.15 shows the ferroelectric hysteresis loops measured on the ferroelectric stacks grown on GdScO₃ and DyScO₃ substrates with 200nm thick BTO layers, together with results from a BTO single crystal³⁸, where (a) Polarization-electric field hysteresis loops of BaTiO₃ thin film capacitors (2000 Å) grown by PLD on GdScO₃ and DyScO₃ with SrRuO₃ top and bottom electrodes. The inset shows the loop hysteresis of an unstrained bulk BaTiO₃ single crystal for comparison. (b) Temperature dependence of the lattice parameters of strained SrRuO₃/BaTiO₃/SrRuO₃ capacitor structures grown by PLD on DyScO₃ substrates and GdScO₃ substrates. The in-plane ($\parallel$) and out-of-plane ($\perp$) lattice constants of the BaTiO₃ thin films, SrRuO₃ bottom electrode, and underlying substrates are shown. The lattice parameters of the SrRuO₃ film on DyScO₃ could not be resolved because SrRuO₃ and DyScO₃ are isostructural with very similar lattice parameters. The change in slope at high temperature indicates a phase transition. The error bars ($\pm$ SD) of the measured lattice constants are shown to the left of each curve. The measured values of the out-of-plane lattice constant of biaxially strained BaTiO₃ are compared with theoretical predictions with and without a ferroelectric transition. The hysteresis loops are shifted in the positive voltage direction. This imprint effect is probably due to the asymmetric interfacial properties of the top and bottom electrodes to the BaTiO₃ films³⁹.

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Figure 2.15 (a) Polarization-electric field hysteresis loops of BaTiO₃ thin film capacitors (b) Temperature dependence of the lattice parameters of strained SrRuO₃/BaTiO₃/SrRuO₃ capacitor structures grown by PLD on DyScO₃ substrates and GdScO₃ substrates

Another case of strain effects was demonstrated in SrTiO₃/BaTiO₃ superlattices by Tenne⁴⁰. Using ultraviolet Raman spectroscopy, they showed that one-unit-cell-thick BaTiO₃ layer in BaTiO₃/SrTiO₃ superlattices was not only ferroelectric (with T_c as high as 250 Kelvin) but also polarized the quantum paraelectric SrTiO₃ layers adjacent to them. A T_c was tuned to ~500 K by varying the thicknesses of the BaTiO₃ and SrTiO₃ layers, in strained multiple layers. In Figure 2.16 (a), a cross section HRTEM image of the superlattice shows alternating layer of 5 unit cells of BaTiO₃ and 4 unit cells of SrTiO₃⁴⁰. The interface roughness is confirmed within 1 unit cell. In Figure 2.16 (b), T_c determined by the Raman data, X-ray diffraction (XRD), and the phase-field model are shown as a function of the BaTiO₃ and SrTiO₃ layer thicknesses. The XRD measurement provides an additional confirmation of the Raman results, where a change in the temperature dependence of the out-of-plane lattice constant can be taken as an indication of T_c . The T_c increases with increasing n as the dipole-dipole interaction in BaTiO₃ layers becomes stronger, whereas large m suppresses T_c by reducing the coupling between the BaTiO₃ layers. By changing the values of n and m , T_c is tuned from 151 to

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638 K; that is, from 250 K below to 235 K above the bulk value of BaTiO₃. The higher-than-bulk T_c is due to the strain in the BaTiO₃ layers, just as strain enhances T_c in single-layer ferroelectric films. When the strain is partially relaxed in sample (BTO8/STO4) 40, T_c drops almost to the bulk BaTiO₃ value.

Figure 2.16 (a) is the HRTEM image of BTO₅/STO₄ superlattice. (b) The T_c of superlattices is plotted as function of n value of BTO_n/STO_m superlattice.

2.3 Magnetism in Transition Metal Oxides

Comparing with ferroelectricity in transition metal oxides, ferromagnetism is more complex, such as spin, charge and orbital structure of metal ions. In this section, a brief introduction of modern magnetic oxides is presented. The first part classifies magnetic oxides according to magnetic mechanism. After that more focus is placed on to the mix-valence manganite, which is ferromagnetic oxide used as the magnetoelectric superlattices in the present study.

2.3.1 Classification of Magnetic Oxides

The use of magnetic oxides in electronics technology has become common. To classify these magnetic oxides, three types of magnetic coupling are referred as superexchange, double exchange and RKKY coupling they are illustrated in Figure 2.17.

Figure 2.17 Magnetic coupling in oxides. Schematic illustrations of (a) superexchange, (b) double exchange, and (c) RKKY coupling.

Superexchange (or Kramers-Anderson superexchange) is the strong antiferromagnetic coupling between two next-to-nearest neighbor cations through a non-magnetic anion, that was formally developed by Anderson⁴¹. Superexchange is an important effect in ionic solids where 3d and 2p orbitals of transition metals interact. It is described through a simple valence bonding argument, how antiferromagnetic ordering occurs. Figure 2.17 (a) shows a schematic illustration of the superexchange effect in $LaMnO_3$. Each of the Mn^{3+} ions contains four 3d electrons and when these atoms bond, with some degree of covalence and a mediating O^{2-} anion, the only way that hybridization can take place is with the donation of electrons from the oxygen to the manganese ions. By Hund's rule, the spin of the electron donated to the left Mn-ion must be the same as the spins in the Mn-ion, which leaves an electron of the opposite spin in the oxygen p-orbital to be donated to the right Mn-ion. By the same argument, this bonding can only take place

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if the spins of the right Mn-ion are opposite to the left Mn-ion. The oxygen-mediate bonding leads to a collective antiparallel spin alignment of nearest neighbor Mn-ions.

In physics, the fundamental mechanism of interaction between unlocalized electrons can attribute to double exchange process. In 1951, Zener proposed an explanation of this behavior in terms of his theory of indirect magnetic exchange between 3d atoms ⁴². If parent manganite like LaMnO_3 is doped with Sr or Ca on the La-site, a mixed valence compound is created. Double exchange describes the magneto-conductive properties of these mixed valence compounds and delineates the mechanism for hopping of an electron from one site to another through the mediating oxygen atom. Again, because the O^{2-} ion has full p -orbitals, the movement from one ion through O^{2-} to another ion is done in two steps. This idea is explored extensively for the case of the widely studied oxide ferromagnet $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ which has Mn^{3+} and Mn^{4+} ions (Figure 2.17 (b)). Assuming the ligand field is relatively small and filling the 3d orbitals following the Hund's rule the Mn^{3+} and Mn^{4+} ions with electrons as shown with the dark blue arrows. In such materials, electron conduction proceeds by this double step process by which one of the electrons on the Mn-sites jumps back and forth across the oxygen. The electron is thus delocalized over the entire M–O–M group and the metal atoms are said to be of mixed valency. This is aided by the fact that spin-flips are not allowed in electron hopping processes and thus it is more energetically favorable if the magnetic structure of the two Mn-ions is identical; therefore, ferromagnetic alignment of moments is achieved.

Comparing traditional ferrite or magnate, dilute magnetic oxides (DMO) is straitforward way to make oxides being magnetic. Dilute magnetic oxides (DMO) are wide-bandgap materials that behave ferromagnetically when doped with a few percent of a

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magnetic 3d cation.⁴³ The magnetism of DMO is depicted as RKKY coupling. The RKKY exchange (named after the work of Ruderman and Kittel, Kasuya, and Yosida)^{44, 45} is not based on the relationship between bonding and magnetism, but instead is the concept that a local moment can induce a spin polarization in a surrounding conduction electron sea. Such studies have showed that the spin polarization of the conduction electrons oscillates in sign as a function of distance from the localized moment and this spin information can be carried over relatively long distances (Figure 2.17 (c)).

2.3.2 Strain Effects in Mixed Valence Manganite Thin Film

Magnetic and electrical properties of manganite thin film are greatly manipulated by strain because of their nature of spin, charge and orbital ordering. For example, strain-dependent magnetic phase diagram of epitaxial $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films is observed.⁴⁶ The metal-insulator transition was found to be suppressed by biaxial strain in manganite epitaxial thin film.⁴⁷ Additionally, the magnetic anisotropy of manganite thin films was also found to be manipulated by strain in manganite thin films by Suzuki.⁴⁸

Theoretically, Millis et al⁴⁹ proposed an analytical model to describe the effects of biaxial strain (ϵ_{xx} and ϵ_{yy}) on the magnetotransport properties of colossal magnetoresistance CMR manganites. In this model, the Curie temperature (T_c) depends on two parameters: (1) the bulk compression $\epsilon_B = 1/3(2\epsilon_{xx} + \epsilon_{zz})$ (assuming $\epsilon_{xx} = \epsilon_{yy}$), and (2) the biaxial distortion $\epsilon_* = 1/2(\epsilon_{zz} - \epsilon_{xx})$, where $\epsilon_{xx} = (a_{xx} - a_{\text{bulk}})/a_{\text{bulk}}$ and $\epsilon_{zz} = (a_{zz} - a_{\text{bulk}})/a_{\text{bulk}}$ are the pseudocubic in-plane and out-of-plane strain, respectively. Experimentally, a direct way of introducing strain is to grow manganite thin film on different substrates showing a variety of in plane lattice constants.

An intensive work was reported by Adamo et al⁴⁶. They grew (001) $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

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thin films on different single crystal substrates, varying the substrate-induced biaxial strain from -2.3% to +3.2%. The influence of biaxial strain on the temperature dependence of the resistivity $\rho(T)$ of the thin films grown on various substrates is shown in Figure 2.18. The data clearly indicates that strain has a significant effect on the metal-insulator (MI) transition temperature. In the case of thin films with a small amount ($|\epsilon_{xx}| \leq 0.6\%$) of strain (SrTiO_3 , LSAT, and NdGaO_3), the low temperature resistivity values $\rho < 0.1 \text{ m}\Omega\cdot\text{cm}$ are comparable to those measured on single crystals, confirming the high quality of these samples. The MI transition temperature (T_{MI}) is higher than 390 K for the samples grown on NdGaO_3 ($\epsilon_{xx} = -0.5\%$) and LSAT ($\epsilon_{xx} = -0.4\%$). The film grown on SrTiO_3 ($\epsilon_{xx} = +0.6\%$) shows a T_{MI} around $370 \pm 10 \text{ K}$. T_{MI} is reduced as the magnitude of the substrate mismatch increases, as in the case of the film on DyScO_3 ($\epsilon_{xx} = +1.6\%$). The film deposited on LaAlO_3 ($\epsilon_{xx} = -2.3\%$) shows an insulating behavior over the entire temperature range, in agreement with previous work.^{50, 51} The films grown on GdScO_3 ($\epsilon_{xx} = +2.3\%$), SmScO_3 ($\epsilon_{xx} = +2.7\%$), and NdScO_3 ($\epsilon_{xx} = +3.2\%$) show room temperature resistivity values of $\approx 1 \text{ }\Omega\cdot\text{cm}$. Due to their high resistivities these $\rho(T)$ curves have been measured over a reduced range of temperatures and are not given in Figure 2.18 (a). In Figure 2.18 (b), the magnetization is plotted, after subtracting the magnetization of the bare substrates. The samples were cooled down to 10 K in an applied field of 1000 Oe. The data were taken during warming up. For the films grown on the rare earth scandate substrates, no magnetic field was applied due to the large paramagnetic background signal. For the other samples, 1000 Oe was also applied during warming. The circles indicate the Curie temperature, defined as the temperature where the $M(T)$ of the film first deviates from $M(T)$ of the bare substrate.

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Figure 2.18 (a) Resistivity vs. temperature behavior, at zero applied magnetic field, of 22 nm thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films on different substrates (10 nm thick on NdScO_3). (b) The temperature dependence of the magnetization normalized at 10 K of samples cooled in a 1000 Oe field of $H = 1000$ Oe. Circles indicate the Curie temperature, T_C .

2.4 Multiferroics

Multiferroics are defined for materials which exhibit more than one ferroic order parameter simultaneously. Searching multiferroic materials has been an exciting topic for decades, since the magnetic order induced ferroelectricity⁵² or superconductivity⁵³ shows great potential on novel device design and applications. However, the physical mechanism of ferroelectric and ferromagnetic phenomena counteract naturally. In ferromagnetic transition metal oxide, partially filled d-shell is favored to fulfill exchange coupling between metal ions. This process also promises the high conductivity simultaneously as the ferromagnetic phase arises. However, the high dielectric property is the feature of ferroelectric material, in which empty d-shells prevent electrons hopping and result in low leakage current. Because of this fundamental contradiction, few truly 'multiferroic' materials exist in nature, but the 'magnetoelectric' coupling of magnetic and electrical properties is not clear. In Figure 2.19, the terms of “multiferroics” and “magnetoelectric”

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are shown schematically. The relationship of multiferroics and magnetoelectric is incompletely overlapping. By the original definition, a single-phase multiferroic⁵⁴ material is one that possesses two or all of the ‘ferroic’ properties: ferroelectricity, ferromagnetism and ferroelasticity. Moreover, the classification of a multiferroics has been broadened to include antiferroic order. Magnetoelectric coupling, on the other hand, may exist whatever may be the nature of magnetic and electrical order parameters. It can occur in paramagnetic ferroelectrics, shown in Figure 2.19. Magnetoelectric coupling may arise directly between the two order parameters, or indirectly via strain.

Figure 2.19 The relationship between multiferroics and magnetoelectric materials. Ferromagnets (ferroelectrics) form a subset of magnetically (electrically) polarizable materials such as paramagnets and antiferromagnets (paraelectrics and antiferroelectrics). The intersection (red hatching) represents materials that are multiferroics. Magnetoelectric coupling (blue hatching) is an independent phenomenon that can, but need not, arise in any of the materials that are both magnetically and electrically polarizable. In practice, in is likely to arise in all such materials, either directly or via strain.

2.4.1 Two-phase System in Multiferroics

An alternative strategy for engineering enhanced magnetoelectric effects is to introduce indirect coupling, via strain⁵⁵, between two materials such as a ferromagnet and

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a ferroelectric. Each phase may then be independently optimized under conditions at room temperature performance and coupling limitation. Figure 2.20 shows that strain coupling requires intimate contact between a piezomagnetic (or magnetostrictive) material and a piezoelectric (or electrostrictive) material. Schematically illustrated in Figure 2.20, these two phase systems can be realized in the form of composite (a), laminates or epitaxial multilayer (b) and fiber/rod composite.

Figure 2.20 Strain-mediated magnetoelectric coupling in two-phase systems. (a) particulate composite, (b) 2-dimensional thin-film heterostructures, and (c) composite or epitaxial pillars.

Among these methods, most two phase multiferroics of polycrystalline or ceramics are categorized as particulate composite. For example, to achieve high density as well as strong magnetoelectric coupling nickel ferrite (NFO) and PZT powder were hot-pressed and spark plasma sintered into ceramic composite, shown as Figure 2.21, reported to have a large improvement in the magnetoelectric voltage coefficient⁵⁶.

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Figure 2.21 Scanning electron microscopy (SEM) images of (a) polished surface and (b) fractured surface of the NFO-PZT composite ceramics.

On the other hand, a nanostructured $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ ferroelectromagnet exhibiting coupling between ferroelectric and magnetic order parameter was reported⁵⁷. This two phase multiferroics is representatively considered as the nano-pillars in Figure 2.20 (c). In Figure 2.22, transmission electron microscopy (TEM) study resolves these hexagonal patterns to be arrays of CoFe_2O_4 pillars with 20- to 30-nm diameters embedded in a BaTiO_3 matrix (Figure 2.22 (a)). A CoFe_2O_4 volume fraction of $\sim 35\%$ was estimated from such planar section images. Cross-section TEM reveals that the pillars go through the thickness of the film, and high-resolution images reveal the heteroepitaxy between the CoFe_2O_4 and the BaTiO_3 lattices. Plan-view electron diffraction patterns are given in Figure 2.22 (b). Together with cross-section diffraction patterns, the orientation relationship: $[100] \text{ SrTiO}_3 // [100] \text{ SrRuO}_3 // [100] \text{ BaTiO}_3 // [100] \text{ CoFe}_2\text{O}_4$ was also reported⁵⁷.

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Figure 2.22 (a) TEM planar view image showing the CoFe₂O₄ nanostructures in the BaTiO₃ matrix. (b) Electron diffraction pattern of (a), illustrating the in-plane heteroepitaxy between CoFe₂O₄ and BaTiO₃.

Compared with the results of two phase multiferroics, epitaxial thin-film heterostructures could permit precise magnetoelectric study, because crystallographic orientation, layer thickness and interfacial roughness can be controlled accurately. However, ferroelectric layers can generate strains in the order of 1% in magnetic epitaxial layers owing to lattice constant mismatch.

2.5 Growth of Oxide Thin Films

A critical part of this research lies in fabricating high quality oxide thin film which should deliver desired features. For this purpose, laser molecular beam epitaxy (MBE) is utilized for growing complex oxide thin films. In the following section, a brief introduction about the history of development of laser MBE technique and basic epitaxy modes to clarify the epitaxy mechanism are presented.

2.5.1 Development of laser Molecular Beam Epitaxy (MBE)

Pulsed-laser deposition (PLD) has been used for the synthesis of complex oxide

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materials, superlattices, and well controlled interfaces. The use of a pulsed laser to induces the stoichiometric transfer of a material from a solid source to a substrate. Pulsed laser evaporation for film growth from powders of SrTiO_3 and BaTiO_3 was achieved first time in 1969⁵⁸. In 1983, Zaitsev-Zotov et al. reported superconductivity in pulsed-laser evaporated $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ films after heat treatment.⁵⁹ The real breakthrough for PLD, however, was its successful application to the in situ growth of epitaxial high temperature superconductor films in 1987 at Bell Research Lab⁶⁰.

Since then, PLD has been used extensively in the growth of these high-temperature cuprate and numerous other complex oxides, including materials that cannot be obtained via an equilibrium route. Early on, it has been shown that the processes in the growth of materials from a PLD plume were fundamentally different from those found in thermal evaporation⁶¹. As the PLD process became better controlled and more sophisticated, the term “laser MBE” was introduced to describe a PLD system in which layer-by-layer growth was achieved and monitored by RHEED. This terminology is somewhat inaccurate, as a laser plume always contains a combination of ions, electrons and neutral particles and not a molecular beam. Nevertheless, ‘laser MBE’ has been used successfully to go beyond the co-deposition of all components of a complex oxide by instead deposition single layers of SrO and BaO sequentially⁶² and intercalating SrO layers in manganites⁶². The detail technique of laser MBE is conceptually simple, and the details are introduced in next chapter of experimental set up.

2.5.2 Epitaxial Crystal Growth and Strain of Thin Film

Laser MBE technique is referred to high vacuum crystal growth, in which species are transported from source to substrate in high vacuum environment. The extreme growth

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conditions make observation of growth difficult, and greatly affect growth modes. In this section a brief overview of typical epitaxy modes as well as strain effect are presented.

It is generally accepted that there are three may be possible distinguished modes of crystal growth on surfaces. These modes are illustrated schematically in Figure 2.23. First one is layer-by-layer, or Frank-van der Merwe mode (seeing Figure 2.23 (a)). Since the atoms are more strongly bound to the substrate than to each other, the first atoms to condense form a less tightly bound second layer. Hence the layer growth mode is obtained, provided the decrease in binding is monotonic toward the value for a bulk crystal of the deposit.

The layer plus island or Stranski-Krastanov growth mode (seeing Figure 2.23 (b)) is an “intermediate” case. After forming the first few monolayers, the subsequent layer growth is unfavorable and islands are formed on top of this intermediate layer. There are many possible reasons for this mode to occur and almost any factor which disturbs the monotonic decrease in binding energy characteristic for layer-by-layer growth may be a possible factor. Last one is island or Volmer-Weber mode (seeing Figure 2.23 (c)), where small clusters are nucleated directly on the substrate and then grow into islands of the condensed phase. This happens when the atoms or molecules of the deposit are more strongly bound to each other than to the substrate. This mode is displayed by many systems of metals growing on insulators⁶³⁻⁶⁵, including many metals on alkali halides, graphite and other layer compounds.

Within these crystal growth modes, the layer-by-layer growth is generally known as the favourite growth mode for thin film epitaxy, especially in fabrication of nano-scale thin film. The surface roughness is under control in monolayers range, because the atoms

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are more strongly bound to the substrate or previously completed atomic layer than to each other. Then the crystal growth is achieved by completing one by one monolayer and promises an atomic level smooth surface.

Figure 2.23 Schematic representation of three typical crystal growth modes, (a) layer-by-layer or Frank-van der Merwe, (b) layer plus island or Stranski-Krastanov, and (c) island or Volmer-Weber modes, θ notes surface coverage in monolayers (ML).

Epitaxial growth refers to extended single-crystal film formation on top of a crystalline substrate. Epitaxy is of great interest for the work in this research and has been one of the most important developments in the field of semiconductor processing in the last century and has given rise to the information technologies and current computing abilities. There are two major types of epitaxy, homoepitaxy and heteroepitaxy. As the name implies, homoepitaxy refers to the growth of a material on a substrate of that same material, for example doped-Si on a Si substrate. The film in this case can be of very high quality, but have a different doping or functional nature from the substrate. The second type of epitaxy, heteroepitaxy, refers to the case where the film and substrate are different materials, but have similar structures that help guide the growth of the film. This is the growth process used throughout this thesis. Figure 2.24 illustrates the two typical growth

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conditions in heteroepitaxy. If the film material has exactly the same lattice parameter as that of the substrate or of different material with very small lattice mismatch, interfaces can be formed where there is little disruption of the structure across the interface. If, however, the film and substrate materials are different and the lattice parameters are slightly more mismatched, it is possible to form one of two types of interfaces. Figure 2.24 (a) illustrates the so-called strained-layer epitaxy. This sort of structure occurs for most very thin films with a certain substrate mismatch especially if both the substrate and film have the same crystal structure. Figure 2.24 (b) illustrates relaxed epitaxy. In this case the lattice mismatch is somewhat larger, and the film and substrate materials might even have different crystal structures resulting in a relatively quick relaxation of the film material to its bulk structure through the formation of defects, like dislocations, that accommodate interfacial strain in the system and lead to a relaxed film⁶⁶.

Figure 2.24 Schematic illustration of heteroepitaxy (a) strained and (b) relaxed epitaxial layers of a lattice mismatched heterostructure. The misfit dislocation is marked by arrow existing at the heterointerface of (b).

3. Experimental Procedures

3.1 Laser Molecular Beam Epitaxy (MBE)

Laser MBE also known as pulsed-laser deposition (PLD) is one of the most versatile techniques for oxide film fabrication. Though significant development of this technique began in late 1980s, yet this is now a widely used deposition approach for film growth, especially in the oxide thin film research. Earlier, PLD was popularized as an oxide film-growth technique through its success in growing epitaxial high temperature superconducting films ⁶⁷. In this technique, shown in Figure 3.1, a pulsed-laser is focused onto a target of the material to be deposited. For sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material. The ablated material is ejected from the target in a forward-directed plume.

Figure 3.1 Schematic diagram of a pulsed laser deposition system.

Pulsed-laser deposition has several attractive features, including stoichiometric transfer of material from the target, generation of energetic species, hyperthermal reaction

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between the ablated cations and molecular oxygen in the ablation plasma, and compatibility with background pressures ranging from ultra high vacuum (UHV) to 100Pa. Epitaxial oxide films can be deposited with PLD using single, stoichiometric targets of the material of interest, or with multiple targets for each element. As with evaporation, the film-growth process can be controlled at the atomic level using PLD. In addition, epitaxial growth with deposition rates in the order $100\text{\AA}/\text{s}$ has been demonstrated with this technique⁶⁸.

3.2 Reflection High-Energy Electron Diffraction (RHEED)

Reflection high-energy electron diffraction (RHEED) is an important tool in surface science because of its high surface sensitivity, and the ability of monitoring thickness of film for in-situ growth. A RHEED equipped with PLD system has been set up in our lab and epitaxial growth can be realized according to the RHEED oscillation.

The principle of RHEED is utilizing the diffraction of electrons by surface atoms and provides information of the periodic arrangement of the surface atoms. Figure 3.2 (a) shows a schematic drawing of the RHEED geometry. The incident electron beam (e-beam) strikes the sample surface at a grazing angle θ_i . The electrons are monoenergetic with a typical energy of $E \sim 10\text{--}50\text{ keV}$. The electron gun and phosphor screen (which acts as the detector) are located far from the sample to avoid any interference with the deposition process. In this geometry, electrons are scattered from the crystal surface, resulting in a characteristic diffraction pattern on the phosphor screen, shown in Figure 3.2 (b). This pattern is instantaneously displayed and can be used to define the crystallographic surface structure of, for instance, a growing thin film.

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Figure 3.2 (a) Schematic view of the RHEED geometry. (b) Typical RHEED pattern from a single crystal substrate.

The electrons with tens of KeV order energy are focused and incident onto the surface as shown in Figure 3.3. Then, the electrons are scattered by the periodic potential of the crystal surface, which results in a characteristic diffraction pattern on the screen. The combination of grazing incidence and strong electron-substrate interactions reduces the penetration depth of incident electrons to a few monolayers. The diffracted intensity is displayed directly on a screen, so the information is available instantly, i.e, real-time analysis is possible. Furthermore, RHEED arrangement in UHV chamber allows it to be used for in-situ observation of laser MBE thin film growing process.

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Figure 3.3 Elastic scattering model of RHEED intensity oscillation in 2 dimensional epitaxial growth.

3.3 High Resolution X-ray Diffraction (XRD)

PHILIPS X’pert-MRD (Materials Research Diffractometer) shown in Figure 3.4 has been used for the characterization. It is designed for measuring high quality epitaxial thin films grown on substrates, which include a wide variety of electronic, optoelectronic and photonic materials. The instrument is routinely used for high precision lattice parameter determination, rocking curves, super lattice from multilayer, glancing incidence X-ray diffraction and X-ray reflectivity. In triple axes configuration, this instrument has an intrinsic resolution of ~ 5 arcsec, making them well suited for measurements on nearly perfect crystals. The movement of sample can be described in Figure 3.4. There are five freedoms of motions: X, Y, Z, Θ , ω can be adjusted. Recently, some novel characterization methods have attracted intensive attentions which are XRR and RSM.

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Figure 3.4 (a) PHILIPS X'pert-MRD, (b) setup of X-ray tube and diffractometer, (c) schematic illustration of operation of high resolution XRD.

3.4 Atomic Force Microscopy (AFM)

In order to observe the surface roughness and topography of substrates and deposited thin films, atomic force microscopy (AFM) micrographs have been taken with a Digital Instruments, Inc. Nanoscope III A. The surface morphology has been taken in tapping mode with Si_3N_4 tips under atmosphere. The tip size is 2nm. Typical data taken from AFM

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height include atomic steps and root mean square (RMS) roughness.

2.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) analysis has been performed on the thin films to investigate the microstructures. TEM has the atomic resolution real space imaging of materials. The morphology, crystallographic structures as well as the chemical information of the thin films could be provided. The microscopy employed in this study is JEOL 2010 and JEOL 2100F, operated at 200kV, and Philips CM300 operated at 300kV.

As shown in Figure 3.5, a TEM is composed of an illumination system, sample stage, an objective lens system, a magnification system and a data collecting system. The electron gun is the key part of illumination system. LaB₆ wire thermionic emission source and field emission source have been used in JEOL 2010 and JEOL 2100F, respectively. The latter is better for performing high coherent lattice imaging, electron holography and high resolution microanalysis. The sample stage could allow in situ observation of non-structural phenomenon induced by annealing, low temperature or electromagnetic field. The objective lens system is the heart of high resolution TEM which determines the limit of imaging performance.

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Figure 3.5 The configuration of conventional transmission electron microscopy.

The main techniques used with TEM included: 1. conventional imaging (bright field, dark field images); 2. selected area electron diffraction pattern (SAD); 3. convergent-beam electron diffraction (CBED); 4. phase contrast images (high resolution TEM); 5. Z-contrast imaging; 6. energy-dispersive X-ray spectroscopy (EDX); and 7. electron energy loss spectroscopy (EELS). In this report, conventional bright field imaging SAD and HRTEM techniques are used to study the microstructures of thin films and manganite/titanite interfaces.

3.5 Physical Properties Measurement System (PPMS)

The Physical Property Measurement System (PPMS) is a versatile, state-of-the-art instrument that is capable of measuring a broad range of magnetic, electronic and thermodynamic materials properties, shown as Figure 3.6. This system allows

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measurements in a controlled temperature and magnetic field environment, with temperatures ranging from 0.3 - 400K (with a 3He insert) and magnetic fields from 0 - 7T. The entire system is computer controlled, allowing programmed temperature, current, or field sweeps during a measurement.

Figure 3.6 A physics properties measurement system comprised of computer control assembly and a low temperature cryostat (liquid He tank).

The vibrating sample magnetometer (VSM) model P525 has been used to characterize the magnetism of sample. The VSM liner motor transport uses a uniquely designed liner motor to vibrate sample. By oscillating the sample near a detection coil, basic measurements are performed with synchronously detecting the voltage of coil. The system is able to resolve the magnetization change of less than 10^{-6} emu at a data rate of 1 Hz by using a compact gradiometer pickup coil configuration, relatively large oscillation amplitude (1 - 3 mm peak) and a frequency of 40 Hz.

3.6 Ferroelectric and Impedance Spectroscopy Measurement

Hysteresis loops (P - E) have been measured using Precision Pro Ferroelectric Analyzer (Radiant Technologies, Albuquerque, NM) with high voltage interface. Different durations are set for P-E hysteresis measurements. For this, the Hysteresis test standard is

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established by the CHARGE software package on the original RT66A. The stimulus takes the form of a single triangle wave. One cycle is applied to the sample to ensure that the sample starts in a known location for the measurement loop. A delay of one second occurs to allow slow parasitic effects to settle to their quiescent states. The measurement loop is then executed. Since the delay is fixed at one second, only two parameters establish the entire test: V_{Max} and the number of points to use for the test. As noted above, the number of points determines the period of the loop. The output voltage profile for the Hysteresis test and three of the four parameters are shown in Figure 3.7.

Figure 3.7 Output waveform for the hysteresis test.

In addition, in measuring $P(E)$ hysteresis loops several kinds of artifacts can arise. Some of these are entirely instrumental, and some arises from the effects of conductive (leaky) specimens. Hysteresis circuits do not measure polarization P directly, rather, they measure switched charge Q . For an ideal ferroelectric insulator $Q = 2P_rA$ $Q = 2P_rA$ where P_r is the remanent polarization and A is the electrode area for a parallel-plate capacitor. For a somewhat conductive sample $Q = 2P_rA + \sigma E_a t$, where σ is the electrical conductivity, E_a is the applied field, and t the measuring time. Thus Q in a pulsed measuring system depends on the pulse width.

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Impedance spectroscopy of the dielectric films has been measured by an Agilent 4294A precision impedance analyzer over 100 - 1M Hz and 25 - 300 °C at the ac oscillation level of 100 mV. Each measured temperature was kept constant with an accuracy of ± 1 °C. In terms of following equation, $\sigma' = \frac{d \cos \theta}{A|Z|}$ where d is the sample thickness, A is the top electrode area, θ is the impedance phase angle and $|Z|$ is the absolute impedance value.

4. Results and Discussion

4.1 SrTiO₃ (001) Single Crystal Substrate Treatment and Atomic Level

Epitaxy of SrTiO₃ and BaTiO₃

4.1.1 SrTiO₃ Single Crystal Substrate Treatment

It is known that a typical perovskite oxide structure consists of two alternating planes as shown in Figure 4.1. For the most common commercial substrate, SrTiO₃ (001) includes either SrO or TiO₂ at the top most surface. However, two different surface terminations show different properties. In order to grow the atomically flat thin film and desired interface, single phase terminated SrTiO₃ substrate should be first prepared for nano-device fabrication. From the perspective of surface energy and chemical stability, TiO₂ terminated surface is more stable⁶⁹⁻⁷². Thus it is important to remove the top most SrO layer without damaging the TiO₂ plane. There was no well-satisfied solution until 1994⁶⁹ to solve this problem. Kawasaki and co-workers used buffered HF (BHF) with critical pH value to remove the SrO surface without disturbing TiO₂, and this result was identified by unit cell height terraces using AFM. Following them, in 1998, Koster⁷⁰ optimized this process by forming strontium hydroxide before BHF etching. In this study, the same experimental procedures were followed in our laboratory. Furthermore, the improvement contributed by post etch thermal annealing under oxygen environment in atmosphere pressure was studied. This approach was investigated by AFM and RHEED, and the results were found to be comparable.

Figure 4.1 ABO₃ perovskite Structure with two possible terminating planes of (001) plan SrTiO₃ surface.

Substrates were firstly cleaned with acetone and ethanol, followed by 10 minutes ultrasonic soak in Di-water to form the hydroxide of the top most SrO. The most critical step was the chemical etching by homemade buffered HF (BHF) (NH₄F: HF = 87.5:12.5) solution, its pH value was carefully monitored by pH meter to a pH value of 5.5. Finally, the Lindberg tube furnace was used to anneal these substrates at 950 °C for 5 hours in oxygen atmosphere environment. High quality AFM image is presented in Figure 4.2. Clear and sharp boundaries between terraces appear clearly on the sample surface. The enlarged micrograph is shown in Figure 4.3, in which heights of the sample surface is dropped from the left to right step by step with unit-cell scale indicated by the brightness reduction. On the right, two cross section lines scanned along the location marked with “a” and “b” in micrograph are given. Terraced structure is observed again and the step heights is identified to be one and two unit cell height (3.905 Å) with 0.4 and 0.8 nm respectively.

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Figure 4.2 AFM image is based on fully treated SrTiO₃ substrate. The terraced structure is obtained from this atomic flat surface.

Figure 4.3 Enlarged morphology of fully treated substrate surface, two cross section lines are given scanned at the marked locations.

For comparison, the RHEED diffraction pattern taken from as-received commercial SrTiO₃ (001) substrate without any treatment except normal cleaning by acetone and ethanol is presented in Figure 4.4. From this diffraction pattern, only rough streak lines are

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observed which are (01), (00), (01) rods. This RHEED can only give the single crystal orientation. Figure 4.5 presents diffraction pattern from ideal smooth surface displaying very sharp Bragg spots and Kikuchi lines. Furthermore, there is Laue ring appearing on the top of Figure 4.5 (b), this high resolution diffraction signals are observed for ideal smooth surfaces only, which shows the quality of the substrate.

In conclusion, single terminated ideal smooth surface of SrTiO_3 substrates have been reproducibly obtained. The most critical steps are the hydroxylation of top most SrO followed by its dissolution in BHF. Post-etching oxygen annealing is found to be important to repair surface damage by the BHF solution. This process can also be useful to other similar perovskite materials. The surface morphology results from AFM and microstructure results from RHEED show optimized condition of the SrTiO_3 by terraced structure and sharp diffraction pattern respectively. This assures a quality substrate which could be used to fabricate nano-devices and other artificial nanostructures.

Figure 4.4 RHEED diffraction pattern of SrTiO_3 (100) as-received substrate without special treatment.

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Figure 4.5 RHEED diffraction patterns from different crystal orientation observed on fully treated SrTiO_3 (100) substrate, each image presents sharp Bragg spot and clear Kikuchi lines.

4.1.2 Atomic Homoepitaxial of SrTiO_3 Thin Film Using Laser MBE

Ideal smooth single phase terminated SrTiO_3 (100) substrate with TiO_2 surface has been obtained using BHF etching and additional oxygen annealing. SrTiO_3 is the best lattice matching substrate with stable chemical property for epitaxial growth of many transition metal oxides. In this section, different crystal growth modes have been studied

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and the parameter is affecting growth modes are investigated. Intensity oscillations of RHEED diffraction patterns for two-dimensional growth are observed up to hundred of cycles. The morphology of epitaxial thin film is measured by AFM.

Thin film growth mode is very sensitive to growth conditions, such as the growth temperature, oxygen pressure, laser frequency and power. With RHEED monitoring, it becomes possible to study the growth mode in-situ by varying substrate temperature and pressure. The most important physical parameter is substrate temperature. The substrates were loaded in epitaxy chamber which was pumped to 10^{-6} Pa without oxygen induced. The substrate was heated up to growth temperature with ramp rate of 10 degrees per minutes, and the in situ annealing was performed at growth temperature for half an hour. In this period oxygen valve was carefully turn on and oxygen environment was maintained at 10^{-1} Pa. Before growth, the laser energy was calibrated at 200mj and 1Hz, using an energy meter. Figure 4.6 presents the clear RHEED oscillations indicating the two-dimension layer-by-layer growth mode for different substrate temperature is (a) at 550°C and (b) at 580°C. It is worth to investigate the morphology of the deposited thin films. The AFM images of fully treated substrate in (a) and deposited thin film on it in (b) are shown in Figure 4.7, respectively. Experimental results of AFM and in-situ RHEED intensity oscillation show the remarkable atomic level smoothness of the fabricated epitaxial thin film.

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Figure 4.6 Specular RHEED intensity from the growth surface during deposition of SrTiO₃ on fully treated SrTiO₃ (100) substrate at different temperature is (a) 550 °C and (b) at 580 °C.

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Figure 4.7 AFM images of fully treated SrTiO₃ (100) substrate (a) and homoepitaxial SrTiO₃ thin film (b).

4.1.3 Heteroepitaxy and Ferroelectric Property of Single Crystalline BaTiO₃ Thin Film on SrTiO₃ (001) Substrate

The study of ferroelectric materials in different forms has a notable increase in the past three decades. The scientific and technological implications of ferroelectric materials, particularly thin films, are evident by the great number of applications in different technological fields⁷³. Thin films of BaTiO₃ have been widely investigated for their ferroelectric properties as well as for the possibility of their uses in many applications. The possibility of their use in form of integrated capacitor is of particular interest with the current semiconductor technology. However, some issues like orientation control, oxygen concentration, processing method and critical dimension have strong influence on the structural and ferroelectric properties. In this research, BaTiO₃ is the ferroelectric component in the multiferroics superlattices to couple the magnetic oxide together. Before growing multiple layers, heteroepitaxy of BaTiO₃ is investigated, and ferroelectric property of epitaxial BaTiO₃ thin film is examined.

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Heteroepitaxy of BaTiO₃ thin films were carried out in two dimensional growth mode by adjusting growth parameters using the treated SrTiO₃ (001) single crystal substrates. The growth presented the similar in-situ RHEED behaviors as homoepitaxy of SrTiO₃ discussed earlier, but the crystalline nature of heteroepitaxial thin film was different because of lattice mismatch. In Figure 4.8, the result of X-ray diffraction 2θ-ω scan is shown, in which the four Bragg peaks are attributed to SrTiO₃ substrate and BaTiO₃ epitaxial layer, respectively (as marked different crystal planes). It is seen clearly, the hetero-epitaxial layer of BaTiO₃ follows the *c*-axis crystal orientation of SrTiO₃ substrate. Additionally, the lower angle of peak position of BaTiO₃ film manifests the compressive strain in the epitaxial layer imposed by the SrTiO₃ substrate due to 2.2% lattice mismatch. The thickness of BaTiO₃ films of 355 nm is measured by prism coupling technique.

Figure 4.8 X-ray diffraction pattern of BaTiO₃ thin film grown on SrTiO₃ (001) single crystal substrate showing the crystalline texture and low mosaic spread.

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Electrical properties were measured using interdigital electrodes on the films. Metal electrodes were formed by photo lithography technique and the lift-off method. Two metal layers of 10 nm Ti and 60 nm Au were deposited in sequence using electron beam deposition technique to assure good adhesion. The resistance of electrodes was $7.4 \times 10^{-6} \Omega$ cm. According to the thickness of 355 nm, the width between digit fingers of 5 μm was considered accuracy to determine the ferroelectricity and dielectric permittivity in the BaTiO₃ films. Shown in Figure 4.9, the ferroelectric hysteresis loops are measured at different applied voltage. The remnant polarization values are found to be $+P_r = 8.47 \mu\text{C}/\text{cm}^2$ and $-P_r = -7.71 \mu\text{C}/\text{cm}^2$ in the representative hysteresis loop at ± 12 V applied voltage. The shape of a loop is directly related to the crystalline characteristics of the BaTiO₃ films, growth mechanisms and the thermal history of the heterostructure.

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Figure 4.9 Ferroelectric hysteresis loops of BaTiO₃ epitaxial film at different applied voltages of 35, 27.5, 20, 12.5 and 8 V.

Dielectric property of the BaTiO₃ thin film was examined by capacitance versus electric field measurement. Figure 4.10 shows the capacitance variation versus the applied electric field. When the capacitance (i. e. dielectric constant) of a capacitor is a function of the applied DC field, it is understood to be belonging to the nonlinear class of dielectrics^{74, 75}. Such nonlinearity is characterized by the tunability (K) of the capacitor. Tunability of a capacitor at an applied bias of E can be calculated using the following relationship

$$K = \frac{C(0) - C(E)}{C(0)} \times 100\%$$

,where the C(0) is the capacitance at zero applied bias and C(E) is the capacitance at an applied bias in volts. It has been observed that the BaTiO₃ single layer film shows nearly 29.7% tunability when the applied bias is 4.5 V. Similar hysteresis in the polarization versus electric field curve (Figure 4.9) has also been observed. Studies have shown that

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tunability of dielectric constant is affected by the strain present in the films⁷⁶. On the other side, the plots of dielectric loss tangent as function electric field and a hysteresis behavior typical of ferroelectric capacitor are shown in the Figure 4.10.

Figure 4.10 Capacitance versus electric field curve of epitaxial BaTiO₃ film measured using interdigital electrodes. The right axis represents the dielectric loss tangent.

4.2 Epitaxial Growth and Magnetic Properties of CoFe_2O_4 on SrTiO_3 (100) and MgO (100) Substrates without Buffer Layer

4.2.1 Introduction

In recent years, Co ferrite (CoFe_2O_4) has attracted much attention because of its interesting electronic and magnetic properties as well as potential applications in magnetoelectronics and magneto-optical devices^{77, 78}. These attractive properties can be explained by their complicated crystal structure. It is known that the spinel structure has generic molecular formula AB_2X_4 , where X is an anion and A, B are cations. Spinel ferrites are a large and commercially important class of magnetic oxides with common formula MFe_2O_4 , where M is a divalent (often transition metal) cation. The magnetic properties of these compounds are sensitive to the distributions of the transition metals among the cation sites in the structure⁷⁹. Co ferrite has an inverse spinel structure in which 8 tetrahedral cation A sites are occupied by eight Fe^{3+} ions, while the 16 octahedral cation B sites are randomly occupied by eight Co^{2+} and eight Fe^{3+} ions. However, the intrinsic properties of Co ferrite should be investigated using high quality single crystal.

Recently, a lot of research has been focused on the preparation of Co ferrite by various techniques including borax flux, sputtering, molecular beam epitaxy and pulsed laser deposition⁸⁰⁻⁸³. While the properties of bulk Co ferrite have been studied and utilized for many years, there has been relatively little work devoted to the growth and properties of its thin films. With high quality single crystal thin films, many interesting and useful properties of Co ferrite are found. With little lattice mismatch of -0.38% between two MgO unit cells and one CoFe_2O_4 unit cell, epitaxial Co ferrite thin film is conveniently grown on the MgO (001) single crystal substrate. However, the magnetic properties of Co

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ferrite thin film is affected by the interaction between the film and the substrate^{84, 85}. A variety of substrates and buffer layers have been attempted at thin film fabrication using different deposition methods.

In this section, the growth of quality single crystal Co ferrite thin films on MgO (100) and SrTiO₃ (100) substrates is reported. Firstly, two different growth modes of Co ferrite thin film on MgO (100) substrate were carried out by varying oxygen pressure. The different growth mode is determined by the surface energy. For the two-dimensional case of Frank–van der Merwe growth, single atoms attach preferentially to single crystal site in substrate resulting in atomic smooth surface. That means strong influence of interface energy on epitaxial thin film growth. On the other hand, in the 3-dimensional Volmer–Weber growth mode, the adatom-adatom interaction is stronger than those of the adatom with the surface, leading to the formation of three-dimensional clusters or islands. It is obvious from the above discussion that the strong surface energy is crucial. Secondly, highly strained Co ferrite thin films were grown on SrTiO₃ (100) substrate with the layer-by-layer growth mode as monitored by the RHEED. Modulation of lattice parameters by varying the growth temperatures was measured using high-resolution XRD. The result indicates that the interesting magnetic properties of Co ferrite thin films can be affected by the film growth conditions.

Co ferrite thin films were grown on commercially available MgO (100) and SrTiO₃ (100) single crystal substrates, with one side polished. Lattice constant and mismatching with Co ferrite of these two substrates are listed in Table 1. A KrF excimer laser (COMPex 205 Fluorine from Lambda Physik) with a wavelength of 248 nm was operated at energy density of 1 J/cm² and pulse duration of 25 ns with repetition rate from 1 to 4 Hz. A 2-inch

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ceramic target was placed 5.5 cm away from the substrate. The Co ferrite thin film was grown on MgO (100) substrate under oxygen pressure of 2.0×10^{-5} Pa and 2.5×10^{-3} Pa. The substrate temperature was fixed at 600°C. In addition to the best lattice matching substrate of MgO, *c*-axis oriented SrTiO₃ was also used to deposit highly strained Co ferrite thin films. The growth conditions were varied with substrate temperatures ranging from 600 °C to 750 °C, and the oxygen pressure was fixed at 2.5×10^{-3} Pa. Post deposition in-situ annealing was carried out for 30 min under oxygen environment.

Material	Lattice Constant (nm)	Lattice Mismatch
CoFe ₂ O ₄	0.8392	-
MgO	0.4212	-0.38% (tensile)
SrTiO ₃	0.3905	6.9% (compressive)

Table 1 Lattice constants of MgO, SrTiO₃ and CoFe₂O₄ are listed with calculated lattice mismatch of MgO and SrTiO₃ with CoFe₂O₄. Here, the lattice mismatch of MgO and SrTiO₃ substrates are calculated to be -0.38% (tensile) and 6.9% (compressive), respectively.

Crystallinity and surface morphology of the films were characterized by in-situ RHEED and ex-situ high resolution X-ray diffraction (XRD), X-ray reflectivity (XRR) and atomic force microscopy (AFM).

4.2.2 Results and Discussion

Two series of Co ferrite thin films on two different single crystal substrates were grown and studied. As mentioned above, MgO (100) substrate has very small lattice mismatch with Co ferrite (Table 1) that should enable the Frank-van der Merwe (layer-by-layer) growth to occur if the growth temperature and the oxygen pressure are optimized. The similar growth of Fe₃O₄ films grown on MgO (100) by PLD was reported⁸⁶.

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In the progress of epitaxy, clear RHEED patterns from single crystal are shown in Figure 4.11. RHEED image of Figure 4.11(a) with clear streaky lines is captured under high oxygen pressure of 2.5×10^{-3} Pa. This typical fine streaky RHEED diffraction pattern demonstrates that the growth mode is the two-dimensional layer-by-layer growth mode with atomically smooth surface. On the contrary, the three-dimensional diffraction character is clearly seen from the RHEED pattern in Figure 4.11 (b). Therefore, the epitaxy mode of Co ferrite under oxygen deficient environment is the island or Volmer-Weber growth mode. This behavior is observed throughout the whole growth process, and it can be explained by the oxygen deficiency existing in Co ferrite thin film which influences the lattice structure of this complex compound oxide. AFM observation of the two thin films deposited under different oxygen pressure is shown in Figure 4.11 (c) and (d), respectively, and AFM results are in good agreement with these of RHEED. The film deposited at higher oxygen pressure (2.5×10^{-3} Pa) shows very small roughness (0.439 nm rms) whereas roughness of around 2 nm (rms) is exhibited for films deposited at 2.0×10^{-5} Pa.

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Figure 4.11 RHEED and AFM images of CoFe_2O_4 thin films grown at oxygen pressure of 2.5×10^{-3} Pa (left) and 2.0×10^{-5} Pa (right) on MgO substrates. The rms values of two films are 0.4 and 2.9 nm, respectively.

Layer thickness, interface and surface roughness of the two films grown on MgO (100) substrate were analyzed by XRR, as shown in Figure 4.12 with the best fitting curves. Some key parameters which dominate the simulation results including film density, thickness, surface, and interface roughness are listed in Table 2. The density of Co ferrite thin film is assumed to have the same value as that of bulk Co ferrite. Figure 4.12 (a) shows the result of the film deposited with rich oxygen environment, whereas the result of the film deposited under oxygen deficient environment is given in Figure 4.12 (b). Figure 4.12 (a) shows a gradual decline of reflectivity when the X-ray incident angle increases beyond a critical angle, and “fringes” can be seen in the curve. However, in Figure 4.12 (b), a sharp drop in the reflectivity is observed and no “fringes” exist. This phenomenon is

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attributed to the different roughness of the two films. Smooth film has a gradual decline of reflectivity with the increase of incident angle and continuous “fringes” in the curve is induced by the X-ray interference between upper and bottom surfaces. On the other hand, rough surface will result in a sharp drop and no interference “fringes” appear. The XRR reveals the same features observed in AFM. The thickness of the smooth Co ferrite film is calculated to be of 59 nm using the average value of the fringe space.

Figure 4.12 Typical XRR curves (solid line) along with best fitting data are plotted (dash line) of two CoFe₂O₄ thin films deposited on MgO substrates under different oxygen pressures of 2.5×10⁻³ Pa (a) and 2.0×10⁻⁵ Pa (b), respectively.

Oxygen	Layer	Layer	Surface	Interface
Pressure	Density	Thickness	Roughness	Roughness
(Pa)	(gm/cm ³)	(nm)	(nm)	(nm)
2.5×10 ⁻³	5.3	59	0.5	0.2
2.0×10 ⁻⁵	5.3	59	1.1	3.0

Table 2 Boundary conditions of XRR simulation of the two samples deposited on MgO including layer density, thickness, roughness of surface and interface. The layer density of CoFe₂O₄ thin film is assumed the same as bulk value. The thickness of two films was set equal to each other as 59 nm, the roughness of the films deposited under lower oxygen pressure is set much higher in order to match the experimental curve.

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It is well known in the thin film research that many interesting physical properties and novel phenomena are closely related and originated with high strain at interface between the thin film and the substrate. In this light, the highly strained Co ferrite thin films were also investigated and epitaxially grown on SrTiO_3 (100) substrate with a strong compressive strain of 6.9% as listed in Table 1. To make sensible comparison to Co ferrite on MgO (100), oxygen pressure for Co ferrite on SrTiO_3 (100) substrate was fixed at 2.5×10^{-3} Pa. The substrate temperatures of SrTiO_3 (100) were carefully changed from 600 to 750 °C. Figure 4.13 shows the in-situ RHEED diffraction patterns in sequence of epitaxial stages. Figure 4.13 (a) is taken from SrTiO_3 (100) substrate before deposition, indicating the atomically smooth of the substrate surface as shown by streaky pattern. The layer-by-layer growth mode is exhibited when the growth temperature is less than 700 °C, evidenced by the streaky RHEED pattern in Figure 4.13 (b). However, when the substrate temperature is higher than 700 °C, the RHEED pattern is transformed to the transmission diffraction mode as shown in Figure 4.13 (c), indicating that the two dimensional surface is covered with crystal Co ferrite islands. The experimental results clearly demonstrate that the substrate temperature affects markedly on crystallinity and growth mode on Co ferrite grown on the SrTiO_3 substrate.

Figure 4.13 RHEED patterns of different deposition stages in sequence: (a) the initial stage of pre-deposition: SrTiO_3 , (b) CoFe_2O_4 thin film with substrate

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temperature at less than 700 °C and (c) substrate temperature beyond 700 °C. The epitaxy mode is transformed from layer-by-layer mode to island mode with substrate temperature beyond 700 °C.

The effect of substrate temperature on the crystallinity of Co ferrite thin films grown with different temperature is further investigated by high resolution XRD. In wide range of 2θ scan, only SrTiO_3 (200) and (400) peaks and those of CoFe_2O_4 are observed. This experimental result shows that Co ferrite are epitaxially grown on SrTiO_3 (100) substrate with the preferred c-axis orientation. The out-of-plan lattice parameters of Co ferrite thin films are determined by narrow 2θ scan in the range of $40^\circ - 50^\circ$. As shown in Figure 4.14, 2θ scan curves are aligned to the SrTiO_3 (200) peaks by the vertical dashed line. With the increase of the substrate temperature, the peak position of the epitaxial thin film moves with respect to the substrate peak except for the curve at 750°C. The out-of-plane lattice parameters of Co ferrite thin films are calculated and listed in Table 3. If the unit cell volume of Co ferrite thin films is assumed to be unchanged (i.e, kept as a constant), the in-plane lattice parameters would be relaxed with higher growth temperatures from the compressive strain imposed by the substrate due to the lattice mismatch. However, the correlation between the lattice parameters and growth temperatures can be well controlled for the growth temperature below 700°C. The growth mode changed at high temperature can be seen by the splitting of the Co ferrite thin film (400) peak at 750°C, which is in a good agreement with the RHEED observation. Furthermore, for the out-of-plane orientation of Co ferrite thin film, the best rocking curve with full width at half maximum (FWHM) of 0.75° is obtained.

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Figure 4.14 XRD 2θ scan for epitaxial CoFe_2O_4 thin films deposited with increasing substrates temperatures from 600 to 700 °C. The peak shift of CoFe_2O_4 (400) plane with the increase of substrate temperature is observed.

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	600°C	650°C	700°C	750°C
2θ (deg)	42.46	42.87	43.26	42.98
dc (Å)	8.511	8.433	8.361	8.412

Table 3 Effect of growth temperature on the 2θ value of CoFe₂O₄ (400) plane and calculated lattice constant of samples grown on SrTiO₃.

Magnetic properties of Co ferrite thin films were examined using vibrating sample magnetometer (VSM) in physical properties measurement system (PPMS). The measurements were performed at room temperature with transverse magnetic field applied to samples surfaces. The magnetic hysteresis loops of two Co ferrite films grown on MgO (□) and SrTiO₃ (○) shows distinguishing magnetic behaviors (Figure 4.15). The saturated magnetic moment of film grown on SrTiO₃ substrate was estimated to be 93 emu/cm³ at applied magnetic field of 20k Oe, comparing with smaller value of 69 emu/cm³ offered by MgO sample. Simultaneously, the different coercive fields of 7045 and 2598 Oe were identified for SrTiO₃ and MgO substrates, respectively. The different magnetic performances are attributed to the strain effect introduced by the substrates, although under identical growth conditions. Interestingly, noticeable kinks in the curve of SrTiO₃ sample appeared when applied magnetic field was set closely to zero. That generally suggests the superposition of two hysteresis loops, which are identified with different coercive filed. In the case of Co ferrite on SrTiO₃, huge lattice mismatch of 6.9% resulted in a highly strained interfacial layer that shows different coercive.

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Figure 4.15 Magnetic hysteresis loops measured in room temperature on Co ferrite films grown on different substrates of MgO (□) and SrTiO₃ (○), respectively.

As discussed earlier, the crystallinity of epitaxial thin films are strongly correlated to the growth temperature (seeing Figure 4.14). In Figure 4.14, the manipulation of lattice constants of Co ferrites thin films is proved by X-ray diffraction measurements. Spontaneously, the variation of crystalline structure will affect the physical appearance in those epitaxial films. In Figure 4.16, the magnetic hysteresis loops were measured on Co ferrite films grown on SrTiO₃ substrates at different temperature of 600 °C (□), 650 °C (○) and 700 °C (Δ). Obviously, only sample fabricated at the highest temperature of 700 °C showed developed hysteresis loop with remarkable magnetic moment. According to characteristics of crystallinity and magnetism, growth temperature of 700 °C assured the quality Co ferrite thin film.

Figure 4.16 Magnetic hysteresis loops obtained on Co ferrite films grown on SrTiO₃ substrates at different temperature of 600 °C (□), 650 °C (○) and 700 °C (Δ).

4.2.3 Summary

In summary, Co ferrite thin films on Mg (100) and SrTiO₃ (100) substrates with different lattice mismatch and interfacial strains are epitaxially grown. The two key parameters of oxygen pressure and substrate temperature have been investigated and optimized, to achieve the two-dimensional single crystal layer-by-layer growth mode. The oxygen pressure plays an important role in the epitaxial growth mode of Co ferrite thin films on MgO substrate. The *c*-axis oriented Co ferrite thin films have also been successfully grown epitaxially on the highly compressive strained SrTiO₃ substrate, without buffered layer, by the two-dimensional layer-by-layer growth mode. Significant modulation of strain in epitaxial thin films by growth temperate has been studied by high-resolution XRD, and high quality Co ferrite thin films have been obtained with the FWHM of only 0.75°. The magnetic examination determined the quality Co ferrite thin film grown

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on SrTiO_3 substrate at 700 °C. Although, the room temperature magnetism of Co ferrite is attractive for making two phase multiferroics, heteroepitaxy of layered superlattice is impossible because of the huge lattice mismatch of 6.9% between Co ferrite and SrTiO_3 substrate.

4.3 Investigation of Room-Temperature Ferromagnetism in Co-doped $\text{SrTiO}_{3-\delta}$ Thin Film Grown on SrTiO_3 (100) Single Crystal Substrate

4.3.1 Introduction

Recently, diluted magnetic oxides (DMOs) exhibiting ferromagnetism (FM) at room temperature (RT) have attracted significant interest and been intensively studied for potential applications in spintronics devices. Experimental reports of Co-doped TiO_2 , ZnO and SnO_2 have claimed to exhibit ferromagnetism with Curie temperature higher than room temperature. The physical mechanism of magnetic ordering in DMOs is attributed to the interaction between magnetic cations and the hydrogenic electrons formed by intrinsic defect of oxygen vacancies. However, the debate on origin of surprisingly high magnetic moment per transition-metal cation in doped oxide thin film has still on and been not clear, even the effects of secondary phase or clusters have been screened out with proved by different characterization methods. Another confusing question is that some DMOs show their higher Curie temperature only when they are in thin film form.

It is well know that oxygen vacancy often plays an important role altering the electronic structure and having impact on the properties of transition metal oxides⁸⁷. More recently, claims of ferromagnetism in undoped oxide thin films could be well explained by point defects dominated by oxygen vacancy in undoped TiO_2 and In_2O_3 thin films on different substrate material deposited by pulsed-laser deposition (PLD). However, the attention have to been paid to its asymmetric structure of thin film from substrate to surface of thin film, and interaction originating from interface between thin film and substrate also cannot be ignored in the system. The unexpected side effects on substrates under ultra high temperature and vacuum environment of the PLD growth conditions have

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not been systematically studied.

SrTiO₃ (STO) is probably best known for its high dielectric constant and has been integrated with silicon process⁸⁸⁻⁹². It also has been widely used as substrate for growth of high quality thin films of perovskite oxide such as high T_c superconductors, ferroelectric and ferromagnetic material. Making STO magnetic is a considerable attraction that would open a new way for spintronics device by integration with silicon technology. Although high-mobility conduction induced by oxygen vacancy has been reported on the STO substrate^{93, 94}, there is no further investigation on magnetic contribution on substrate. In this section, starting with epitaxy of Co 3% doped SrTiO_{3- δ} thin film on STO (100) single crystal substrate, we also examine the possible magnetic effect to substrate, giving a clue of anomalous correlation between magnetization verse thickness of Co-doped SrTiO_{3- δ} thin films fabricated with same growth conditions by our laser molecular beam epitaxy (MBE) system, and the study of STO substrate treatment demonstrated another origination of magnetism from contaminated substrate as well as thin film.

4.3.2 Results and Discussion

A series of Co-doped SrTiO_{3- δ} thin films with thickness 100, 200 and 400 nm were prepared. This Co doped SrTiO₃ ceramic target was purchased from MTI Corporation, www.mtixtl.com. In the growth process, the vacuum pressure was set to 1.0×10^{-4} Pa in order to form oxygen vacancies with necessary concentration simultaneously. During deposition, the surface morphology is monitored by in-situ RHEED. A typical RHEED intensity oscillation is shown in Figure 4.17. Each cycle of oscillation in the figure yields the completion of one unit cell growth, and the strong undamped oscillations indicate perfect layer-by-layer epitaxial growth. Calculated from the average of periods of

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oscillations, the growth rate was determined to 19 ablations per monolayer ($\sim 3.9\text{\AA}$). In comparison with MBE, nonlinear growth mode is observed and surface relaxation between each laser ablations is illustrated as inset (a) of Figure 4.17. It is seen from that figure this RHEED intensity increases within each intervals between pulses and dropped suddenly as response of mass arriving of atoms triggered by laser ablations. This behavior can be explained with the growth kinetics theory and birth-death models of epitaxy. The RHEED pattern with only streaky lines indicates the ideal smooth surface and two dimensional growth modes.

Figure 4.17 In-situ RHEED intensity oscillations of the Co-doped $\text{SrTiO}_{3-\delta}$ thin film epitaxially grown on STO (100) substrate with two dimensional layer-by-layer mode and each period indicates the completion of one monolayer. Inset (a) is zoom in analysis of first period manifesting surface relaxation within intervals of ablations. Inset (b) shows the RHEED pattern with streaky lines, implying the ideal smooth surface.

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The ex-situ analysis of crystallinity was carried out using high resolution X-ray diffraction (HR-XRD). Figure 4.18 shows the characterization of 100 nm Co-doped $\text{SrTiO}_{3-\delta}$ thin film with angle XRD scan from 45.5 to 47 degree, the inset is the rocking curve at the peak of (200) plane from the thin film. The two peaks are attributed to (200) plane of STO single crystal substrate and epitaxial Co-doped $\text{SrTiO}_{3-\delta}$ thin film, respectively. C-axis lattice parameters of the substrate and thin film are determined by their peaks' position of (200) plane as 3.906 Å and 3.943 Å. The result indicates the bigger unit cell of Co-doped $\text{SrTiO}_{3-\delta}$ thin film than that of STO substrate, and it suggests that Co cation prefers to substitute the Ti site instead of Sr site. If not the peak of thin film would shift to the opposite direction corresponding to a reduced lattice parameter of thin film. The full width at half maximum (FWHM) of the (200) peak is measured as 0.26° which suggests the high crystallinity of the film. The 2θ - ω XRD scan confirms that there is no second phase. It is therefore concluded from the above experimental results that the Co-doped $\text{SrTiO}_{3-\delta}$ thin films have been epitaxially grown on STO (100) substrate with two dimension layer-by-layer growth mode without any second phase.

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Figure 4.18 High resolution XRD curve of 100nm Co-doped $\text{SrTiO}_{3-\delta}$ grown on STO (100) substrate. The offset peak position of thin film originating from the expanded unit cell which can be explained by substitution of B site Ti by Co. Inset shows rocking curve at the (200) plane of the thin film.

To investigate the magnetic property of these Co-doped $\text{SrTiO}_{3-\delta}$ thin films, several magnetic hysteresis loops were measured with applied magnetic field parallel to the plane of thin film. Some typical results are shown in Figure 4.19. After subtracting background diamagnetism of the substrate, the $M(H)$ curves of 100, 200, and 400 nm films are marked as (1), (2) and (3) in the figure, respectively. All the films used in the magnetic measurement were grown under same conditions. It can be seen from the figure that all films are ferromagnetic above room temperature, and the saturated magnetic moments increase with the increase of thickness from 100 to 400 nm. The almost linear correlation

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between the saturated magnetization with thickness of thin films is depicted as inset in Figure 4.19, which matches well with the common expectation of more magnetic moment as response to increased dosage of magnetic $3d$ cations. However, the argument is that a considerable magnetization (0.916×10^{-5} emu) still exists even when the thickness of ferromagnetic thin film is reduced to zero following the trend above, indicating excluding unique magnetic contribution of Co cation. The similar behaviors of unexpected high magnetic moment per dopant was observed when the concentration of dopants became low. This has been reported in literature in various DMOs thin films^{95, 96}. The most possible explanation is the magnetic contribution existing at the interface between the thin film and substrate, which can be attributed to lattice mismatch or strain between substrate and thin film. In this case, the average moment per Co cation of 100 nm thin film is 2.3 times higher than 400 nm, although the dopants concentration and growth conditions are identical. However, the $42 \mu_B$ per square nanometer can be calculated with extrapolated magnetization divided by area of substrate ($5 \times 10 \text{ nm}^2$), which is much lower than the supposed $200 \mu_B \text{ nm}^{-2}$. Furthermore, from lattice matching point of view, the growth of 3% Co-doped $\text{SrTiO}_{3-\delta}$ thin films on SrTiO_3 can be regarded as quasi-homoepitaxy because of less than 1% mismatch as mentioned before. The experimental results of RHEED pattern and intensity oscillations gave very sharp interface which would not introduce much defects and stress. In order to test the role of the interface, an additional treatment of top side polishing was performed on the sample (1) of 100 nm film. After polishing, ferromagnetism at room temperature was still observed, although the interface was supposed to be polished away completely. However the reduced magnetic moment is consistent with the loss of the STO on the surface of substrate by polishing. This observed

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phenomenon supports our initial suspicion on the ferromagnetism in the magnetic thin film systems and imply there might exist another origin of the magnetism.

Figure 4.19 Magnetization versus magnetic field curves measured at 300K for the films with thicknesses varying from 100 (1), 200 (2) and 400 nm (3) are showed after subtracting the back ground diamagnetic signal of substrate. The strong linear correlation of magnetization as a function of thin film thickness is given in the inset.

The sample grown with thicker film had to experience longer thermal cycle at the fixed growth rate. To evaluate this thermal effect, a blank substrate was loaded into the vacuum chamber under the same growth procedure, but without laser ablation. In this case, the same thermal cycles for growth of the 400 nm thin film, were reproduced on blank SrTiO₃ single crystal substrates with vacuum pressure set as 1.0×10^{-4} Pa. After the magnetic characterization, an additional $500^{\circ}\text{C} \times 24$ hour post-annealing in oxygen flow rate of 300 sccm and atmosphere pressure was carried out on this treated substrate. The curves of magnetization verse magnetic field after subtraction of background diamagnetic

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moment are shown in Figure 4.20. The curves marked as (4) and (5) are the results of the Sample (4) annealed under high vacuum of 1.0×10^{-4} Pa with 680°C for 3 hour, Sample (5) followed by additional oxygen atmosphere annealing 500°C for 24 hr. As showed in (a), the clear ferromagnetic signal is observed in Sample (4) by the high vacuum during the process, in contrast to the negligible ferromagnetism appearing in Sample (5). The inset in Figure 4.20 (a) shows a smaller field region of the hysteresis loops, the coercive field of Sample (4) can be identified around 220 Oe. To compare the magnetic moments between the thin film sample and blank substrate with the same thermal cycle and growth conditions, two hysteresis loops were plotted together in Figure 4.20 (b): Curve (3) for the 400 nm Co-doped $\text{SrTiO}_{3-\delta}$ thin film and Curve (4) for vacuum annealed blank SrTiO_3 substrate. Clearly, the two curves almost fully overlapped implying that the magnetization in this thin film should be almost originated from the substrate instead of magnetic cation. Thus, the next question is about the source for the dielectric SrTiO_3 single crystal substrate be magnetized. Is it defects or extrinsic contamination? It is generally known that defects or secondary phase is easily generated in DMO when magnetic ions with high concentration are introduced. However, in this case, Co ions is doped with only 3% and the crystallinity of epitaxial thin film confirms the absent of any secondary phase, thus magnetic signal may originate from the contamination in the thin film samples.

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Figure 4.20 (a) Magnetic hysteresis loops measured on blank STO substrate which was treated with the same thermal cycle under high vacuum conditions as growing 400nm thin film (4), with additional oxygen anneal at atmosphere pressure (5). The inset shows a smaller field region of the hysteresis loops. (b) The comparison of magnetic performance between treated blank STO substrate (4) and the sample grown with 400nm thin film (3). (c) Magnetization measured at 10K on the same treated blank STO substrate before (6) and after (7) back side polishing.

During the thin film epitaxial growth in the laser MBE system, substrates were directly put on stainless steel sample holder by silver paint. Contamination would arise when the system is operating under ultra high temperature close to 700°C. Under such conditions, the dopants of iron could diffuse into the substrate from stainless sample holder

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as a side effect⁶. In order to clarify this possibility, we measured the magnetization of the treated blank SrTiO₃ substrate before and after polishing its back side. The result is shown in Figure 4.20 (c). The two magnetization versus magnetic field curves $M(H)$, measured on the same blank SrTiO₃ substrate at 10K before polishing the backside (Curve 6) and after polishing (Curve 7). Only 25% magnetization loss can be observed after polishing the backside, but it should mostly disappear if the contamination really occurred. In order to investigate another possibility of intrinsic defects of oxygen vacancies, additional gentle anneal in oxygen atmosphere was carried out on a treated SrTiO₃ substrate. The magnetization was measured twice as in Figure 4.20 (a): Curve (4) and (5) are before and after annealing in oxygen environment, respectively. It is surprising that the ferromagnetic ordering was developed in high vacuum and destroyed by subsequent annealing in oxygen atmosphere. The above experimental results clearly show that the magnetic moment in treated blank SrTiO₃ substrate originated from oxygen vacancies.

To estimate the SrTiO₃ substrate, a variety of substrates imported from different manufacture were investigated by thermal treatment. And only the crystal made by Shinkosha Co. of Japan shows consistence on magnetic behavior after thermal treatment. Additionally, this product is accepted as best quality in commercial market. The above results indicate a unreliable magnetic performance in Co-doped SrTiO₃ thin film, that is not proper to be used in further study on multiferroics superlattice.

4.3.3 Summary

In summary, to understand the origin of magnetism in DMOs, a series of high quality 3% Co-doped SrTiO_{3- δ} thin films have been fabricated using laser MBE technology operating under high vacuum condition. All the samples have showed room temperature

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ferromagnetism and the magnetization have exhibited unexpected large magnetic moment. The unreasonable magnetization is attributed to the poor quality STO single crystal substrate initially used, which is against normal understanding in DMO thin film systems. With elimination of oxygen vacancies by additional thermal annealing in oxygen atmosphere, the magnetic signals are erased from the blank STO substrate treated in high vacuum annealing. The possibility of contamination from the stainless substrate holder had also been clarified. To examine variety of STO substrates purchased from different vendors, Co-doped $\text{SrTiO}_{3-\delta}$ thin films have been grown again under the same conditions. The thin film sample grown on high grade STO substrate made by SHIKOSHA (JAP) does not show any magnetic signal. This result can't support the reliable ferromagnetism in Co-doped $\text{SrTiO}_{3-\delta}$ thin films. The choice of substrate for growth of oxide thin film is essential, because extreme epitaxy environment may generate impurity phase in substrate. Many high dielectric oxides have been claimed to exhibit magnetic property at room temperature, most possibly attributed to defects, and that is inconsistent with some theoretical predictions.

4.4 Growth and Structure Properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ ($x=0.2, 0.3, 0.45$) Thin Film Grown on SrTiO_3 (001) Single Crystal Substrate

4.4.1 Introduction

Mixed valance manganites have attracted intensive studies for decades ^{5, 8}, in which the cubic perovskites with the composition of $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ [R: a trivalent rare-earth (RE) and A: a divalent alkaline-earth (AE) cation] is the most attractive. With modulation of hole concentrations of x , the strong correlation between ferromagnetism and metallic conductivity as well as insulator-metal transition ⁹⁷ has been realized in the bulk crystals of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO). This phenomenon is well explained by the Zener's double-exchange interaction model and mostly developed by Anderson in 1950s ^{98, 99}. The double-exchange interaction model indicates that the coexistence of the Mn^{3+} and Mn^{4+} results in inter-site spin interaction and electron transfer simultaneously via center O^{2-} anion. With improvement of sample preparation techniques, the colossal magnetoresistance (CMR) ¹⁰⁰ effect and the half-metallic property ^{101, 102} were observed on high quality single crystal thin films. In this material 100% spin polarized conduction electrons promise huge magnetoresistance (MR) on the magnetic tunneling junction (MTJ) structure which has two electrodes of ferromagnetic layer separated by an insulating layer ¹⁰³. This material shows high potential to be used as magnetic memory applications ^{102, 104}. However, the device performance strongly depends on the properties of thin films, such as surface, interface, strain and oxygen contents.

In epitaxial manganite thin films, strain plays an important role in induced magnetic phase transition ¹⁰⁵, magnetic anisotropy ¹⁰⁶ and its microstructure ^{107, 108}. To date the strain effects have been intensively studied, and many parameters for epitaxial thin films have

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been identified to have influences such as thickness¹⁰⁹, oxygen contents¹¹⁰, doping concentration¹¹¹ and lattice mismatch with substrates¹⁰⁵. To quantify strain effect, characterization of lattice distortion c/a (c and a is out-plan and in-plan lattice constant of thin films, respectively) is a straightforward method. After a systematic study of manganites super-lattices¹¹²⁻¹¹⁵, the fundamental concept based on “orbital physics” has been developed and summarized by Y. Tokura¹⁶. In this model, the coupling between spin and lattice degree of freedoms gives rich magnetoelectronic phenomena, and the magnetic phase transition against lattice distortion can be well explained.

Among these factors, oxygen content influences the magnetic and electric properties of manganites thin films in two different ways. Firstly, from lattice distortion point of view, oxygen deficiency shows the tendency to expand the unit cell volume of cubic perovskite with ABO_3 structure by changing attractive force of two neighboring manganese ions to repulsive force when center oxygen cation disappears. On the other hand, both spin-orbital coupling of electrons in 3d orbitals and double exchange interaction are strongly related with the oxygen content. The former effect shows strong correlation with lattice distortion as a function of oxygen content. The latter of double exchange interaction would occur under the condition of the center oxygen bridging two neighboring manganese ions. In this research area, systematic studies have been carried out on bulk materials, and the magnetic phase diagram versus lattice distortion has been given based on various of spin-orbital ordering condition^{16, 111}. Although giant magnetoresistance has been realized in these bulk manganites materials, magnetic devices, for example MTJ, but they suffer much lower Curie temperature¹¹⁶. Besides the high strain induced magnetic phase transition in the epitaxial thin film, the intrinsic defects may

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play an important role in degradation of the device performance when the epitaxial conditions are not optimized.

In this section, our efforts are concentrated on fabrication of highly epitaxial LSMO thin films on STO (001) substrates using laser molecular beam epitaxy (MBE) technique. Systematic study on epitaxial conditions has been carried out by varying oxygen pressure under fixed growth temperature. The results of rocking curve characterization show achieved the minimal full width at half maximum (FWHM) from (002) plane of thin films to be 0.02° only. With reference to the quality of commercial STO substrate used in this study, this value indicates a nearly perfect epitaxial growth. It is known that hole doping level can be modulated by changing the strontium concentration x of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Various thin films with x varying from 0.2, 0.3 to 0.45 have been grown under the optimized conditions, and systematic change of lattice parameters can thus be obtained. Finally, discussion on effects on crystallinity of epitaxial thin films is given, and an extremely low FWHM of 0.02° has been measured from the sample of LS2001. Based on the experimental high resolution XRD characterization, some structural imperfections are attributed to the substrate used.

LSMO thin films are grown on commercial one side polished STO (001) substrates made by Shinkosha Co. of Japan. A computer controlled KrF excimer laser (COMPex 205 Fluorine from Lambda Physik) with a wavelength of 248 nm was employed at energy density of 1 J/cm^2 and a pulse duration of 25 ns with the repetition of 1 ~ 2 Hz. Sintered LSMO ceramic targets of various Sr^{2+} concentration ($x=0.2, 0.3$ and 0.45) were placed 5.5 cm away from the substrate. The growth was performed with oxygen pressure (P_{O_2}) of 10^{-4} ~ 5.0 Pa and the STO substrate temperature of 780°C . The detailed growth conditions are

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described in Table 4. Film growth mode and thickness were in-situ monitored by reflection high energy electron diffraction (RHEED). In-situ anneal of film after growth was carried out for 30 min with the same P_{O_2} and temperature as during growth, and was followed by rapid cooling down.

Sample	x	P_{O_2} (Pa)	2θ (deg.)	FWHM(deg.)	FWHM	c/a
ID	(film/substrate)					
LS30O4	0.3	5.0×10^{-4}	45.985	0.052	1.4	1.010
LS30O3	0.3	1.5×10^{-3}	46.090	0.264	6.6	1.008
LS30O1	0.3	5.0	46.943	0.030	1.3	0.990
LS20O1	0.2	5.0	46.788	0.020	1.1	0.994
LS45O1	0.45	5.0	47.520	0.036	1.0	0.979

Table 4 List of growth conditions and film properties of Sr²⁺ doping level, oxygen pressure, peak position of (002) plane by 2θ , FWHM of rocking curve, normalized FWHM, lattice distortion of c/a .

The orientation and out-of-plane lattice constant (c -axis length) of all the thin films were examined by XRD 2θ - ω scan (Philips X’pert-MRD, Cu $K\alpha$ line). The crystallinity of thin films was estimated using rocking curve measurement by analyzing FWHM of the peak of (002) plane, where the ω axis is scanned alone with analyzer crystal being utilized.

4.4.2 Results and Discussion

Crystal growth mode can be affected by various factors which are not only the growth conditions but also the materials. It is generally accepted that there are three possible crystal growth modes that can be distinguished by observing surface morphology. However, only layer-by-layer growth mode can ensure ideal crystal structure and atomic

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level sharp interface at the epitaxial heterostructure. When using laser MBE technique to grow transition metal oxides, oxygen pressure P_{O_2} and growth temperature T_g are two dominant parameters to determine oxygen content of epitaxial thin film¹¹⁷. Besides the growth conditions, strain induced by the lattice mismatch between thin film and substrate also plays a crucial role in growth mode¹¹⁸. Because of the near 1% lattice mismatch between STO (3.905 Å) and LSMO (3.87 Å), cubic-on-cubic type of epitaxial arrangement would be realized for LSMO thin films grown on STO single crystal substrate with c -axis orientation. During the film growth, RHEED system was operated to in-situ monitor the surface morphology, and it was observed that all these films were grown with the layer-by-layer mode.

In Figure 4.21 (a), typical RHEED intensity oscillations are presented. Each cycle of oscillation marks the completion of one monolayer LSMO growth. By calculating the average of oscillations periods, the growth rate was determined to be 26 ablations per monolayer (3.87Å). The growth was stopped immediately when the thickness of 100 nm was achieved for all films. As seen in the figure, RHEED intensity increases within each interval between pulses and drops suddenly to the response of mass arriving of atoms triggered by laser ablations. This behavior can be well explained by the growth kinetics theory and the birth-death model of epitaxy^{119 120}. In comparison with the conventional thermal MBE, laser MBE has its typical feature of nonlinear growth. Significant surface relaxation procedure can be observed within each interval of laser pulses. A high resolution illustration for the first epitaxy period is inserted into Figure 4.21 (a). Another key evidence of epitaxial growth is in-situ RHEED pattern, which is given in Figure 4.21 (b) and (c). Figure 4.21 (b) is observed on STO substrate just before the epitaxial growth,

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while Figure 4.21 (c) is the pattern for the epitaxial thin film. Only streak lines appear on both patterns indicating the ideal smooth surface of the substrate and the two dimensional growth mode of the epitaxial thin film. These RHEED features can further provide the evidence for the cluster free thin films, otherwise the pattern would change to transmission mode with island spots taking place of streak lines. However, the streaky lines on the RHEED pattern of epitaxial thin film expand gradually along its damped oscillation, indicating step flow growth mode¹²¹.

Figure 4.21 In- situ RHEED intensity oscillations in (a), the inset is the zoomed of first oscillation period. The RHEED pattern of STO substrate before deposition in (b) and of LSMO thin film during deposition in (c).

Ex-situ examination for crystalline nature was performed using high-resolution XRD for all samples. Figure 4.22 shows the stacked charts of wide angle 2θ - ω scans around (002) plane for 3 films, and the charts are aligned by the peak of (002) plane from

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STO substrate. These three films with the same fixed Sr doping level of $x=0.3$ were grown under a fixed growth temperature of 780 °C and varying oxygen pressure from 10^{-4} in (a) to 10^{-3} in (b) and to 5.0 Pa in (c). Very clear Bragg peaks appear without the observation of any second phase. The diffraction peaks attributed to LSMO thin films show great sensitivity to oxygen pressure. When oxygen pressure was less than 10^{-3} Pa, diffraction peaks, of curves (a) and (b) distributed on the left side of STO substrate. However, the peak position switched to right in rich oxygen environment of 5.0 Pa. Eventually, in the much richer oxygen environment of 5.0 Pa, the peak of LSMO thin film is switched over the right side of STO substrate. This behavior reveals the very different lattice distortion of these epitaxial layers when different oxygen contents are introduced. It is known that out of plane lattice parameter can be calculated based on 2θ value of the Bragg peak position, therefore the relative position of Bragg peaks between the thin film and the substrate indicates lattice distortion of a strained thin film if in plane lattice parameter of the thin film is assumed to be equal to that of the substrate.

Figure 4.22 Stacked charts of wide angle 2θ - ω scans around (002) plane of LSMO thin films grown at temperature of 780 °C and varying oxygen pressure from 10^{-4} to 5 Pa. The red arrows indicate the oscillations due to diffraction from interface and surface of epitaxial layer.

It is generally agreed that the magnetic and electrical behavior of mixed valence manganites reflect the ratio of Mn^{3+} and Mn^{4+} cations that can be controlled by Sr^{2+} doping in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system. In this study, different thin films with various x were deposited under the optimized growth condition of 780°C and 5.0 Pa P_{O_2} .

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Figure 4.23 shows the results of 2θ - ω scan for the films with the increase of doping concentration from top of 0.2 in (a), to middle of 0.3 in (b) to bottom 0.45 in (c) . Due to high P_{O_2} , all the Bragg peaks of the plane are located at the right side of substrate. As observed, the thin film (002) peak moves away from substrate (002) peak with increasing doping concentration. This behavior indicates that a smaller out of plane lattice constant is induced with more Sr^{2+} dopant.

Figure 4.23 Estimation of *c*-axis lattice constants modulated by strontium doping concentration of 0.2, 0.3 and 0.45 by 2θ-ω scans.

Normally, the commensurate epitaxy refers to a parallelly aligned interface between substrate and epitaxial layer on an atomic basis, which can result in a fully strained thin film with same in-plane lattice constant as substrate. However, the strain energy introduced by misfit between epitaxial layer with substrate would be released via misfit dislocations when reaching the critical thickness. As a result, the epitaxial layer becomes relaxed and a misfit of in-plane lattice constant exists. To identify the in-plane lattice parameter of epitaxial layers, the most straightforward way is to map the two dimensional reciprocal space of asymmetric plane, in which a direct indication of lattice relaxation, *R*, can be yielded. Then, the in-plane lattice constant can be determined by taking into account *R* which varies from 0 to 1, referring to fully strained or relaxed conditions. In Figure 4.24, there are two images of reciprocal space mapping around (103) plane which are observed on two representative samples: LS30O4 and LS30O1. Figure 4.24 (a) is

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obtained on sample LS30O4, which was grown under high oxygen pressure of 5 Pa. In contrast, the result of LS30O1 grown with high oxygen deficiency is shown in Figure 4.24 (b). As seen in both figures, the diffraction peaks of the substrate and the epitaxial layer are aligned vertically to the sample surface. This behavior reveals the fully strained epitaxial layers, consequently the in-plane lattice parameters of thin films are verified to be identical with the substrate.

Figure 4.24 2-D reciprocal space mapping around asymmetric plane of (103) obtained on sample: LS30O4 (a) and LS30O1 (b).

Figure 4.25 shows the interface between epitaxial LSMO film and SrTiO_3 substrate obtained on sample LS20O1. The planar sharpness is less than 1nm, that implies a good epitaxial growth. In the whole film, no defects and grain boundaries could be detected, yet the crystal units are clearly identified. The lattice parameter in (010) plane is estimated to

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be 0.39 nm near the interface and the surface of epitaxial LSMO film as showing in Figure 4.25 and Figure 4.26, which is an indication of coherent strain in the film. This observation also matches well with XRD results of a fully strained thin film without lattice relaxation. On the other hand, two dimensional layer-by-layer growth mode is suggested by the sharp interface and surface. By combining XRD and TEM characterizations, the coherent strain is further confirmed in the manganite film with perfect epitaxial growth. This makes the sample a good candidate for the study of the electronic properties. The single crystalline character helps to attribute the resistivity and carrier concentration change to the intrinsic properties of manganite, without any contribution from grain boundaries and structural dislocations. This nearly defect free structure also could be an ideal platform to examine the conductivity based on the electron-lattice coupling, because the chance for electrons being trapped in the structure defects is largely reduced.

Figure 4.25 A cross sectional high resolution transmission electron microscopy (HRTEM) image of the interface between LSMO_0.2 and SrTiO_3 substrate

Figure 4.26 The cross sectional HRTEM of the LS20O1 film surface

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Lattice distortion and normalized FWHM of films are plotted as a function of oxygen pressure and Sr^{2+} doping concentration, respectively. In Figure 4.27 (a), a strong correlation between lattice distortion (c/a) and P_{O_2} is represented as solid squares (■). The c/a shows a tendency to decrease with the increasing P_{O_2} . This behavior indicates that uniaxial compressive strain of LSMO epitaxial layers along [001] direction is changed to tensile strain when P_{O_2} is higher than 10^{-1} Pa. On the other hand, FWHM are examined by ω scan along (002) plane for both the films and the substrate. On the right y-axis of Figure 4.27 (a), open circles (○) indicate “normalized” $\text{FWHM}_{\omega f/\omega s}$ calculated by dividing of FWHM of the thin films over the corresponding value for the substrate. The purpose of taking into account the crystallinity of substrate is to screen out the variation of different STO substrates used. As described, there is no evident correlation between FWHM and c/a ratio. Comparable good crystallinity can be obtained for the two films with the highest and the lowest P_{O_2} . There are diffracted waves between upper and lower boundary of the epitaxial layer with perfect crystalline structure¹²². In addition, ultra-smooth surface and sharp interface can be supported in these high quality films. However, the poor performance of crystalline mosaic is seen on sample LS30O3. As shown in Figure 4.27 (a), both extremely low and rich oxygen contents could achieve highly crystalline structures, although the lattice constants could be very different. But gradually increased oxygen pressure may break the balance and contribute to non-uniform distributed oxygen vacancies. The correlation of lattice distortion c/a and Sr^{2+} concentration is plotted in Figure 4.27 (b). Stronger tensile stress is developed with smaller c/a ratio.

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Figure 4.27 Correlation of lattice distortion c/a and $\text{FWHM}_{\omega_f/\omega_s}$ of epitaxial films vs.: (a) growth oxygen pressure P_{O_2} and (b) Sr^{2+} doping concentration.

To investigate the epitaxial thin films, lattice constant is considered as one of the most important parameters for physical properties in transition metal oxides. For example, the ferroelectricity phase transition can be manifested by the change of lattice constant, and similarly, the behavior of magnetic phase transition is also affected by the change of

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lattice constant. However, to evaluate the quality of the epitaxial thin film, it is not enough to only review the lattice constant. To further estimate the degree of crystallinity in the epitaxial thin film, the rocking curve measurement should be carried out by ω scan around Bragg peaks, and the smaller value of FWHM indicates, the better quality of the epitaxial thin film. But more information could be found from the rocking curve besides the value of FWHM. Thus, analysis of rocking curve profiles on both epitaxial layer and substrate can reveal the effect of substrate on the crystallinity of highly epitaxial thin film. In Figure 4.28, the rocking curves obtained from two thin films of LS30O4 and LS30O1 are plotted side by side. The upper two curves, (a) and (c), are the performance of films, the result of additional measurements on the corresponding substrates, (b) and (d), are also given at the bottom. As summarized in Table 4, these two films are grown under very different conditions, and the difference of oxygen pressure is four orders. A considerable difference in lattice constants has been found in these two films, in spite of comparable values of FWHM. Upon further careful examination of curve profiles, the difference is obvious: comparing Figure (a) with (b), a much broadening profile appears at bottom of curve (a) marked by two arrows, but the top profiles of two rocking curves are nearly the same, with the two samples exhibiting similar FWHM values. This phenomenon was also recorded for the whole epitaxial thin film and was imaged combining two layers. The under layer was thought to be a thin fully strained buffer layer, above which a fully relaxed epitaxial layer was well grown with much less defect. As a result, the final appearance of rocking curve was a superposition of two independent curves attributing to different layers. But this explanation may not be suitable in this study, because the nearly perfect epitaxy has been achieved in the films.

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The profile of rocking curve can be affected not only by the epitaxial layers but also by the substrate. In Figure 4.28 (b), a small peak is observed to shift to the left side of major peak (marked by an arrow). Usually, when split peaks appear in the rocking curve of an epitaxial thin film, the epitaxial growth process would be regarded in spreading orientations, but whether the divergence is attributed to the epitaxial growth procedure or to the substrate requires further investigation. To answer this question, the substrate quality was estimated and the result of ω scan is presented in the lower part of the rocking curve of the film, as shown in Figure 4.28 (b). It is seen that the curve of epitaxial layer is almost duplicated from substrate, and clearly there are similar weak peaks appearing at the same position. Therefore, it is further evident that the fully epitaxial growth films have exactly identical crystallographic orientation with the substrate.

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Figure 4.28 Rocking curves of sample LS3004 and LS3001 around (002) planes: upper two curves, (a) and (b), are the performance of thin film, compared with the substrates, (c) and (d), in the bottom.

4.4.3 Summary

In this section, we have focused on the fabrication of highly epitaxial LSMO thin films on STO single crystal (001) substrates using laser molecular beam epitaxy (MBE). Systematic studies on epitaxial conditions have been carried out by varying oxygen pressure as well as growth temperatures. The results of rocking curve characterization show that the minimal FWHM for (002) plane of thin films is as small as 0.02° . In reference to the quality of commercial STO substrate used in this study, the value indicates that the perfectly epitaxial result has been achieved. It is known that hole doping level can be modulated by changing the strontium concentration of x in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Various thin films with x of 0.2, 0.3 to 0.45 have been successfully grown under the optimized conditions. A correlation of lattice parameter to strontium concentration x has also been observed. Finally, the discussion of influence on crystallinity of epitaxial thin films is presented. Based on the evidences of high resolution X-ray diffraction (XRD) characterization, some structural imperfections are attributed to the substrate used.

4.5 Growth and Properties of Fully Strained Multiferroics

Superlattices: $[(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3)_{4n}/(\text{BaTiO}_3)_{3n}]_m$

4.5.1 Introduction

The coupling of electric and magnetic properties in solid states was predicted by Pierre Curie in 1894¹²³. The co-existence of ferroelectricity and magnetism in materials called magnetoelectric multiferroics can be thought as the extension of this concept. Magnetoelectric multiferroics show fantastic attraction in electronic device applications, such as memory storage, transducers and actuators, since there is an additional degree of freedom on magnetic polarization as well as electrical tuned magnetic domains. Unfortunately, to date few materials have been found to exhibit strong magnetoelectric effect^{124, 125}. This is due to the contradictory mechanisms of ferroelectricity and magnetism. To most studied transition metal oxide perovskites, both ferroelectric and ferromagnetic phases can be found among this family. When ferroelectric phase appears, B site cation prefers empty d-shells and shifts from center to corner spontaneously^{31, 126}. On the contrary, ferromagnetic phase is developed with characteristics of highly spin ordering that must be assured by partially filled d-shells, for example of mixed-valence manganites⁵.

Although this fundamental contradiction obstructs the search for strong coupling magnetoelectric multiferroics, recently the interest in this field revives¹²⁷ due to some exciting advances, such as the discovery of high- T_c (curie temperature) in “induced-multiferroics” cupric oxides¹²⁸, attractive feature of spin frustration prototypes in TbMnO_3 ¹²⁹, TbMn_2O_5 ¹³⁰, compared with the most studied BiFeO_3 ¹³¹ and BiMnO_3 ¹³², which are combining A-site long range polarization and B-site magnetic ordering. The materials

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mentioned above can be categorized as single phase multiferroics, where magnetoelectric coupling originates from the same material. Otherwise, an alternative route to achieve strong magnetoelectric effect has also been well studied in parallel by integrating independent ferroelectric and magnetic material together, which is called two phase multiferroics. The enhanced magnetoelectric coupling can be expected in this artificially designed materials when considerable strain effects exist. This indirect magnetoelectric coupling has been realized in many ways, e.g., composites¹²⁵, nanostructures⁵⁷ and epitaxial heterostructures¹³³. Hetero-epitaxy has been known to permit strong strain effect with precisely controlled crystallographic orientation. Furthermore, the highly epitaxial layer by layer grown multiple films could be claimed as superlattice¹³⁴, if the heteroepitaxial relationship presents in nanoscale, which could result in enhanced properties and intriguing effects^{40, 135-137} in highly strained system only. Another advantage of these two-dimensional thin film materials is their application potential in integrating with silicon technology^{88, 138}.

Recently, magnetocapacitance effect has been reported in the perovskite-superlattice, composing of representative ferroelectric BaTiO_3 (BTO) and ferromagnetic $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO)¹³⁹. However, it is arguable that the observed magnetocapacitance effect may not originate from the coupling of ferroelectricity and magnetism. An evidence of magnetocapacitance without magneto coupling was found by theoretical computation when magnetoresistance and Maxwell-Wagner effect were taken into account¹⁴⁰. On the other hand, a trilayer-superlattice, composed of all insulating perovskites LaAlO_3 , LaFeO_3 and LaCrO_3 , was investigated by computational modeling more recently¹⁴¹. The result suggested a large switchable polarization due to epitaxial

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strain as well as coupling of magnetic ions. It is well known that strain in the heteroepitaxial thin films plays a crucial role to affect the material performance. For example, tremendously enhanced ferroelectric property has been observed in highly epitaxial SrTiO_3 (STO) and BaTiO_3 (BTO) superlattice⁴⁰, even ferroelectric phase appeared in high dielectric STO attributing to strain effect¹⁴². However, the epitaxial strain can only be controlled carefully under certain conditions. Otherwise the misfit dislocation would appear to release excess stress and the crystallinity would decline greatly.

In this section, fully strained superlattices designed for strong magnetoelectric effect were successfully fabricated using laser molecular beam epitaxy (MBE) technique. The ferroelectric and magnetic components were BTO and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO), respectively. The substrate used was STO single crystal with *c*-orientation. The epitaxial condition was well optimized to obtain layer-by-layer (Frank-van der Merve) growth mode which was in-situ monitored by reflection high energy electron diffraction (RHEED) system. Only thickness ratio of 4/3 between LSMO and BTO layers was found to be able to ensure fully strained epitaxial relationship due to the lattice mismatch between epitaxial layer and substrate. By fixing the thickness ratio, the super-lattices can be named as $[\text{LSMO}_{4n}/\text{BTO}_{3n}]_m$, in which *n* can be 2, 3 and 4. The superstructure was identified by the satellite peaks in high resolution X-ray diffraction (XRD) pattern, which attributes to super-lattice parameters. In addition, the comparison on superlattice parameters between experimental results and calculated results confirmed the fully strained epitaxial growth. Both ferroelectric and ferromagnetic properties were observed on these multiferroics superlattices.

All the films were grown on commercial one side polished STO (001) substrates from

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Shinkosha Co. of Japan with the dimension of $10 \times 10 \text{ mm}^2$. A computer-controlled KrF excimer laser (COMPex 205 Fluorine from Lambda Physik) with a wavelength of 248 nm was employed at energy density of 1 J/cm^2 and a pulse duration of 25 ns with the repetition of 1 ~ 2 Hz. Sintered BTO and LSMO ceramic targets were placed 5.5 cm away from the substrate and switched alternatively in the operation of multiple-layer-epitaxy by a program controlled stepper motor. The growth was performed with oxygen pressure (P_{O_2}) of $8 \times 10^{-1} \text{ Pa}$. The substrate temperature varied from 680°C to 780°C during growth of BTO and LSMO layers, respectively, to achieve a two-dimensional layer-by-layer growth mode and optimum quality. Diffraction pattern, intensity oscillation cycles, epitaxial mode and layers thickness were strictly monitored and controlled by reflection high-energy electron diffraction (RHEED). In-situ annealing of films after growth was carried out for 30 min with the same P_{O_2} and temperature as growth, and was followed by rapid cooling down. The crystal orientation and out-of-plane lattice constant (c -axis length) of all the thin films were examined by XRD 2θ - ω scan (Philips X'pert-MRD, Cu $K\alpha$ line). To estimate mosaicity of epitaxial layers, rocking curve measurements were also carried out by scanning ω with fixing of 2θ position of diffractometer.

4.5.2 Results and Discussion

The hetero-epitaxial thin film growth always faces the challenge of strain that originates from lattice mismatch between epitaxial layer and substrate and results in a critical thickness in epitaxial thin film. According to bulk values, lattice mismatches between STO substrate and super-lattice constituents of BTO and LSMO are 2.2% and -0.7%, respectively. It can be seen that the lattice mismatch attributing to BTO generate much more strain compared to LSMO. As a result, the potential weak points may arise

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from the BTO layers in the FE/FM superlattice. In Figure 4.29, this strained-layer superlattice accompanying with its strain conditions are schematically illustrated.

In Figure 4.29 (a), isolated (unstrained) BTO and LSMO layers are plotted alternately, and the corresponding strain status, compression of BTO and tension of LSMO, are also marked. This in-plane strain of the epitaxial layer, also called coherency strain in growth, would alter the out-of-plane lattice constant due to invariable crystal volume. As indicated in Figure 4.29 (b), d_{BTO} , the BTO layers in the strained superlattice is thicker than unstrained layers, but tension force reduces the thickness of LSMO layer (d_{LSMO}). Since the epitaxial layer aligns strictly in-plane with substrate at atomic level in the circumstance of fully epitaxial growth, both in-plane lattice constants of BTO and LSMO would be identical as STO substrate. However, this fully strained epitaxial growth is considerably limited by the critical thickness h_c , above which the layer-by-layer growth mode switches to the 3-dimensional island (Stranski-Krastanov) growth mode¹⁴³, accompanying with mass of misfit dislocations. The detailed strain status of individual super-lattice layer is shown in Figure 4.29 (c), where much more compressive stress is imposed on BTO layers due to the big lattice mismatch.

In this strained system, the excess stress will be accumulated at the interface of the film and the substrate while the superlattice builds up, which is schematically plotted in Figure 4.29 (d). Generally, the strain energy of a fully strained super-lattice without misfit dislocation can be denoted as $E_{\text{strain}} = n(k_A d_A \varepsilon_A^2 + k_B d_B \varepsilon_B^2)$, where n is the number of super-lattice layers, d_A and d_B are the layers thickness, k_A and k_B are the relevant elastic constants, ε_A and ε_B are the strain referring lattice distortion. This equation assumes a superposition of the strains,

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which is proportional to ϵ^2 , in individual layers. Before the growth of superlattice, efforts were taken to optimize the growth conditions for both LSMO and BTO¹⁴⁴. However, the optimum growth temperatures were remarkably different under the oxygen pressure of 8×10^{-1} Pa. To ensure layer-by-layer growth and high crystalline quality, the thin film was epitaxially grown under a temperature as low as possible to avoid the formation of clusters. In the progress of epitaxy, the growth temperature was set at 680° for BTO layers and switched to 760° for LSMO. By varying the temperature of substrate, the 2-D layer-by-layer growth was confirmed by RHEED observations.

Figure 4.29 Schematic illustration of layered grown LSMO/BTO superlattice on STO (001) substrate; (a) strain conditions of each layers where compressive or tensile stress force on BTO and LSMO respectively, (b) lattice distortion due to strain, (c) strain energy attributing to each layers, (d) excess stress as function of layer thickness.

Figure 4.30 shows the in-situ RHEED patterns and the simultaneous intensity oscillations in the growth of super-lattice [LSMO₈/BTO₈]. On the top of the figure, there are three diffraction patterns taken with the same azimuth angles of [010], from: (a) STO

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substrate before epitaxy; (b) the 1st LSMO layer and (c) the 1st BTO layer. The streak and sharp RHEED pattern suggests atomic level smooth surface as well as sharp interfaces. By recording brightness of diffraction spot, the RHEED intensity varies spontaneously with the surface morphology of thin film and each oscillation indicates the completion of one unit cell growth. The RHEED intensity oscillated as the function of epitaxial time from the growth of first LSMO layer, as shown in Figure 4.30, until the completion of the eighth circle. This means that eight LSMO monolayers have been epitaxially grown. After switching the target from LSMO to BTO, laser ablations were triggered again to grow BTO on top of LSMO. Certainly, the thickness of BTO layer was also controlled as 8 monolayers. The epitaxial growth rates of LSMO and BTO were identified to be different by comparing the period of oscillations. The growth rates of LSMO & BTO layers were estimated to be 27 and 17 seconds per unit cell, respectively. Although the sharp RHEED patterns and oscillations of intensity show the evidence of epitaxial growth of first several layers, the oscillations are damped gradually and the RHEED pattern is evolved from streaks into spots, indicating a 3-dimensional island growth mode of the film to its critical thickness.

Figure 4.30 Top: In-situ RHEED observation of diffraction patterns indicating atomic level smooth surface; (a) STO substrate exactly before epitaxy, (b) completion of first epitaxial layer of LSMO, (c) following BTO layer heteroepitaxy on under layer of LSMO. Bottom: RHEED intensity oscillations as function of growth time suggest the completion of every unit cells, in which thickness was precisely monitored by counting oscillation cycles as marked by index on top of every maximum.

To estimate the critical thickness and evaluate the growth mode, the evolution of RHEED pattern is shown in Figure 4.31 by comparing the diffraction patterns of different BTO layers in the growth of $[\text{LSMO}_8/\text{BTO}_8]$ super-lattice. Two series of patterns resulting from different azimuth angles, $[010]$ on top and $[110]$ of bottom, were analyzed. In the first column, the patterns of STO substrate are also shown as benchmark of ideal smooth surface. As illustrated in Figure 4.29 (d), the excess stress will accumulate with the growth of the strained layers. As a result, the epitaxial relationship of this highly strained super-lattice may break due to unsustainable stress. In Figure 4.31, by taking RHEED patterns of

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BTO layers, which contribute most strain, from different azimuth angles of [110] and [101], the growth mode transition from layer-by-layer to islands growth is observed. Compared to the performance of RHEED patterns taken after completion of first (BTO1) and third (BTO3) BTO layer, weak spots appear to overlap with streak lines after third BTO layer deposited. The spotted pattern is resulted from the transmission of electrons through 3-D clusters at the film surface. It is shown that at the moment of third BTO layer completion, the diffraction mode is still dominated by atomic smooth surface, but relaxation in epitaxial layers is detected as well. Therefore, the critical thickness of [LSMO₈/BTO₈] super-lattice can be identified. Eventually, RHEED diffraction patterns switched to 3-D transmission mode featured by 3-D clusters is shown in Figure 4.31 BTO8 pattern.

Figure 4.31 Evolution of RHEED patterns, taken with two azimuth angles of [110] and [010] on STO substrate and completion of 1st, 3rd and 8th BTO layers, suggest the transforming of growth mode from 2-D layer by layer growth to 3-D islands growth as well as relaxation of layered superstructure.

To further estimate the crystallinity of the relaxed “superlattice” of [LSMO₈/BTO₈],

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out-of-plane lattice constant and rocking curve measurements are carried out on high resolution X-ray diffractometer. The results are shown in Figure 4.32. From 2θ - ω scan around STO (002) plane, there are three distinguished peaks attributed to STO substrate, super-lattice constituents of BTO and LSMO, as marked in the figure. The c -axis lattice parameters calculated according to Bragg peak position are 3.904Å for STO substrate, 3.99Å for BTO and 3.87Å for LSMO, which matches well with bulk values.

In this case, independent appearance of both characteristic peaks of BTO and LSMO proves a two phase composite rather than layered superstructure, although two materials were alternately deposited by sourcing from different targets. To understand this phenomenon, a growth model is thus proposed. Indicated by RHEED pattern evolution, the surface morphology of multiple-layer film declined due to accumulated strain energy. Consequently, the under layer would be exposed in relaxed surface¹⁴³. Then two different surfaces would be simultaneously offered for the incoming atoms. Homoepitaxy would be naturally preferable compared with heteroepitaxy. Driven by this intention, incoming atoms would concentrate in the area, where homoepitaxy occurred to build up islands. In subsequent growth, BTO and LSMO would grow as mixed clusters instead of strained layers, but not the strained super-lattice.

Table 5 lists the peak position of (002) planes as well as the out-of-plane lattice parameter a_{rel} , (relaxed), for substrate and relaxed epitaxial layers. The lattice parameters under fully strained condition were also calculated, in which fully strained growth permits the same in-plane lattice parameters of epitaxial layers and substrate. The expected c -axis lattice parameters of fully strained BTO and LSMO epitaxial layers were calculated under the assumption of the unit cell volume kept as constant. The results of a_{str} (strained) in

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Table 5 show extended out-of-plane lattice parameter of BTO as well as shortening of LSMO in comparison with relaxed condition. To investigate the mosaicity of epitaxial films, rocking curve measurements were performed, in which diffractometer was fixed at peak position of rocking substrate only. It was surprising to find that both epitaxial films showed comparable performance with substrate, indicating almost perfect epitaxy. As shown in the inset of Figure 4.32, a FWHM value of 0.013° is obtained by analyzing the rocking curve of BTO (002) plane, a strong evidence of an excellent experimental performance.

Figure 4.32 XRD 2θ scan carried out on relaxed “super-lattice” around STO (002) plane revealed three characteristic peaks attributing to STO substrate, LSMO and BTO independently. Also, a Rocking curve obtained on BTO (002) plane is showing as inset, by which a FWHM value of 0.013° is yield.

To achieve strong magnetoelectric coupling, coherent hetero-interfaces shall be achieved in fully strained FM/FE super-lattice. By referring to the equation of strain energy, the strain energy sums up all energy attributing to both compressive and tensile

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force. However, the excess stress is compensated because of opposite forces subjecting to compressed or tense layers, which are in this case BTO and LSMO, respectively. Thus, minimal excess stress can be achieved by modulating the individual layer thickness. In this case, reduction of relative thickness of BTO layers is the most straightforward way to balance the excess stress induced by large lattice mismatch, which is schematically illustrated in Figure 4.29.

To minimize the strain energy, the thickness ratio between LSMO and BTO layers was adjusted to 4:3 in following growth. The super-lattices can be accordingly denoted as $[\text{LSMO}_{4n}/\text{BTO}_{3n}]$, $n = 2, 3$ or 4 . In the growth of these redesigned super-lattices, all the conditions were kept unchanged. As expected, the layer-by-layer growth mode conducted the epitaxy all the way through the completion of 16 superlattice periods, as shown by the sharp RHEED patterns similar to the patterns in Figure 4.30. This encouraging result shows the success of layered super-structure with atomic smoothed interfaces. Ex-situ high resolution XRD investigations were carried out to evaluate the crystallinity of these superlattices.

Figure 4.33 shows a stacked chart of the 2θ - ω scan performed on these super-lattices of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]_{16}$, where 16 indicates the repetition of superlattice period. From top to bottom, the n value increases from 2, 3 to 4, yielding the different super-lattice parameters, Λ . All the curves are aligned according to the peak of STO (002) plane. Each curve shows recognizable satellite peaks that appear periodically with certain interval ($\Delta\eta_m$) corresponding to different super-lattice parameters. As shown in Figure 4.33, the most intensive satellite peaks of every curve are defined as 0 order satellite peak (S.L.0), besides which high order satellites peaks are marked. In Table 5, the calculated average $\Delta\eta_m$ shows

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a strong linear relationship with n .

By comparing Figure 4.32 and Figure 4.33, it is noted that the individual diffraction peaks attributed to the two constituents of BTO and LSMO disappear in Figure 4.33, but the satellite peaks prevail. This observation reveals the layered superstructure, and suggests strongly coherent interfaces, which appear periodically as sharp atomic planes in diffraction with X-ray wave¹³⁴. The average lattice parameter for a single perovskite unit cell in superlattice can be extracted from the zero order super-lattice peak near the STO (002) peak¹⁴⁵. It is seen from Table 5 that the average lattice parameters, a_{SL} , corresponding to the 2θ values of zero order superlattice peaks vary in the range of a_{LSMO} to a_{BTO} , and the experimental super-lattice parameter, Λ_{exp} , can be figured out by multiplying average lattice parameter by number of unit cells per super-lattice period, which are 14 ($n = 2$), 21 ($n = 3$) or 28 ($n = 4$) depending on the n value.

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Figure 4.33 Stacked chart of 2θ scans performed on redesigned super-lattice: [LSMO_{x4n}/BTO_{x3n}] x16, where n increases from top to bottom. All the curves are aligned by the benchmark of peaks of STO (002) plane, beside which orders of satellite peaks distributed corresponding to different super-lattice parameters.

Films	2θ(002)			a _{rel}	a _{str}	
				(relaxed)	(strain)	
BTO	45.24			3.99	4.167	
LSMO	47.46			3.87	3.802	
S.L.	2θ(SL0)	a _{S.L.}	Δη _m	Λ _{rel}	Λ _{str}	Λ _{exp}
				(relaxed)	(strain)	(experimental)
n=2	46.66	3.968	2.33	54.9	55.42	55.56
n=3	45.69	3.966	1.53±0.07	82.35	83.14	83.29
n=4	45.72	3.963	1.06±0.01	109.8	110.8	110.9

Table 5 Experimental 2θ values of epitaxial BTO, LSMO and the superlattices with different n values are listed. The average and standard deviation of intervals of satellite peaks, $\Delta\eta_m$, are calculated according to the performances of 2θ scan. Utilizing the lattice parameters of BTO and LSMO, two types of prediction for superlattice parameters are concluded depending on relaxed or strained epitaxy conditions, respectively. In comparison with estimated values, experimental result of superlattice parameters perfectly match with the prediction in fully strained condition.

An alternative method used to estimate the superlattice parameter is to sum up both layer thickness of constituents in one super-lattice period, which is depicted in the formula: $\Lambda=N_Aa_A + N_Ba_B$, where N_A and N_B are the numbers of unit cells for each constituent materials, a_A and a_B are corresponding lattice parameters. As discussed earlier, there are two possible out-of-plane lattice parameters for epitaxial layers depending on whether the epitaxial layer is in relaxed or strained condition. Two types of super-lattice

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parameters, Λ_{rex} (relaxed) and Λ_{str} (strained) can also be acquired from relaxed or strained condition. The experimentally obtained super-lattice parameter, Λ_{exp} (experimental), perfectly matches the estimated value in fully strained condition with only 0.1 Å difference. These results strongly show that the layer-by-layer grown super-lattices are fully strained and perfect epitaxy.

To further confirm the epitaxial relationship, the 2-D reciprocal space mapping (RSM) measurements were carried out using high resolution XRD, where 2-axes measurements were performed by scanning 2θ over certain range of ω ¹⁴⁶. The RSM of representative super-lattice of $[\text{LSMO}_8/\text{BTO}_6]_{16}$, on symmetric (002) plane is shown in Figure 4.34 (a) and on asymmetric (103) plane in (b). The perfect epitaxy reveals fully strained epitaxial layers with parallel aligned interface on an atomic basis, and they share the identical in-plane lattice parameter with substrate. In the reciprocal space, this fully strained epitaxy is expected with the same Q_x value of scattering factor. As shown in Figure 4.34, all the diffraction peaks attributed to STO substrate and epitaxial super-lattice are aligned normally to sample surface in both symmetric and asymmetric planes, indicating the identical in-plane-lattice parameter of substrate and epitaxial layers. Thus, the artificially designed perovskites super-lattices, $[\text{LSMO}_{4n}/\text{BTO}_{3n}] \times 16$, are once again confirmed to be fully strained.

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Figure 4.34 2-axis scans around both symmetric (002) plane; (a), and asymmetric (103) plane; (b), resulted two reciprocal space maps, in which diffraction peaks attributing to STO substrate as well as superlattice can be identified as marked. Notice that, the behaviors of all the peaks aligning normal to sample surface are exhibited on not only symmetric plane but also asymmetric plane.

In order to investigate the hetero-interface, high resolution transition electron microscopy (HRTEM) is employed. In Figure 4.35, a typical TEM image is taken using transition mode showing the electron diffraction pattern on film of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]_{16}$ with $n = 2$. The diffraction spots split in the out-of-plane direction, not in-plane, indicating exactly epitaxial growth of the heterostructures that evidences again the fully strain condition.

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Figure 4.35 The selected area electron diffraction pattern of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]^*16$ with $n = 2$.

The periodicity of the SL ($n = 2$) sample was examined by bright field TEM image and the intensity distribution is given in Figure 4.36. A total of 16 periods are identified and the thickness of the LSMO and BTO layers are 3.1 nm and 2.3 nm respectively. These values are nearly the same with the as-designed ones. In Figure 4.36 (b), a micrograph is taken on the sample ($n = 4$), where the BTO and LSMO layers are marked.

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Figure 4.36 (a) Bright field TEM image of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]^*16$ superlattices with $n = 2$. (b) Micrograph of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]^*16$ superlattices with $n = 4$.

To further investigate the hetero-interface, a simulation using multislice method was done according to the experimental result. In Figure 4.37 (a), a HRTEM image is taken with defocus value of 36 nm on the sample of $n = 4$, and (b) is the zoom in image of the heterointerface from the same sample, in which top layer is BTO and bottom is LSMO and a white dot line is drawn along the interface for visual assistance. Obviously, BTO and LSMO layers show different space group. Generally, LSMO is treated as pseudocubic, but it is rhombohedral physically. In the simulation, space group of P_{4MM} and R_{3MH} were used in the indexing of the SAED of the superlattices, and the zone axis was determined to be $[211]$. The simulation results are shown in Figure 4.37 (c) and (d), overlapping with the TEM images. In (c) of BTO layer, the blue cycles present Ba^{2+} and the purple is Ti^{2+} . On the other side, simulation of LSMO layer is shown in (d), where Mn^{3+} or Mn^{4+} cations are indicated by orange, the blue and green represent La^{3+} and Sr^{2+} , respectively. According to the simulation and experiment results, a $(\text{La,Sr})\text{O-MnO}_2\text{-BaO-TiO}_2$ type interface is suggested as evidenced by HRTEM investigation. The influence on the magnetoelectric coupling in the multiferroic heterostructures can be refereed to very recent publication¹⁴⁷.

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Figure 4.37 (a) HRTEM image taken with defocus value of 36 nm on the sample of $n = 4$, (b) Zoom in image of the heterointerface separating LSMO and BTO on the same sample, top layer is BTO and bottom is LSMO and a white line is drawn along the interface for visual assistance, and (c) HRTEM simulation of BTO layer. The blue atom is Ba, the purple atom is Ti. (d) HRTEM simulation of LSMO layer. The orange atom is Mn, the blue and green atoms are La and Sr, respectively.

Magnetism of these magnetoelectric superlattice was examined using physical properties measurement system (PPMS). To identify the Curie temperature, T_C of ferromagnetic phase, magnetization was measured in wide temperature range from 300K to 10K in zero field cooling mode, when a constant magnetic field was applied parallel to the sample surface. In Figure 4.38, normalized magnetization (M) of three superlattices are plotted versus temperature (T), where the symbols of $\blacksquare$, $\bullet$ and $\blacktriangle$ represent the samples with different n value of 2, 3 and 4 respectively. As the repetition of superlattice period is

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fixed at 16 for every film, then the larger n value indicates larger total manganite thickness. Consequently, a strong magnetization will appear on the superlattice film with larger n value. However, to estimate the magnetism of ultra thin manganite layers due to different superstructure, normalization of measured magnetization is necessary, since the interfaces, strain condition and the critical thickness of magnetic phase can influence the magnetic property on epitaxial thin films. In this case, all the measured results are divided by the n value accordingly. As a result, the comparison of magnetization is shown in Figure 4.38, in which different magnetic performances are observed. Interestingly the strong magnetic signal is still observed on the superlattice film with large n value, although normalization has been done. This result implies a strong magnetic exchange coupling occurs in the manganite layer with large n value or thickness. This phenomenon may be attributed to the interface effect where the magnetic coupling is destroyed. Spontaneously, this effect becomes weak with increasing thickness. Some research groups have reported the existence of critical thickness in magnetic oxide thin film. On the other side, this physical mechanism also determines the transition temperature of ferromagnetic phase of these superlattices. From Figure 4.38, the highest Curie temperature of 200K is identified on the sample with n of 4, but the other two samples only result in a Curie temperature of 150K.

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Figure 4.38 Normalized magnetization is plotted as function of temperature measured under zero field cooling mode on the superlattice films.

Normalized magnetization (in unit of 10^{-5} emu) versus magnetic field curves measured at 10k for the superlattices with n value varying from 2 (■), 3 (●) and 4 (▲) are shown in Figure 4.39 after subtracting the background diamagnetic signal of substrate. The strong linear correlation of normalized magnetization as a function of n is observed. The two curves obtained from samples of $n = 2$ and 3 show similar performance, which means a dominated interface effect. However, all superlattices exhibit similar coercive field of about 500Oe.

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Figure 4.39 Normalized magnetization verse magnetic field curves measured at 10K for the superlattices with n value varying from 2 (■), 3 (●) and 4 (▲) are showed after subtracting the back ground diamagnetic signal of substrate.

In-plane ferroelectric characteristic was examined using Precision Probe ferroelectric testing system. Top interdigit electrodes were fabricated by photolithography and electron beam deposition techniques. The 5 μm space was defined between each metal digit. The metal electrodes were composed of 10 nm Ti and 60 nm Au to assure good adhesion. In Figure 4.40, ferroelectric hysteresis loops were measured on multiferroic superlattice $[\text{LSMO}_{4n}/\text{BTO}_{3n}]_{16}$ superlattices with $n = 4$ at different applied electric fields. These curves show a linear lossy dielectric, that is attributed to two factors. As designed, not only dielectric material of BaTiO_3 but also conductive manganite of LSMO was grown to form the layered superstructure. Consequently, the ferromagnetic component of LSMO was suspected to channel the leakage current in the multiferroic superlattices.

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Figure 4.40 Ferroelectric hysteresis loops of the multiferroic superlattice [LSMO_{4n}/BTO_{3n}]*16 superlattice with n = 4 at different applied electric fields.

In Figure 4.41, the capacitor system of multiferroics superlattice is systematically illustrated, where red and green arrows represent tunneling and channeling current, respectively. When in-plane electric field was applied on the superlattice, the leakage current tunneling through dielectric BaTiO₃ layer was channeled through conductive LSMO layer and collected by the negative terminal finally. In addition, the leakage current may tunnel further when an intensive electric field is applied. In this light, a leaky capacitor model is presented to explain the linear dielectric loss. In Figure 4.41 (b), one superlattice unit, which is the bi-layer of LSMO/BTO hetero-structure, is modeled by connecting a capacitor and resistor in parallel. On the other side, the ferroelectric property of the multiferroic superlattice is also influenced by the critical thickness, as in thin ferroelectric films. As introduced in literature review (seeing section 2.2.2.1), the critical thickness of ferroelectric films has been reported by many researchers^{32, 148-151}. Although,

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there is no generally accepted value to be referred to, the thickness of individual BTO layer is considerable small, that are 2.5, 3.7 and 4.9 nm according to Table 5 in this research.

Figure 4.41 (a) In-plane capacitor system of multiferroics superlattice is applied with electric field using interdigit electrodes, where red and green arrows represent tunneling and channeling current, respectively. (b) Leaky capacitor model is illustrated by connecting dielectric BTO and conductive LSMO layers in parallel.

4.5.3 Summary

In this section, a new class of multiferroics with ferroelectric BTO and ferromagnetic LSMO superlattice structure has been achieved. The new class of superlattice multiferroics is different with traditional single phase multiferroics or composites. By taking advantage of laser MBE technique, monolayer growth is realized on STO (001) single crystal substrate to achieve layered superstructure. Due to lattice misfit, the optimized thickness ratio between compressive and tensile layers is identified to be 3/4 for these highly strained superlattices. The layered perovskites superlattices with building blocks of $[LSMO_{4n}/BTO_{3n}]_m$ ($n = 2, 3$ to 4) have been successfully built up to 16 superlattice periods. Proved by the in-situ RHEED observations and ex-situ high resolution XRD characterization, the commensurate epitaxy promises the fully strained hetero-interfaces

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connecting ferromagnetic and ferroelectric materials. In further characterization of physical properties, both ferroelectric and ferromagnetic behaviors are evidenced on these multiferroic superlattices.

5. Conclusions and Recommendations

In this thesis, the fabrication of nano-scaled epitaxial transition metal oxide materials, characterization and the properties have been investigated systematically. A new class of multiferroic superlattices has been achieved by laser MBE technology. In physics, these atomic aligned magnetoelectric interfaces lead to a new way to study the magnetoelectric coupling in a strongly correlated electron system. In this chapter, the main conclusions and recommendations are given.

5.1 Conclusions

5.1.1 Substrate Treatment and Layer-by-layer Epitaxy of Titanite Oxide

Thin Films Using laser MBE Technique

In this study, single crystal SrTiO_3 substrate is utilized to grow variety of oxides thin films. The single phase terminated SrTiO_3 substrate has been prepared by wet etching method. Homemade buffered HF ($\text{NH}_4\text{F}:\text{HF}$) solution with critical pH value of 5.5 is used to remove the surfaced SrO without touching TiO_2 . An additional thermal annealing under oxygen atmosphere has repaired the surface damage caused by wet etching process. The surface morphology of treated SrTiO_3 substrates has been investigated using AFM and RHEED. The terraced structure is observed on the sample surface, where the step height of terraces is identified to be unit cell height. The sharp RHEED pattern has been obtained on this treated surface, which assure the further atomic layer growth.

Through manipulating growth parameters of temperature, oxygen pressure and growth

Chapter 5 Conclusions and Recommendations

rate, atomic mono-layer epitaxy has been achieved, as evidenced by RHEED intensity oscillations. After examining the homoepitaxy techniques, heteroepitaxy BaTiO₃ have also been carried out to achieve quality ferroelectric thin film on the treated SrTiO₃ (001) single crystal substrates. The growth BaTiO₃ shows the similar in-situ RHEED behaviors as homoepitaxy of SrTiO₃, but the crystallinity of heteroepitaxial thin film is different because of lattice mismatch. The characterization of high resolution X-ray diffraction presents highly oriented epitaxial growth and low degree of crystalline mosaicity. In further ferroelectric measurements, the typical ferroelectric hysteresis loops are observed on this epitaxial BaTiO₃ film at different applied electric fields. Simultaneously, dielectric property of the BaTiO₃ thin film has been examined by capacitance versus electric field measurement. In conclusion, the substrate treatment is essential to assure the quality interface and atomic mono-layer growth. On the treated single crystal SrTiO₃ substrate, two dimensional epitaxial modes have been achieved on both homoepitaxy as well as heteroepitaxy of BaTiO₃. The crystalline and ferroelectric characteristics are investigated.

5.1.2 Preparation and Property Investigation of Ferromagnetic Transition Metal Oxide Thin Films

Ferromagnetic oxides have been intensively studied in this thesis, because quality oxide thin film with reliable ferromagnetism is critical for realizing the magnetoelectric coupling in multiferroic superlattice. With the objective of searching magnetic transition metal oxide in form of epitaxial thin film, three of important oxide materials have been fabricated and investigated including Spinel Co ferrite CoFe₂O₄, diluted magnetic oxide (DMO) of Co-doped SrTiO₃ and mix-valence manganite La_{1-x}Sr_xMnO₃.

Among the family of ferrite materials, cobalt ferrite (CoFe₂O₄) is unique in that it has

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the highest values of magneto-crystalline anisotropy and magnetostriction. For the epitaxial growth of cobalt ferrite, the issues of lattice parameter and crystal symmetry mismatch with the substrate are of considerable importance. Co ferrite thin films on Mg (100) and SrTiO₃ (100) substrates with different lattice mismatch and interfacial strains are epitaxially grown without buffer layer. The two key parameters of oxygen pressure and substrate temperature have been investigated and optimized, to achieve the two-dimensional single crystal layer-by-layer growth mode. The oxygen pressure plays an important role in the epitaxy growth mode of Co ferrite thin films on MgO substrate. The *c*-axis oriented Co ferrite thin films have also been epitaxially grown on the highly-compressive strained SrTiO₃ substrate, without buffered layer, by the two-dimensional layer-by-layer growth mode. Significant modulation of strain in epitaxial thin films by growth temperature has been studied by high-resolution XRD, and high quality Co ferrite thin films have been obtained with the FWHM of 0.75 °. The magnetic examination determines the quality Co ferrite thin film grown on SrTiO₃ substrate at 700 °C. Although, the room temperature magnetism of Co ferrite is attractive for making two phase multiferroics, heteroepitaxy of layered superlattice is impossible because of the huge lattice mismatch of 6.9% between Co ferrite and SrTiO₃ substrate.

Recently, diluted magnetic oxides exhibiting ferromagnetism (FM) at room temperature (RT) have attracted significant interest and been intensively studied. Because of the minimal lattice mismatch, a series of 3% Co-doped SrTiO_{3-δ} thin films have been grown on SrTiO₃ substrates using laser MBE technology operating under high vacuum condition. All the samples show room temperature FM and the magnetization with unexpected large magnetic moment when the thin film is thinner. The unreasonable

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magnetization is found to arise from the SrTiO_3 substrate. With the refilling of oxygen vacancies by additional thermal annealing in oxygen atmosphere, the magnetic signals disappear from the blank SrTiO_3 substrate which is once treated in high vacuum annealing. The possibility of contamination from the stainless substrate holder has also been clarified. To examine variety of SrTiO_3 substrates purchased different vendors, Co-doped $\text{SrTiO}_{3-\delta}$ thin films have been grown again under the same conditions. The thin film sample grown on high grade SrTiO_3 substrate made by Shiksha Co. of Japan does not show any magnetic signal. This result suggests that the unreliable ferromagnetism in Co-doped $\text{SrTiO}_{3-\delta}$ thin films. The choice of substrate for growth of oxide thin film is essential, because extreme epitaxy environment may generate impurity phase in substrate. Many high dielectric oxides have been claimed to exhibit magnetic property at room temperature, most possibly attributed to defects, and that is inconsistent with some theoretical predictions.

After evaluation of Co ferrite and Co-doped $\text{SrTiO}_{3-\delta}$ mix-valence manganite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films have been epitaxially grown on STO single crystal (001) substrates using laser MBE technique. Systematic studies on epitaxial conditions have been carried out by varying oxygen pressure as well as growth temperatures. The results of rocking curve characterization show that the minimal FWHM for (002) plane of thin films is as small as 0.02° . In reference to the quality of commercial STO substrate used in our study, this value indicates that the perfectly epitaxial result is obtained. It is known that hole doping level can be modulated by changing the strontium concentration of x in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Various thin films with x of 0.2, 0.3 to 0.45 have been successfully grown under the optimized conditions. A correlation of lattice parameter to strontium concentration x

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has also been observed. Finally, the discussion of influence on crystallinity of epitaxial thin films is presented. On the evidences of high resolution X-ray diffraction (XRD) characterization, some structural imperfections are attributed to the substrate used.

5.1.3 Growth and Properties of Fully Strained Multiferroics

Superlattices: $[(\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3)_{4n}/(\text{BaTiO}_3)_{3n}]_m$

A new class of multiferroics with ferroelectric BTO and ferromagnetic LSMO superlattice structure has been developed. The new class of superlattice multiferroics differs from traditional single phase multiferroics or composites. By taking advantage of laser MBE technique, monolayer growth has been realized on STO (001) single crystal substrate to achieve layer-by-layer grown superlattice. By analyzing the behaviors of RHEED and the strain energy due to huge lattice misfit, the optimized thickness ratio between compressive and tensile layers has been found to be 3/4 for these highly strained superlattices. The layered perovskites superlattices with building blocks of $[\text{LSMO}_{4n}/\text{BTO}_{3n}]_m$ ($n = 2, 3$ to 4) have been successfully built up to 16 superlattice periods. Proved by the in-situ RHEED observations and ex-situ high resolution XRD characterization, the perfect epitaxy reveals fully strained superlattice. In further characterization on ferroic properties, both ferroelectric and ferromagnetic behaviors are shown in these multiferroics superlattices.

5.2 Recommendations

In this thesis, a variety of oxides thin films are fabricated using laser MBE techniques. Fundamentally, the growth of quality transitional metal oxide materials is the most important part of the research works. The sample characteristics including atomically

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controlled structure and unexplored physical properties strongly correlate to the growth mechanism. Because of extreme conditions of ultra high vacuum, high temperature and ultra fast laser ablation, atomistic understanding of the epitaxial growth process of metal oxide surfaces is a challenging work in front-line material research. Generally, RHEED system is mostly employed in laser MBE for in-situ monitoring crystal surface. In this light, a high performance RHEED system made by STAIB INSTRUMENTS has been ordered and will be installed soon. This RHEED gun provides dedicated electron optics systems for diffraction studies, in the range of 10 to 30 keV. By combining electrostatic and magnetic elements, the gun produces a high brightness, small size, and low divergence beam, with extremely low outgassing. And the unique features of beam blanking and beam rocking allow the precise adjustment and variation of the incidence angle using electronic controls, without moving the sample. Additionally taking advantage of the data acquisition software of RHEED vision, which performs both image processing and real time analysis, this solid RHEED system will assist us in carry through the deeper investigation on material growth.

In this artificially designed material, the atomic coherent heterointerfaces are the core of magnetoelectric effects. Although the periodically grown heterointerfaces are believed to enhance the multiferroic property, the complicated fabrication process and production cost may impose some obstacles for device application of superlattices. Consequently the multilayer structure may be a more practical way to simplify the periodic superstructure without scarifying the physical properties. As we know, both ferroelectric and ferromagnetic materials hold great potential for applications as new generation of memory devices, such as FeRAM and MRAM which are typical sandwich capacitance

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structures. With an ambitious of combining the best qualities of ferroelectric and magnetic memory devices, a prototype magnetoelectric tunneling junction with fast low-power electrical write operation, and non-destructive magnetic read operation has been fabricated and synthesized.

This nano-size magnetoelectric tunneling junctions consisting of magnetic electrodes of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and Fe_3O_4 and the barrier layer of ferroelectric BaTiO_3 have been grown on SrTiO_3 (001) single crystal substrates using laser molecular beam epitaxy (MBE). RHEED and TEM studies reveal that the trilayers are heteroepitaxial with abrupt interfaces. After lithography and ion milling processes, magnetoelectric junction device is finalized. In figure Figure 5.1, the device design of the magnetoelectric tunneling junction is schematically illustrated in (a) and the microscopy image of the finalized device is shown as (b). At the early stage investigation, the junction exhibits nonlinear current-voltage characteristics and changes in junction resistance with applied field, which is attributed to different coactivity of the two magnetic layers. Magnetoresistance $\sim 1\%$ at 10 K is observed, shown as Figure 5.1 (d), that is lower than would be expected for a highly spin-polarized system. Two current versus voltage, curves measured under different temperature of 300K and 10K using AC transport measurement system of PPMS, manifest a typically rectifying property of this hetero-structure, as shown in Figure 5.1 (c). On the other hand, the manipulation of tunneling current is also achieved by turning the polarization orientation of the ferroelectric barrier layer.

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Figure 5.1 (a) A tunneling magnetoresistance (TMR) junction designed with sandwich structure, where epitaxial layers of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (bottom electrode) BaTiO_3 (Barrie layer) and Fe_3O_4 (top electrode) are continuously grown using laser molecular beam epitaxy (MBE) to 30nm, 2nm and 15nm respectively. After lithography and Ion milling, the active area in top layer of Fe_3O_4 is defined without exposure of bottom electrode. To isolate top metal electrode, amorphous LaAlO_3 of 400nm is deposited at room temperature in vacuum chamber after secondary mask. A lift-off procedure is carried out to expose the active area of top Fe_3O_4 layer. The TMR device is finalized after third patterning and electron beam deposition of 100nm gold pad. (b) Two IV curves were measured under different temperature of 300K and 10K using PPMS, (c) and manifest a typically rectifying property of this hetero-structure, and (d) Magnetoresistance $\sim 1\%$ at 10 K is also shown.

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