Oxygen pressure-mediated cation stoichiometry, microstructure, and properties of epitaxial perovskite thin films

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**Oxygen Pressure-Mediated Cation
Stoichiometry, Microstructure, and
Properties of Epitaxial Perovskite Thin
Films**

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A Thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of

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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 _____

LI ZHIPENG _____

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Summary

Transition metal oxides, especially those with perovskite structure, have attracted great attention due to their rich and useful physical properties, such as high temperature superconductivity, ferroelectricity and ferromagnetism. Functional perovskite films have profited greatly from the steady advances in thin film growth technologies, which allow nanoscale engineering in order to fabricate oxide electronics devices.

Within the family of perovskite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.2 < x < 0.5$) compounds are viewed as one of key building blocks of oxide spintronic devices due to their desirable properties, such as colossal magnetoresistance (CMR) and half metallicity. When they are used as electrodes in combination with ferroelectric barrier layers, highly spin-polarized multiferroic tunnel junctions can be formed. However, cation off-stoichiometry at the epitaxial interfaces between manganites and other materials can lead to interfacial dead layers, severely reducing the performances of the tunnel junction devices. In this work, transmission electron microscopy (TEM) and synchrotron-based spectroscopies were used to demonstrate that oxygen vacancies serve as a critical factor for modifying the cation stoichiometry in pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films. Near the manganite/ SrTiO_3 interface, A-site cations (La/Sr) are in excess when oxygen vacancies are induced during the film growth, partially substituting Mn cations. Simultaneously, Sr cations migrate

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towards the film surface and form a SrO rock-salt monolayer. Consequently, a gradient of the Mn nominal valence, varying from +3.6 to +3.2, is observed along the film growth direction through quantitative analysis of electron energy loss spectra, leading to anomalous magnetic properties. The results narrow the selection range of useful oxygen pressures during deposition, and demonstrate that accurate interface and surface cation stoichiometry can only be achieved after oxygen vacancies are eliminated in films during growth. This finding suggests that oxygen pressure serves as a tuning parameter for the interfacial dead layers and, hence for control over device performance.

In addition, we studied growth, microstructure and properties of perovskite superlattices composed of ferromagnetic $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ and ferroelectric BaTiO_3 . Increasing demand for spintronic devices, such as high-density memory elements, has generated interest in magnetoelectric coupling and multiferroic materials. The manipulation of electron spin by ferroelectric polarization or vice versa, can generate an additional degree of freedom besides electric and magnetic ordering, leading to the possibility of four-state memories. In artificial heterostructures, magnetoelectric coupling occurs only near the interfacial area. Due to the high interfacial area to volume ratio, multiferroic multilayer/superlattice is viewed as one of the most efficient ways to enhance the magnetoelectric coupling coefficient. However, both ferroelectric and ferromagnetic properties are difficult to be maintained when materials are shrunk to ultrathin layers. Interface dipoles and spin modulations are thought to create dead layers in ferroelectricity and ferromagnetism, respectively. Whether these dead layers are intrinsic has so far

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been controversial. In this work, we demonstrated that the degradation of multiferroic properties in the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ superlattices is strongly correlated to the local strain fields and cation nonstoichiometry induced by cation defects. This conclusion was arrived by combining the atomic-scale electron microscopy, piezoelectric force microscopy and low-temperature magnetism measurements. When the defects, such as pure edge dislocations and planar defects, were eliminated by increasing oxygen pressure during the film growth, both robust ferroelectricity and ferromagnetism were observed. Therefore, we conclude that the presence of cation defects has been the major obstacle limiting the functionalities of multiferroic superlattices with ultrathin ferroic layers and high oxygen pressure is required to deposit films with nearly bulk ferroic properties.

In summary, this work offers a well-documented insight into another critical growth parameter (besides the well-studied laser fluence effect) that can result in off-stoichiometric pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin films and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ multiferroic superlattices. Controlling the oxygen pressure during growth is crucial to achieving better interfaces, surfaces and microstructures, paving the way for fabrication of complex oxide devices with high performances.

Chapter 1 Introduction

1.1 Motivation

Complex oxides with perovskite structure exhibit a wide spectrum of physical properties, such as high temperature superconductivity, ferroelectricity and ferromagnetism.¹ This richness attracts intensive research on their fundamental physics and chemistry as well as on possible device applications. Furthermore, inspired by the success of silicon-based microelectronics devices, perovskites have been integrated in silicon memory chips to achieve data storage, as in the ferroelectric random access memory (FeRAM). Recently, by utilizing ultrathin multiferroic materials (with both ferroelectric and magnetic properties) as barrier layer in tunnel junction devices, a prototype with four-state memory has been demonstrated.²

The prerequisite for functional oxide devices is the growth of high quality thin films with accurate chemical stoichiometry. Pulsed laser deposition (PLD), which utilizes the evaporation of sintered ceramic targets through focusing a laser on the target surface, is a favorable thin film growth technique due to its ability to preserve the stoichiometry of compound materials of the targets.³ By employing a single crystalline and nearly lattice-matched substrate with an atomically smooth surface, epitaxial thin films with sharp interfaces can be fabricated.

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However, when the material is confined in two dimensions and grown as part of a heterostructure with other materials, the roles of both interface effects and size effects are revealed. Such effects become obvious when the bulk properties begin to deteriorate as the film thickness decreases.^{4,5} When such thin films are applied in oxide-based multiferroic devices, these effects can result in film properties that are degraded far away from those of bulk materials. Taking strontium-doped lanthanum manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) as an example: the bulk material displays colossal magnetoresistance and half-metallicity with a metal-to-insulator transition temperature of 370 K.⁴ So, when it is combined with an ultrathin dielectric layer to form a multilayer structure, giant tunneling magnetoresistance (TMR) above room temperature is expected to occur.⁶ However, this does not actually happen; the TMR of thin film manganites decreases rapidly with increasing temperatures to low values at room temperature. One possible reason for this effect is the suppressed ferromagnetic ordering near the interface due to interface reconstruction, such as charge transfer, resulting in an electrical dead layer.^{7,8} Another reason is related to extrinsic effects induced by cation nonstoichiometry. Although oxygen nonstoichiometry can be removed by post-deposition annealing, cation mobility is very limited in close packed perovskite structures, which restrict their recovery to stoichiometric composition.⁹ The chemical elements that form cations are deposited from the laser-ablated target materials. Therefore, the laser energy density or *laser fluence* on the targets should be crucial for cation stoichiometry in the thin films.^{3,10} With atomic scale electron energy loss spectroscopy (EELS) and a pulsed laser deposition set-up with well-optimized growth conditions, Muller and Huang

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revealed that the metallic ferromagnetism at room temperature can be stabilized in five-unit-cell-thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) layers in pulsed laser deposited LSMO/ SrTiO_3 superlattices, when the cation defects are eliminated by optimizing the laser fluence on ceramic targets.¹¹ This shows how the growth conditions mediate the interface and surface cation stoichiometry, defects and the corresponding physical properties; understanding the details of the growth process is therefore crucial for the achievement of perovskite heterostructures and devices with desirable properties.

Beside the laser fluence effect on cation stoichiometry, it is worth considering that the tendency to neutralize the positive charges brought by oxygen vacancies during film growth may serve as a driving force for local cation nonstoichiometry and structural defects. Fister *et al.* observed that the strontium surface segregation in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films increases as oxygen partial pressure decreases, implying that oxygen vacancies are somehow involved in the cation nonstoichiometry.¹² However, the role of oxygen pressure in determining the local cation stoichiometry and thus physical properties of epitaxial thin films is not completely clarified.

Moreover, integrating the ferromagnetic manganites with ferroelectric titanates can form multiferroic superlattices which have high interfacial area to volume ratio, allowing enhanced magnetoelectric coupling.¹³ To utilize the conventional reflected high energy electron energy diffraction (RHEED) for in-situ thickness monitoring during superlattice growth, low oxygen pressure is preferred to prevent significant scattering of electron beam by gas molecules in the chamber.

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It has also been demonstrated that BaTiO_3 (BTO) films grown at high oxygen pressures exhibit a more coarsened morphology, resulting in lattice strain relaxation and dislocations in the films.^{14,15} Thus, a relatively low oxygen pressure is preferred during film growth. However, because oxygen vacancies lead to cation nonstoichiometry and structural defects,¹⁶ which possibly severely affect the ferroelectricity of the films,^{17,18} a better insight into the effect of oxygen pressure will be critical to obtain good multiferroic properties.

1.2 Objectives

In this work, a variety of techniques were employed to elucidate oxygen pressure effect on interface and surface cation stoichiometry, microstructure, and thus physical properties of epitaxial manganite thin films and manganite/titanate superlattices.

First of all, local chemical information such as distribution of chemical elements at nanometer length scale will be extracted in the thin films which were grown at different oxygen pressures. To achieve this goal, TEM-based imaging and spectroscopy were employed. The prerequisite of obtaining reliable results is that the cross-sectional TEM sample has high quality, i.e. uniform thickness (less than 50 nm thick) and nearly no damaged surfaces. For $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin films, cation stoichiometry and Mn nominal valence are strongly correlated, so, by quantitatively analyzing the Mn nominal valence, the trend in cation stoichiometry change can be deduced. Secondly, to find out whether there is cation surface segregation, the analysis of surface chemical composition is essential. Furthermore, in order to

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understand the interplay between the cation stoichiometry and the physical properties, both transport and magnetic measurement were performed.

To form $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ superlattices, the thickness of each layer should be well-controlled and usually characteristic satellite peaks would be observed in X-ray diffraction pattern and in TEM selected area electron diffraction pattern. Extensive and careful analysis of lattice images will be carried out to identify of the dislocation types. Besides, the impact of microstructure on the multiferroic properties was also studied. To characterize ferroelectricity of the ultrathin BaTiO_3 in the superlattices, piezoelectric force microscopy was used, while the measured ferromagnetic properties included the magnetization vs. temperature curve and the magnetization vs. magnetic field curve. Finally, a mechanism was proposed that can explain how oxygen pressure mediated the structural defects and local stoichiometry of the thin films.

1.3 Major Contributions of the Thesis

This work has shown that, besides laser fluence, oxygen pressure can result in cation off-stoichiometric pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin films and the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ multiferroic superlattices. Maintaining the oxygen stoichiometry *during growth* is crucial to achieving high quality interface, surfaces and microstructure, paving the way for the fabrication of complex oxide devices with high performances.

In this work, TEM and synchrotron-based spectroscopies were used to demonstrate that oxygen vacancies during growth served as a critical factor to

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affect the cation stoichiometry in pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ epitaxial thin films. Local chemical information of the manganite thin films at nanometer scale was obtained with TEM spectroscopy, where the electron beam was focused to a diameter of about 2 nm, and slowly scanned along the thin film growth direction. The distribution of chemical elements was extracted from the normalized intensities of their EELS and energy dispersive X-ray spectrums (EDX). The A-site/B-site cation ratio was found larger than one in the manganite film grown under low oxygen pressure near the interface of the the film and SrTiO_3 substrate. The Mn nominal valence was exacted by quantitative analysis of the EELS Mn $L_{2,3}$ edges and oxygen K edges. These spectral features probe the local density of anti-bonding electron states, which revealed the nature of the chemical bonds and the local valence with nanometer resolution. The profiles of Mn valence are completely different in the samples grown under different oxygen pressures due to their different cation stoichiometries. By using the surface sensitive angle dependent X-ray photoelectron spectroscopy (XPS) with synchrotron light source and element-sensitive Z-contrast STEM imaging with atomic resolution, we found that the oxygen vacancies during film growth can induce strontium surface segregation as well, forming a SrO rock-salt monolayer. A mechanism based on charge neutralization and strain relaxation was proposed.

The magnetic hysteresis loop of the annealed sample grown at low oxygen pressure presents multistep magnetization reversal processes, indicating enhanced inhomogeneity of the magnetic phase. These results demonstrate the importance of oxygen vacancies *during growth* as a source of cation nonstoichiometry near the

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interface and surface of epitaxial thin films. With regard to tunneling devices, the two types of cation nonstoichiometry induced by oxygen vacancies in LSMO during growth can generate an extra insulating and nonmagnetic ‘dead layers’ near the LSMO-barrier interfaces, leading to the reduction of the Curie temperature and conductivity.

To study the multiferrocity of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ superlattices, we used a combination of atomic-resolution electron microscopy, piezoelectric force microscopy and low temperature magnetism measurements, demonstrating that the degradation of multiferroic properties of the pulsed laser deposited manganite/titanate superlattices strongly correlates to the presence of cation defects, including pure edge dislocations and planar defects. The density of these defects can be mediated by oxygen pressure during growth. When the extrinsic defects are eliminated by increasing oxygen pressure during growth, both robust ferroelectricity and ferromagnetism were achieved. Therefore, we conclude that the cation defects are the major obstacle limiting the functionalities of multiferroic superlattices with ultrathin ferroic layers and that high oxygen pressure is required to achieve nearly bulk ferroic properties.

1.4 Organization of the Thesis

Chapter 1 presents the background of the thesis work, motivation and objectives and the contribution of the thesis.

In **Chapter 2**, crystal structure of perovskite is introduced, followed by a discussion on electronic and magnetic properties of perovskite manganites. The

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principle of ferroelectricity in titanate materials is demonstrated by taking the example of barium titanate crystals. The first order and second order ferroelectric transitions explained by the Landau-Ginzburg-Devonshire approach are presented. The impact of defects on ferroelectricity is also briefly discussed.

In **Chapter 3**, an overview of the experimental techniques used in this work is introduced. PLD was employed to fabricate the complex oxide thin films. Both its principle and set-up details are presented. As one of the most important characterization methods, TEM techniques are intensively used in this work. The step-by-step formation of phase contrast image in conventional TEM is firstly explained, followed by a brief introduction of Z-contrast scanning TEM (STEM). The physics of electron energy loss spectroscopy (EELS) and the features of EELS are presented, especially the core-loss region, which is intensively used for the analysis of the oxidation states of transition metal in this work. Afterwards, the principles of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and methods for property measurement are briefly introduced.

In **Chapter 4**, we used synchrotron- and TEM-based spectroscopy to demonstrate that oxygen vacancies serve as a critical factor for modifying the interface and surface cation stoichiometry in pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films. Two types of cation nonstoichiometry were identified. Near the substrate/film interface, A-site cations (La/Sr) were in excess during film growth, concurrent with Mn substitution by La/Sr cations, while a SrO rock-salt monolayer was formed at the film surface. Additionally, the spatial variation of the Mn

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nominal valence was exacted by EELS in the annealed film, leading to anomalous magnetic properties.

In **Chapter 5**, we demonstrated that multiferroic properties of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ superlattices are strongly dependent on cation defects that can be controlled by oxygen pressure during the film growth. Energy filtered TEM (EF-TEM) analysis was performed to disclose the elemental distribution of the chemically modulated layers. HRTEM images taken from both [010] and [110] zone axes revealed the formation of pure edge dislocations and extended planar defects. Piezoelectric force microscopy and low-temperature magnetism measurements then showed the impact of cation defects on the multiferroic properties. This chapter ended with a discussion on the interactions between defects.

In **Chapter 6**, we presented main conclusions and discussed some of the prospects for extending the present study. The measurement of magnetoelectric coupling in manganite/titanate superlattice structure, studying the functionality of observed defects during polarization switching and fabrication of ferroelectric tunnel junction were proposed.

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Chapter 2 Literature Review

2.1 Introduction

Transition metal oxides display a wide spectrum of physical properties. The properties are sensitive to cation doping, temperature, strain, and electric field, leading to complex phase diagrams.¹⁻³ The richness of the physical phenomena has motivated extensive researches and has led to several practical applications. Within the transition metal oxide family, perovskites are of particular interest. They can display high temperature superconductivity, colossal magnetoresistance and ferroelectricity.^{4,5} Taking the ferroelectric perovskites for an example, they have a switchable spontaneous electrical polarization states, which can be used for nonvolatile random access memories. Their piezoelectric and pyroelectric properties have been applied in a wide range of technologies such as transducers, actuators and infrared detectors.⁶ With the advances of thin film growth technologies, different functional perovskites can be engineered together with atomically sharp interface to create new nanostructures and devices, such as high density memories.⁷ This chapter describes the crystal structure of perovskites, and the physics of both ferromagnetic manganites and ferroelectric titanates.

2.2 Crystal Structure of Perovskites

Complex oxides with perovskite structures have a general formula of ABO_3 , as shown in Figure 2.1. Taking $SrTiO_3$ as an example, the A-site (the corners of the

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cubic unit cell) is occupied by Sr^{2+} cations while the B-site (centre of the cubic unit cell) is occupied by the Ti^{4+} cations with empty 3d orbitals.

Figure 2.1 Schematic unit cell of perovskite ABO_3 . The A-site cations are in green color, the B-site cation is in purple color, and the oxygen is in red color.

Low level A-site cation doping can introduce two types of structural distortions to the cubic unit cell. One is the orthorhombic distortion where the BO_6 oxygen octahedra rotate to accommodate the size difference between the cations; the other distortion is the elongation of the octahedra caused by the Jahn-Teller effect.⁸ The distortion degree of the perovskite due to the cation size difference can be characterized by a tolerance factor t , which is defined by the following equation:⁹

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2.1)$$

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where the r_A , r_B and r_O are the ionic radii of the A-site cations, B-site cations, and the oxygen anions. For ideal cubic lattice, $t=1$. In the case of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, where A is the alkaline element, Ca^{2+} (ionic radius is 0.106 nm) doped manganite is more distorted than the Sr^{2+} (ionic radius is 0.127 nm) doped sample, as the t of the former is smaller than that of the latter. The distortion level can affect the conduction bandwidth and the electron hopping, important for the transport and magnetic properties of manganites.

2.3 Electronic and Magnetic Structure of Perovskite Manganites

Perovskite manganites has the same crystal structure as SrTiO_3 , as described in the previous section. For undoped manganites, trivalent lanthanide cations T (e.g., La, Nd) reside at the A-site, while the B-site is occupied by Mn^{3+} cations. By replacing T cations with divalent alkaline elements D, such as Ca^{2+} , Sr^{2+} and Ba^{2+} , electron holes are introduced to the system, modifying the electric and magnetic ground states of the materials.¹⁰

2.3.1 The Electronic and Magnetic Structure

Similar to other transition metal oxides, the incomplete d -shell of the Mn cation contributes to the intrinsic electrical and magnetic properties of manganite.¹⁰ Due to the crystal field effect of the symmetric cubic lattice, the Mn $3d$ orbitals split into t_{2g} and e_g states, and the crystal field splitting energy is about 1 eV. Furthermore, the lattice distortion (Jahn-Teller effect) can induce further degeneration of the t_{2g} and e_g orbitals to d_{xy} , d_{yz} , d_{zx} and $d_{x^2-y^2}$, $d_{3z^2-r^2}$ respectively. However, the ferromagnetic Hund's rule coupling energy (about 2-3

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eV) between them is higher than the crystal field splitting energy, therefore, the high spin state is realized. The crystal-field splitting of the fivefold degenerate 3d orbitals in Mn cations are demonstrated in Figure 2.2.^{11,12} Mn cation has seven electrons in 3d level. For Mn^{3+} and Mn^{4+} , the on-site electrons are all spin aligned, resulting in a net magnetic moment of 4 or $3\mu_B/\text{Mn}$, respectively.

Figure 2.2 (a) Crystal-field splitting of the fivefold degenerate 3d levels into lower t_{2g} and higher e_g levels. The Jahn-Teller distortion of the MnO_6 octahedron further lifts each degeneracy. Here, J_H stands for the Hund's coupling between orbitals. (b) The five d orbitals in the cubic crystal field: e_g orbitals ($d_{x^2-y^2}$, $d_{3z^2-r^2}$) and three t_{2g} orbitals (d_{xy} , d_{yz} , d_{zx}). Adapted from Ref. 11 and 12.

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At low doping level, for example $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x < 0.3$), the compound is a canted A-type antiferromagnetic insulator, with the Mn spins being aligned ferromagnetically in the ab plane but pointing in another direction along c -axis. When electron holes are doped in the e_g band for $0.3 < x < 0.5$, their spin directions are aligned with the t_{2g} electrons.¹³ The carrier hopping from site to site aligns the neighboring spins, resulting in a ferromagnetic and metallic ground state, as demonstrated in Figure 2.3.

Figure 2.3 Schematic spin (arrows) and orbital (lobe) configuration of Mn cations in manganites, **F** stands for ferromagnetic state, **A** stands for antiferromagnetic states. Adapted from Ref. 11.

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2.3.2 Transport and Magnetic Properties

Among perovskite manganites, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) has smaller colossal magnetoresistance than other doped manganites, such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. However, LSMO is the only manganite with a Curie temperature above room temperature when $0.2 < x < 0.5$.^{14,15} Therefore, it shows great potential as a building block for oxide electronics devices.

Figure 2.4 shows phase diagram of LSMO. The ground state of the undoped LaMnO_3 (LMO) is a canted A-type antiferromagnetic insulator in which the Mn spins are aligned ferromagnetically in the ab plane while the spin directions are opposite along the c -axis. When x (the Sr doping level in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) increases, transition of the ground state to ferromagnetic phase occurs. Within the range of $0.1 < x < 0.3$, the temperature driven metal-to-insulator transition is accompanied by ferromagnetic-to-paramagnetic transition. The transition temperature is characterized by the Curie temperature, T_C . Saturated magnetization of the doped manganite is around the nominal value $(4-x)\mu_B/\text{Mn}$. The so-called colossal magnetoresistance (CMR) is most pronounced around the T_C .¹⁶

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Figure 2.4 The schematic temperature-doping phase diagram for the LSMO system, with x indicating the Sr atomic fraction. The FM, PM, AFM, PI and CI denote ferromagnetic metal, paramagnetic metal, antiferromagnetic metal, paramagnetic insulator and spin canted insulator, respectively. Adapted from Ref. 14.

2.3.3 Theoretical Models

To explain the transport and magnetic properties of manganites, the double exchange (DE) mechanism with localized t_{2g} electrons and the itinerant e_g electrons was proposed by Zener in 1951.¹⁷ In this theory, the ferromagnetism of the manganites arises from the interaction between electrons in the incomplete d-shells. As shown in Figure 2.5, the e_g electron in a Mn^{3+} ion transfers to a neighboring Mn^{4+} ion without changing spin direction through the intermediate oxygen ion. There are three assumptions contained: (1) the 3d electrons are well aligned owing to the Hund's law; (2) the spin direction of the hopping electrons will not change;

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(3) the kinetic energy, or the hopping integral of the conduction electrons reaches maximum if the spin directions of both hopping electron and core electrons of the neighboring Mn ions are parallel, which in turn leads to the ferromagnetism. The model gives the electrical conductivity as described in the following equation:

$$\sigma = \frac{x e^2 T_C}{a h T} \quad (2.2)$$

where the x is the doping level, a is the lattice constant, T_C is the Curie temperature, T is temperature, e is the charge of one electron and h is Planck's constant. This equation successfully explains the transport properties of the ferromagnetic metallic regime at low temperature.

Figure 2.5 Schematic diagram of the double exchange mechanism, two degeneracy states are developed when both spins are aligned marked by the arrows in the Mn³⁺ ions. Adapted from Ref. 16.

The double exchange mechanism was further developed by Anderson, Hasegawa, de Gennes and others.^{18,19} The kinetic energy or the hopping integral of the conduction electrons is proposed to be proportional to $\cos(\theta/2)$ (θ is the angle

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between the spin direction of the two t_{2g} electrons in the two neighboring Mn cations).¹⁸ When an external magnetic field is applied, the spin direction of both t_{2g} and e_g electrons in the adjacent Mn cations is aligned, reducing the θ value, increasing the kinetic energy of the electron hopping, and therefore, increasing the conductivity. The double exchange mechanism clearly explains the magnetoresistance phenomena in the manganite system. However, Millis and co-workers found that experimental resistivity values in the LSMO system at high temperatures cannot be explained by using the double exchange mechanism.^{20,21} They proposed that the dynamic lattice distortion, manifested as the Jahn-Teller effect, plays an important role in this phenomenon.

Another scenario to explain the magnetic and transport properties of manganites is the nanoscale phase separation proposed by the Dagotto group.²² This model is based on a standard Hamiltonian model and incorporates a kinetic term, Hund's coupling, antiferromagnetic coupling, electron-phonon coupling and electron-electron interaction. This scenario predicts that the doped manganite is intrinsically inhomogeneous. Many nanoscale clusters coexist with competing phases and the electron transport occurs by percolation. Experimental evidence that supports this model has been obtained by X-ray,²³ neutron scattering,²⁴ and scanning tunneling microscopy.²⁵ The rich physics of manganites is explained to be the competition between the coexisting electronic and magnetic phases, such as ferromagnetic metallic phase and paramagnetic insulating phase, and this balance can be easily modulated by external electric fields, magnetic fields, etc.

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2.4 Perovskite Ferroelectrics

2.4.1 An Introduction to Ferroelectrics

Ferroelectrics are a class of materials that process stable and switchable electrical polarization. By encoding the 0 and 1 of the Boolean algebra by the two polarization states, ferroelectric materials show great potential for application in memory devices. Most ferroelectrics have a perovskite structure which has been discussed in the previous sections. Here, the basic principle of ferroelectricity is introduced by taking BaTiO_3 (BTO) as an example.

In BTO lattice, the tetravalent Ti^{4+} cation occupies the center of the oxygen octahedron, while the O^{2-} and Ba^{2+} ions form an *fcc* type structure. The lattice constant a is 0.401 nm when the temperature is just above the ferroelectric transition temperature of 135°C. Then the average distance between the Ti^{4+} and O^{2-} is 0.2055 nm which is larger than the sum of the Ti^{4+} and O^{2-} ion radii (0.196 nm). As a result, the Ti^{4+} ion has relatively free space to move inside the octahedron. As shown in Figure 2.6, both the oxygen octahedron and Ti^{4+} ion displace in the same direction with respect to the Ba^{2+} ions, but the Ti^{4+} ion moves to the upper part of the octahedron when the applied field points downwards and vice versa. These displacements result in a dipole moment.

The local regions with same polarization direction are called ferroelectric domains. Experimental evidence of the polarization switching by an external applied field is observed in the polarization-electric field loop, as demonstrated in

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Figure 2.7. When the applied field is increased (stages 1 and 2), the size of the domains that are aligned with the field will increase;

Figure 2.6 Perovskite BTO with displacement of the oxygen octahedral and Ti⁴⁺ ion with respect to the Ba²⁺ ions at two opposite polarization states. The red spheres are oxygen ions, the blue sphere in the body center of the cube is Ti⁴⁺ ion, and the grey spheres are Ba²⁺ ions. (From N. Stucki, personal communication, Dec 2012).

while new domains can also nucleate and grow. When complete, all the domains are aligned with the field (stage 3), and the polarization value is saturated. As the field decreases, the polarization decreases but remains nonzero when the field is zero (stage 4). The corresponding polarization value is called remnant polarization $+P_r$. Then the field is increased in opposite direction and the polarization direction is switched at the field value of $-E_c$ (position 5). This value is called coercive field. With further increase of the field, the polarization is saturated again at stage 6. The

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$+P_s$ in the figure is called spontaneous polarization, which is defined as the extrapolation of the polarization at high field to zero field.

Figure 2.7 Polarization vs. electric field loop showing the polarization switching.

Adapted from Ref. 6.

The behavior of the spontaneous electrical polarization in ferroelectrics can be explained by the Landau-Ginzburg-Devonshire approach from a macroscopic perspective.²⁶ We shall choose the origin of the free energy U for the strained, unpolarized crystal to be zero, and the polarization is restricted in one crystallographic axis, then the free energy U can be developed as a function of P :

$$U = -EP + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 \quad (2.3)$$

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where E is the electric field, and α , β , and γ are fit-parameters, explained in more detail below.

To find the equilibrium state, the minima of this equation is obtained when:

$$\frac{\partial U}{\partial P} = -E + \alpha P + \beta P^3 + \gamma P^5 = 0 \quad (2.4)$$

Here α is temperature dependent, taking the form $\alpha = \alpha_0(T - T_0)$, α_0 is a positive constant and T_0 is equal to or lower than the Curie temperature (T_C) as mentioned in the Curie-Weiss law. The order of transition can be classified according to the sign of β .

When β is negative, the transition is called *first order* transition (discontinuous transition) and the γ term should be retained. Then the Equation 2.4 can be written as following for zero applied field:

$$\alpha_0(T - T_0)P_s^2 + \beta P_s^4 + \gamma P_s^6 = EP_s = 0 \quad (2.5)$$

where P_s is the spontaneous polarization. The Curie temperature T_C is defined by the conditions $U = 0$ and $\frac{\partial U}{\partial P} = 0$, then $T_C = T_0 + \frac{3}{16} \frac{\beta^2}{\alpha_0 \gamma}$. The minima of the U corresponding to two stable states with $P_s \neq 0$ can be found out by solving following equation:

$$\alpha_0(T - T_0) + \beta P_s^2 + \gamma P_s^4 = 0 \quad (2.6)$$

The plots of the free energy vs. polarization and the P_s vs. temperature are shown in Figure 2.8. The existence of the metastable phase when $T_0 < T < T_C$ is well explained by the first order transition.

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Figure 2.8 (a) Free energy U vs. P for a first order transition, and (b) plot of P_s vs. temperature for first order transition near when T is near T_C . (From N. Stucki, personal communication, Dec 2012).

When β is positive, the transition is called *second order* transition (continuous transition) and γ term can be neglected. Then we can conclude the equilibrium state of P_s vs temperature when the external field is zero:

$$P_s[\alpha_0(T - T_0) + \beta P_s^2] = E = 0 \quad (2.7)$$

For $T \geq T_0$, $P_s=0$, since βP_s^2 term is positive, For $T < T_0$, the $P_s = \mp \sqrt{\frac{(T_0-T)\alpha_0}{\beta}}$,

therefore, the T_0 is equal to the Curie-Weiss temperature, T_c . The plots of the free energy U vs polarization and the P_s vs. temperature are shown in Figure 2.9.

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Figure 2.9 (a) Free energy U vs. P for a second order transition, and (b) plot of P_s vs. temperature for second order transition near when T is near T_C . (From N. Stucki, personal communication, Dec 2012).

Taking BTO as an example, its ferroelectric phase transition is shown in Figure 2.10. The Curie temperature T_C of BTO is about 135°C . Below T_C , the Ti^{4+} cation occupies the off-center position of the oxygen octahedral. The crystal structure changes from cubic ($T > 135^\circ\text{C}$) via tetragonal ($5^\circ\text{C} < T < 135^\circ\text{C}$) and orthorhombic ($-90^\circ\text{C} < T < 5^\circ\text{C}$) to rhombohedral ($T < -90^\circ\text{C}$).²⁷ Since BTO has a stable ferroelectric phase at room temperature, this material is used as the ferroelectric component in the oxide heterostructures.

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Figure 2.10 Crystal structure, lattice distortion and the direction of the spontaneous polarization vs. temperature of BTO. Adapted from Ref. 27.

2.4.2 Impact of Defects on Ferroelectricity

Due to their switchable polarization, ferroelectrics have great potential to be integrated in nanoscale devices such as high density memories. However, the ferroelectricity significantly degrades as the film thickness decreases below a certain value which is called critical thickness. This degradation often stems from the composition and microstructural inhomogeneities such as dislocations. Alpay and co-workers developed a thermodynamic model based on the Landau-Devonshire formalism and showed that there was a drastic variation in polarization near dislocations due to the coupling of the stress field and polarization.²⁸ These polarization gradients result in strong depolarization field which extend over several nanometers and suppress the ferroelectricity, as shown in Figure 2.11. The

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Jia *et al.* found that the strain field of the $a[011]$ dislocation in the SrTiO_3 substrate can propagate across the interface into a $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ film, leading to a strong reduction of the c – axis parameters and a decrease in local spontaneous polarization.²⁹ Therefore, controlling the defects distribution by optimizing the thin film growth conditions is crucial to achieve room temperature ferroelectricity in ultrathin ferroelectric films.

Figure 2.11 Polarization distribution around periodic misfit dislocations in a (a) 15 nm and (b) 40 nm thick PbTiO_3 films on (001) LaAlO_3 substrate. Individual elements were taken around 0.4 nm. Adapted from Ref. 28.

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Chapter 3 Experimental Techniques

Thin film deposition technology is a key to the creation of modern devices such as high data density memory. There has been a continuous industry-driven demand for high quality films for high-performance solid state devices, requiring a rapid evolution of deposition techniques. Meanwhile, the advances in analytical instrumentation also improve the understanding on the relationship between properties and physics and chemistry of thin films. The important factors that determine the performances of electronic devices are (1) structural perfection, (2) purity and homogeneity of chemical composition and (3) flatness or sharpness of the layer surface/interface. To simultaneously achieve these goals, one of the physical vapor deposition (PVD) methods, called pulsed laser deposition (PLD) was used in this thesis. PLD has been proven to be very effective to grow metastable phases and artificial structures of complex oxides which are very difficult or even impossible to be fabricated by conventional synthesis methods.¹ Characterization of thin films was performed with different analytical methods which probe their microstructure, composition, and electrical and magnetic properties. Transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and electrical and magnetic properties measurements are the main characterization methods used in this thesis.

Chapter 3

3.1 Thin Film Growth Technique: Pulsed Laser Deposition (PLD)

3.1.1 The Principles of the PLD

One of the most versatile techniques for oxide film fabrication is pulsed-laser deposition (PLD). Though significant development of this technique began only in the late 1980s, PLD is already a widely used deposition approach for film growth, especially for oxides.^{2,3} Figure 3.1 shows the configuration of a PLD system. The PLD technique uses a high power laser to melt, evaporate and ionize materials from target surface. In the laser ablation process, a pulsed laser beam is focused on a target by a lens outside the chamber, resulting in a dense vapor beam which is the so called highly luminous "plasma plume". The super saturation of ablated materials arrives at the substrate surface and causes a large number of nucleation sites to help the film grow uniformly with high quality. The substrate is held stationary with 5 cm - 6 cm away from the target. The temperature of the substrate may be selected from room temperature to about 800 °C, depending on particular thin film growth regimes. A processing gas supply is often provided for the inlet of selected gases to produce desired chemical reactions during film growth.

The thin film quality is dependent on many parameters, including substrate temperature, laser energy density and frequency, target-to-substrate distance, base pressure and deposition gas pressure, etc. Substrate temperature is one of the most important factors to the crystallinity of the films.² Normally, an amorphous phase forms when the substrate temperature is below a certain value, while crystalline process begins when the temperature increases above the value.

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One of the main advantages of PLD is the capability for stoichiometric transfer of target materials to substrates when the growth conditions are optimized.¹ With very short laser pulse, the target materials explode towards the substrate, with similar deposition rates, resulting in thin films with the exact composition of the targets. Another advantage is its cost-effectiveness. One laser source can be used for multiple chambers and the laser beam can be directed to different chambers by mirrors and lenses. Furthermore, multilayers and even superlattices can be produced by using different targets.

In spite of these advantages, there are certain drawbacks associated with the PLD technique. The highly directional focused laser beam produces a distribution of deposited materials which is strongly peaked to a narrow solid angle, resulting in poor thickness uniformity over a large area. Another disadvantage is the incorporation of micron to submicron size particles on the film surface after laser ablation. However, a number of solutions can eliminate the particles, which include using a velocity filter, high quality targets and shadow masks. The PLD technique is still somewhat limited to the study of new functional materials in research environments.

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Figure 3.1 A schematic configuration of PLD system.

3.1.2 Pulsed Laser Deposition Setup

All the epitaxial thin films used in this thesis were fabricated by the PLD system located in the Sensors & Actuators Laboratory (Nanyang Technological University, Singapore), see Figure 3.2, using a KrF excimer laser (Lambda Physik LPX 210, Germany) with a wavelength of 248 nm. The width of the laser pulse is 25 ns and the repetition rate can be tuned from 1 to 100 Hz. The laser energy ranges from 0.01 to 1.2 J. The effective pumping speed and the total gas flow control the pressure during deposition. The former is adjusted through a variable restriction between chamber and the turbo pumps. For the background gas, oxygen is used most often. The amount of material ablated from the target surface is determined by the laser energy density and the substrate-to-target distance. To obtain a homogeneous distribution of laser energy in the laser beam, an aperture is used before the focusing lens. By varying both the total laser energy and the spot size on

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the targets, the laser fluency can be adjusted from 1 J/cm^2 to 7 J/cm^2 . The main chamber contains four targets holders that can be rotated for the convenience of growing multilayered samples. During the deposition, the target is scanned both vertically and horizontally to optimize the usage of target surface area and to maintain the uniformity of the deposited thin film thickness. The substrate holder with platinum heating wires can be heated up to 800°C , measured by an *S*-type thermocouple.

The epitaxial films in the present work were deposited at a dynamic oxygen pressure from 1 Pa to 30 Pa. The substrate temperature was varied from 650°C to 750°C . The substrates were cleaned in a sequence of ultrasonic baths in acetone and ethanol, prior to loading into the chamber for deposition. The targets were polished before the deposition process every time to get a clean and smooth surface. A shutter was used to shade the substrate, to allow further cleaning of the target surface by pre-sputtering without contaminating the substrate. A laser energy density of about 2 J/cm^2 was used.

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Figure 3.2 Photograph of the PLD system in the Sensors & Actuators Lab at Nanyang Technological University in Singapore.

3.2 Thin Film Characterization

In this thesis, transmission electron microscopy techniques were intensively used to characterize the crystallographic features as well as the local chemical composition. Surface of the thin films was characterized by X-ray photoelectron spectroscopy. To detect ferroelectricity of the ferroelectric ultrathin films, piezoelectric force microscopy was employed. Ferromagnetism was measured by a physical properties measurement system produced by Quantum Design.

3.2.1 Transmission Electron Microscopy (TEM)

The microscopes that were used in this study include a JEOL 2100F operated at 200 kV (JEOL, Japan) for high resolution lattice imaging, a Philips CM300

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(currently FEI, the Netherlands) operated at 300 kV for elemental mapping using energy filtered transmission electron microscopy, and an FEI TITAN 80-300 (FEI, the Netherlands) for Z-contrast imaging and electron energy loss spectroscopy.

3.2.1.1 Basic Modes in Conventional TEM

The principle of a conventional TEM is similar to that of a light microscope, except that light microscopes use light sources and glass lenses while TEMs use electron sources and magnetic lenses.⁴ The configuration of a TEM is shown in Figure 3.3 (a). The electrons that are emitted from the tungsten Schottky filament are accelerated by a high voltage (80 kV to 300 kV in our case) and focused through two or three sets of condenser lenses onto the specimen. The electron beam is scattered by the specimen, while the diffracted beam is brought back to focus by the objective lens on its focal plane and produces an electron diffraction pattern. The final real space images or diffraction patterns can be projected on a fluorescent screen or CCD-based camera through the objective lens, the intermediate lenses and the projector lenses. Figure 3.3 shows two basic operation modes of conventional TEM: image mode and diffraction mode. These two modes can be obtained by changing the focal length of the intermediate lenses. In image mode, the image plane of the intermediate lenses coincides with the image plane of the objective lens; in diffraction mode, the image plane of the intermediate lens coincides with the back focal plane of the objective lens.

Figure 3.3 Schematic of the TEM illumination in (a) image mode and (b) diffraction mode in a conventional TEM. Adapted from Ref. 4.

3.2.1.2 Phase Contrast Image in High Resolution TEM

The most common imaging techniques in conventional TEM mode are bright field (BF) and dark field (DF) imaging, where the transmitted electron beam forms the image. The objective aperture is positioned around the desired beam to perform the beam selection. When more than one beam are selected, instead of one beam, *phase contrast* image is formed. The conventional high resolution TEM image or lattice image belongs to this kind of image. Due to the interaction between

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electron beams and sample, the transmitted electrons have non-uniform spatial distributions which are strongly phase dependent. Therefore, it is called *phase contrast*. The image contrast arises from the interference between the transmitted beam and the diffracted beams, giving rise to phase contrast. As illustrated in Figure 3.4, the lattice fringes perpendicular to the G vector with spacing of $1/G$, are generated. As the size of the objective aperture increases and more diffracted beams are involved in the interference, there will be more lattice fringes appearing in the final image. It can be seen in Figure 3.4 that the image resolution is dependent on the number of electron beams that are selected in the back focal plane by the objective aperture. However, the diffracted beams at high angle can induce more spherical aberration (C_s) which can degrade the resolution of the image, so only certain size of the objective aperture is used to exclude the highly diffracted electron beams. By utilizing the C_s corrector which can compensate the C_s of objective lens, the size of objective aperture can be increased, allowing increased number of diffracted beam for imaging, resulting in an achievement in spatial resolution which approaches to the information limit.⁴

Figure 3.4 (a) Schematic illustration of the tilted-beam 111 lattice fringes in silicon using transmitted beam and one diffracted beam. (b) The illustration of the many beam image from the interference between transmitted beam and six diffracted beams. Adapted from Ref. 4.

Phase contrast imaging is very sensitive to changes in sample thickness and crystal orientation. Besides, the image contrast is also dependent on the TEM operation parameters, such as the defocus value, and the astigmatism of the objective lens. The interaction of the incident electron beam with the sample, and the convolution of the exit wavefunction and the contrast transfer function (CTF) of the objective lens, result in the final image phase contrast. However, this theory is only true when the sample is thin enough that the amplitude variation does not contribute to the image contrast.^{5,6}

The step-by-step image formation in the high resolution TEM mode is illustrated in Figure 3.5.^{5,7} The incident electrons can be described as a planar wave,

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$\psi_0(\mathbf{r})$. The wave interacts with the projected potential of sample, $\phi_p(\mathbf{r})$, and generates an exit wavefunction, $\psi_e(\mathbf{r})$ that can be approximated as:

$$\psi_e(\mathbf{r}) = \exp [-i\sigma\phi_p(\mathbf{r})] \quad (3.1)$$

where σ is the interaction constant, corresponding to the strength of elastic scattering between electrons and the sample. $\mathbf{r}$ is the vector in real space. A weak phase object approximation (WPOA) in which the sample is thin enough that the electrons are considered to scatter only once, could be applied to light elements. Then the object exit wavefunction is formulated as:

$$\psi_e(\mathbf{r}) = 1 - i\sigma\phi_p(\mathbf{r}) \quad (3.2)$$

When the waves pass through the objective lens, the waves propagating along different directions are transferred differently. The CTF which expresses how electron waves are transferred can be formulated as:

$$T(\mathbf{u}) = \mathbf{F}[t(\mathbf{r})] = A(\mathbf{u})\sin\chi(\mathbf{u}) \quad (3.3)$$

$$A(\mathbf{u}) = \exp \left[-\frac{\pi^2 \Delta^2 \lambda^2 \mathbf{u}^4}{2} \right] \times \exp \left[-\pi^2 \alpha^2 \mathbf{u}^2 (\varepsilon + C_s \lambda^2 \mathbf{u}^2)^2 \right] \quad (3.4)$$

$$\chi(\mathbf{u}) = \pi \varepsilon \lambda \mathbf{u}^2 + \frac{1}{2} \pi C_s \lambda^3 \mathbf{u}^4 \quad (3.5)$$

where $\mathbf{F}$ is the Fourier transform operator, $t(\mathbf{r})$ is the CTF in real space, $A(\mathbf{u})$ is the envelope function of the CTF, $\sin\chi(\mathbf{u})$ is a function of the defocus value ε , the spherical aberration C_s and wavelength λ . Δ is the focus spread and α is the electron beam divergence. $\mathbf{u}$ is the vector in reciprocal space. Among these

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parameters, the defocus value is the main parameter to be determined and other parameters are either instrument constants or vary only little such as Δ and α .

Figure 3.5 The schematic illustration of the step-by-step image formation in high resolution TEM mode. The wavefunctions of the electrons at different phases are shown. Adapted from Ref. 5.

When the electron waves are focused on the image plane, HRTEM images are formed. The intensity distribution in the images can be expressed as:

$$I(\mathbf{r}) = |\psi_e(\mathbf{r}) * t(\mathbf{r})| \approx 1 + 2\sigma\phi_p(\mathbf{r}) * \mathbf{F}^{-1}[T(\mathbf{u})] \quad (3.6)$$

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where $*$ is a convolution.

The convolution of the CTF of the objective lens introduces the non-linear transfer characteristics of the lens, leading to complexity in image interpretation.

3.2.1.3 Z-contrast Imaging in Scanning Transmission Electron Microscopy (STEM)

Compared with the phase contrast image formation by conventional TEM, the interpretation of the Z-contrast STEM image is quite straightforward. Therefore, this technique is widely used in the characterization of interfaces, grain boundaries and structural defects.⁸ In the STEM mode, the electron beam is focused into a narrow spot and raster scans over the sample. The Z-contrast STEM image is formed by collecting the high angle scattered electrons by an high angle annular dark field (HAADF) detector, as shown in Figure 3.6, so this technique is also known as HAADF-STEM.⁴ Due to the high collection angle, the contribution from Bragg diffraction is minimized and the scattering at high angle is essentially Rutherford scattering, resulting in an image intensity nearly proportional to the square of the local atomic number.

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Figure 3.6 Schematic illustration of the electron optics in the HAADF-STEM mode.

Adapted from Ref. 8.

3.2.1.4 *Electron Energy Loss Spectroscopy*

Electron energy loss spectroscopy (EELS) is intensively used in this work to study the valence of transition metals, such as Mn, in complex oxide thin films. EELS is obtained when the incident electrons are collected after they pass through the specimen and their loss in energy is measured, as shown in Figure 3.7. The features in EELS provide information of the electron *inelastic scattering* process. In contrast to the microstructural analysis from electron diffraction patterns generated by the elastic electron scattering, EELS gives information of the local chemical composition and electron density of states of the specimen.^{9,10}

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Figure 3.7 A schematic view of EELS in STEM mode. Adapted from Ref. 8.

Figure 3.8 shows an example of an EEL spectrum containing several features at different energies. The highest peak located around 0 eV is called zero-loss peak and arises from the electrons that pass through the specimen without losing any energy in the scattering. The second part is low-loss region that contains the interband transition and plasmon peaks. The interband transitions result from the excitation of valence electrons to unoccupied energy states. The plasmon peaks are strongly related to the density of the valence electrons, and thus dependent on the specimen composition. Sharp plasmon peaks with widths of few eV can be

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observed in the metallic sample, while broad plasmon features are generated in non-metallic

Figure 3.8 Main features of an EEL spectrum using a high temperature superconductor ($\text{YBa}_2\text{Cu}_3\text{O}_7$) as an example. Adapted from Ref. 10.

samples. The third feature is the core-loss region which reveals the electron excitation from core-states (K, L, M shells etc.) to unoccupied conduction band states. Its energy spreads from about 10 eV to several thousands of eV.⁹ In this thesis, the analysis of core-loss region features, such as the $\text{L}_{2,3}$ of transition metals and the oxygen K edge, were mostly employed to extract the chemical bonding information of the complex oxide thin films.

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The $L_{2,3}$ edges in the core-loss region represent the transitions from initial 2p states to the unfilled 4s- or 3d- states that are allowed by the dipole selection rule. For transition metals, the radial overlap of the initial 2p and 3d is much larger than the overlap of the 2p and 4s states. Additionally, the density of states (DOS) of the 4s bands is significantly lower than that of 3d bands. Therefore, the L edges are mainly determined by the *2p to 3d transitions*. Furthermore, the *spin-orbital* interactions in the 2p shells give rise to the well-separated L_3 ($2p_{3/2}$ to 3d) and L_2 ($2p_{1/2}$ to 3d) edges. For simple perovskite structure, the transition metals are *octahedrally coordinated* by six oxygen atoms which split the 3d states into levels of t_{2g} and e_g symmetry according to the *crystal field theory*.⁹ The $L_{2,3}$ edges are therefore split into t_{2g} levels at lower energy and e_g level at higher energy. For Ti^{4+} cations, the combination of the crystal field splitting and spin-orbital splitting gives rise to four strong peaks, as demonstrated in Figure 3.9. Therefore, the fine structure of transition metal $L_{2,3}$ edges is sensitive to the valence states and its coordination.

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Figure 3.9 Experimental Ti^{4+} $L_{2,3}$ edges recorded in anatase, brookite, rutile and perovskite. Adapted from Ref. 9.

3.2.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to measure the chemical states of surface elements in this work. Part of the XPS work was carried out by a VG ESCALAB 220i-XL spectrometer with an Al $K\alpha$ monochromatic X-ray source located in Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), another part was conducted at the Singapore Synchrotron Light Source (SSLS). The principle of XPS is based on the well-known photoelectric effect discovered by A. Einstein. An atom can absorb energy from incoming photon and emit electrons. The well-defined energy required to emit

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electrons is known as binding energy, E_B . Since the energy of incoming photon, $h\nu$, is known, thus the kinetic energy of ejected electron, E_K , can be calculated:

$$E_B = h\nu - E_K \quad (3.7)$$

By analyzing the kinetic energy of emitted electrons and calculating the binding energy, chemical elements can be identified as each element has an unique fingerprint of binding energy. Moreover, the relative ratio of the elements is calculated by measuring the areas under characteristic peaks and applying the correct sensitive factor. Another useful feature of XPS is that the binding energy of many elements vary, depending on their valence states. When the valence of elements, such as Ti, increases from Ti^{3+} to Ti^{4+} , the corresponding binding energy also increases. This is due to the fact that the nucleus will be less screened and the binding energy tends to increase when the electron density is lowered. Actually, the chemical environments of elements in different structures can also induce different electron densities, and therefore, unique binding energies.¹¹ In this work, angle dependent XPS was used to study the surface composition of epitaxial thin films.

3.2.3 Atomic Force Microscopy

In this work, atomic force microscopy (AFM) is not only used to study the surface roughness of epitaxial thin films, but also to characterize piezoresponse of the ferroelectric films in piezoelectric force microscope (PFM) mode. The AFM models we used in this work were MFP-3D Asylum AFM and Cypher AFM from Asylum Research. As shown in Figure 3.10, an atomically sharp silicon cantilever (probe) is used to do a raster scan on the sample surface. At the same time, a laser

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beam from the light source is focused on the surface of the cantilever, and reflected to a four-quadrant photodetector. When the cantilever is brought near the sample surface, forces which include mechanical contact force, van der Waals force, electrostatic force etc, lead to bending of the cantilever according to Hooke's law. This cantilever bending therefore allows measuring the force by measuring the position of a deflected laser spot on the photodetector. In most cases, a feedback mechanism is employed to adjust the tip to sample distance to maintain a constant force value between sample and tip. Normally, the sample is mounted on a piezoelectric stage that can move the sample in the Z direction to maintain a constant force and the X and Y directions for scanning the sample. After the scanning, the resulted map $Z = f(X, Y)$ can represent the topography of the sample surface.¹²

Figure 3.10 Schematic diagram of AFM. Adapted from Ref. 12.

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In the PFM mode, a conductive AFM tip is used instead of a pure silicon cantilever. It is brought into contact with the surface of piezoelectric materials with a voltage applied between them. Due to the electrostriction effect, the sample surface would contract or expand. Since the AFM tip is in contact with the sample surface, the deformation of the surface can bend the tip upwards or downwards, resulting in an additional deflection compared to the status before the voltage is applied. Thus the cantilever deflection in the Z direction can reflect the voltage or polarization.¹²

3.2.4 Transport and Magnetic Property Measurements

The equipment we used in this work for the transport and magnetic property measurements was a Quantum Design Physical Property Measurement System (PPMS) 6000, which has a temperature range of 1.8 K to 400 K and a maximum magnetic field of 9 Tesla. The four-point probe method was used for the measurement of the sheet resistivity of the thin films. The probe is arranged symmetrically with point spacing of s , as shown in Figure 3.11. Constant current I is applied to the outer probes and voltage V between the two inner probes is measured. Then it can be shown that the resistivity ρ is given by:¹³

$$\rho = 2\pi s \frac{V}{I} \quad (3.8)$$

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Figure 3.11 Arrangement of a four-point probe on a rectangular sample. Parameters a and d are the length and width of the sample, respectively. Adapted from Ref. 13.

The magnetic properties of the samples in this work were measured by the vibrating sample magnetometer (VSM) method. In this method, a sample is placed inside a uniform magnetic field to magnetize the sample. Then the sample is physically vibrated by a uniquely designed linear motor. The induced voltage in the detection (pickup) coil is proportional to the magnetization of the sample.¹⁴ The system has an ability to resolve the magnetization of less than 10^{-6} emu by using a compact gradiometer pickup coil configuration, a relative large oscillation amplitude (1-3 mm peak) and a frequency of 40 Hz. In this thesis, model P525 PPMS VSM magnetometer by Quantum Design was used.

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Chapter 4 Interface and Surface Cation Stoichiometry Modified by Oxygen Vacancies in Epitaxial Manganite Films

4.1 Introduction

Strontium-doped lanthanum manganites ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) exhibit desirable tunable properties, such as colossal magnetoresistance (CMR) and half metallicity, which provide rich opportunities for multifunctional devices.¹ With a Curie temperature of 370 K when x is near 0.3, they are one of the most promising candidate as electrodes in multiferroic tunnel junctions by combining their tunneling magnetoresistance (TMR) with electroresistance (ER) effects,^{2,3} as spin injectors in polymers,⁴ and in solid oxide fuel cells,⁵ due to their chemical stability and near-lattice match with other functional oxides. However, the TMR of manganites decreases rapidly with increasing temperature to low values at room temperature. One possible reason is the suppressed ferromagnetic ordering near the interface due to interface reconstruction, in form of an electrical dead layer.^{6,7} Since the physical properties of manganites strongly depend on their local chemical composition,⁸ extrinsic effects such as the cation off-stoichiometry and the resulting interfacial crystalline imperfections could also lead to insulating and nonmagnetic layers. Thin manganite films with accurate chemical stoichiometry

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down to nanometer length scales are therefore required to ensure high performances of oxide spintronic devices.

Similar to other perovskite materials,⁹⁻¹¹ stoichiometry of manganite films can be varied greatly, depending on the thin film growth conditions. Although oxygen nonstoichiometry can be removed by post-deposition annealing, it is difficult to recover stoichiometric composition of cations due to their low mobility.¹² Hence, the precise control of film growth conditions and the analysis of the corresponding cation stoichiometry in films should be paid close attention so as to achieve desired properties. As revealed by Muller *et al.*¹³ and Kourkoutis *et al.*¹⁴ using advanced atomic-resolution electron energy-loss spectroscopy (EELS),¹⁵ the laser fluence on ceramic targets will be decisive for the local stoichiometry of pulsed laser deposition (PLD) -grown (La,Sr)MnO₃/SrTiO₃ multilayers. The quality of multilayers would deteriorate with increasing laser fluence, resulting in nonstoichiometric A-site (La and Sr) and B-site (Mn) cations, which leads to suppression of interface magnetism. The question then arises, how can the cation stoichiometry be modified, if we tune another main film growth parameter - oxygen pressure? In the available literature, the accepted selection of oxygen pressures used for manganite film growth can be divided into two groups: films grown with oxygen pressure above 26 Pa, with or without post-annealing,¹⁶ and films grown with oxygen pressure around 1 Pa, resulting in films with oxygen vacancies, followed by post-annealing to recover the oxygen stoichiometry.¹⁷ It is worth considering that the tendency to neutralize the positive charges brought by oxygen vacancies during film growth could be the driving force for local cation

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nonstoichiometry which is difficult to recover by annealing. Fister *et al.* observed that the strontium surface segregation in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin films became increasingly pronounced as oxygen partial pressure was decreased, implying that the concentration of oxygen vacancies had a divert influence on the cation nonstoichiometry.¹⁸ In this study, detailed investigation was carried out to clarify the effects of oxygen vacancies on local cation stoichiometry, variation of Mn valence and electrical and magnetic properties of the epitaxial films.

4.2 Experimental

$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) films were grown epitaxially on SrTiO_3 (001) (STO) substrate by using pulsed laser deposition (PLD) with an energy density of 1.5 J cm^{-2} and repetition of 1 Hz. The target material was made by using the conventional solid state route using stoichiometric amounts of La_2O_3 , Mn_2O_3 and SrCO_3 as initial reagents. They were weighed in appropriate proportions and homogenized with isopropyl alcohol in an agate mortar for 1 h. The mixture was dried and then granulated using 4 % polyvinyl alcohol solution as binder agent. Pellets of 20 mm diameter and 5 mm thickness were shaped by uniaxial pressing at 150 MPa. Calcination was carried out in air at 1100 °C with 3 h dwelling. The samples were cooled to room temperature, then ground, pressed into pellets again and sintered in air at 1400 °C for 4h. Powder X-ray diffraction analysis showed that the ceramic target was single phase without any impurity peaks. For the samples to be annealed, the oxygen partial pressure was set to 1 Pa, in order to induce large amount of oxygen vacancies during the film growth. They were grown at 780°C and then post-annealed in a tube furnace at 900°C for 5 h in oxygen flux twice.

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Transport property measurements as a function of temperature were conducted after each annealing. As there were no differences in resistivity and metal to insulator transition temperature, the elimination of oxygen vacancies can be confirmed, which was demonstrated in the next section. The details of both *in situ* reflected high energy electron diffraction (RHEED) and *ex situ* high resolution X-ray diffraction (HRXRD) analysis of the as-grown sample have been described.¹⁹ In order to verify the effect of oxygen vacancies, a reference LSMO film with the same composition was grown at a much higher oxygen pressure (26 Pa), while the other growth parameters were kept the same. TEM specimens were prepared by grinding, dimpling, and ion milling in a Gatan Precision ion polishing system. The specimens were briefly cleaned in oxygen plasma, and transferred directly into the microscope for observation. High resolution transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL-2100F microscope, operated with an electron acceleration voltage of 200 kV. An FEI Titan field emission TEM, also operated at 200 kV, with an attached EDAX EDX detector and a Gatan Tridiem ER EELS detector was employed for EDX and EELS line scans with probe size of 0.5 nm and 2.6 nm steps, in scanning TEM (STEM) mode.

The surface Mn 3s electron band analysis was carried out by using X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB 220i-XL spectrometer with an Al $K\alpha$ monochromatic X-ray source (1486.6 eV). The XPS characterization of Sr 3d was performed at beam line SINS, located in the Singapore Synchrotron Light Source. The incoming X-ray energy was 220.79 eV and the energy resolution

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0.2 eV. The Sr 3d spectra with both normal incidence and grazing X-ray incidence were compared to measure the surface Sr content. A Quantum Design physical properties measurement system (PPMS) was used to characterize the magnetic and transport properties. M-H curve was measured at 5 K with the magnetic field applied in-plane, while the magnetoresistance was measured at their metal-to-insulator transition temperatures, 140 K and 290 K for annealed and reference samples, respectively.

4.3 Results and Discussion

4.3.1 Microstructure Analysis

The two-dimensional layer-by-layer growth mode was monitored by intensity oscillations of the reflected high energy electron diffraction (RHEED) during pulsed laser deposition of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) film, as described elsewhere.¹⁹ High-resolution X-ray diffraction (HRXRD) reciprocal space mapping (RSM) directly measures the in-plane and out-of-plane lattice parameters, strain, as well as the mosaicity of the grown film. The reciprocal space mapping around the (103) plane of the as-grown film indicates its fully strained state. Additionally, an exceptionally narrow full-width at half maximum of 0.02° was observed by measuring the thin film rocking curve, showing that the film is of high quality and low mosaicity. Based on the HRXRD measurements, the in-plane and out-of-plane spacing of the thin film were estimated to be $a=0.3905$ nm and $c=0.393$ nm, respectively.¹⁹

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Here, we present transmission electron microscopy (TEM) studies of the annealed thin film, demonstrating monocrystallinity with high epitaxial quality and excluding the presence of grains/domains that can contribute to degradation in electrical and magnetic properties. Figure 4.1(a) shows a low magnification cross-sectional TEM image of the LSMO/STO couple. The micrograph was imaged with the specimen tilted to the [100] zone axis of STO. According to the TEM images, there is no evidence for the formation of lamellae structures or domains, such as those reported by Lebedev *et al.*²⁰ and Zhang *et al.*²¹. This point is further confirmed by the SAED pattern in Figure 4.1(b), taken from the LSMO layer. The diffraction spots of LSMO are sharp spots rather than curved ones, implying that the pseudocubic structures are not domain-oriented. High resolution TEM in Figure 4.1(c) reveals that the interface between the LSMO and the STO substrate is atomically sharp, and nearly free of misfit dislocations, in agreement with RSM. Figure 4.1(d) shows that the high epitaxial quality is maintained throughout the film until the surface; no grain boundaries were found.

Figure 4.1 Morphology of the annealed LSMO thin film. (a) An overview at low magnification. (b) Selected-area electron diffraction pattern of the LSMO film at the [100] zone axis. (c) HRTEM image of the interface of LSMO with the SrTiO_3 substrate. (d) HRTEM image of the LSMO surface.

The high angular dark field (HAADF) STEM images of the reference sample are shown in Figure 4.2(a-c). The contrast in the HAADF-STEM images is

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proportional to approximately $Z^{1.7}$ (with Z as the atomic number). As the LSMO film has larger average atomic number than

Figure 4.2 HAADF-STEM and conventional TEM images of the LSMO reference sample. (a) Overview of the LSMO film by HAADF-STEM imaging. (b) and (c) HAADF-STEM images of surface and interface area, respectively. (d) Conventional high resolution TEM of the film-substrate interface.

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the single crystal STO substrate, the thin film shows brighter contrast than the substrate. Figure 4.2(d) is the conventional high resolution TEM image of the interface between the film and the substrate. From the images, the high epitaxial quality of the LSMO film is demonstrated.

4.3.2 EELS Analysis of the Local Mn Valence and Chemical Composition

According to the phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, its electrical and magnetic properties are strongly dependent on the Mn nominal valence, which is strongly correlated with the stoichiometry of each element.¹ Therefore, to study the effect of oxygen vacancies during the film growth on local cation stoichiometry, EELS line scans were used to characterize not only the cation content profiles but also the local Mn valence along thickness of the two LSMO films. For the reference sample grown at high oxygen pressure (26 Pa), there is no change in its electrical and magnetic properties before and after the thermal annealing, thus we can conclude that it has no oxygen vacancies. This sample shows properties similar to those of bulk single crystal.²² For the LSMO film grown at low oxygen pressure (1 Pa), the as-grown sample and the one annealed in oxygen atmosphere show completely different physical properties, suggesting the presence of oxygen vacancies in the as-grown film (more details in Section 4.3.4). To directly relate Mn valence to the cation stoichiometry, the oxygen nonstoichiometry in the second sample was firstly removed by high temperature oxygen annealing. After this initial annealing step, further annealing had no effect on transport and magnetic properties of the film, which indicates that the oxygen content has quickly reached saturation.

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The TEM specimens of the reference and annealed samples had relatively uniform cross-sectional thickness of about 40 nm in the studied area, as calculated with low-loss EELS.

The Mn $L_{2,3}$ edge represents the electron transition from Mn $2p_{1/2}$ and $2p_{3/2}$ to unfilled 3d states. A well-established measurement to study the Mn valence is the L_3/L_2 peak ratio in the EELS spectrum. This ratio has been shown to decrease monotonically when the oxidation state changes from +2 to +7.^{23,24} Chemical shifts also occur upon varying the Mn oxidation state. However, given the experimental difficulty of accurately calibrating the energy scale, we will not use the Mn $L_{2,3}$ peak shift to study its oxidation state. Figures 4.3 displays the Mn $L_{2,3}$ edges of the annealed and the reference samples after power-law background subtraction, recorded along the film growth direction. By normalizing the L_2 peaks in Figure 4.3(b) and 4.3(d), a direct visual comparison can be made of the L_3/L_2 ratio at different locations. It is clear that the L_3 peak intensity remains constant from the interface to the middle of the annealed film and then gradually increases towards the surface, as shown in Figure 4.3(c). However, the variation of the Mn L_3 peak intensity in the reference sample is negligible, as indicated by the two parallel red lines in Figure 4.3(d). To quantitatively analyze the Mn valence, the Hartree-Slater cross section function (which is available in Gatan's Digital Micrograph software) is used as a step function to remove the continuum contribution. A 10 eV wide energy window after the L_2 edge is used for scaling purposes. Then, the remaining signals under the L_2 and L_3 lines are integrated within two 11 eV wide windows. Finally, the resulting integrated intensity values are used to calculate the $L_{2,3}$ (L_3/L_2)

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area ratio for a quantitative analysis of the Mn valence. The reference data we used are from Varela *et al.* who use the same analysis method.²⁴ Our calculated $L_{2,3}$ values and the corresponding Mn valence of the annealed and reference samples are plotted in Figure 4.4(a) and 4.4(b) as a function of distance from interface. The Mn valence in the annealed sample remains about 3.6 from the film-substrate interface to the middle of the film and then decreases to 3.2 closer to the surface, while the reference sample has a uniform Mn valence of 3.2 from interface

Figure 4.3 EELS spectrum line scan of the Mn $L_{2,3}$ edges. (a and c) EELS images of the Mn $L_{2,3}$ edges in annealed sample and reference sample. (b and d) Side view of Mn $L_{2,3}$ edges with L_2 peak intensity normalized in annealed sample and reference sample. The red line shows the variation of L_3/L_2 peak intensity ratio.

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Figure 4.4 Variation of Mn nominal valence in LSMO films. (a and b) The exacted $L_{2,3}$ ratio (black) and corresponding Mn valence (red) vs. the distance from the interface in annealed sample and the reference sample, respectively. (c) XPS peak of the Mn 3s band in annealed sample. The energy separation between two peaks indicates ΔE_{3s} .

to surface. To calibrate the EELS Mn nominal valence V_{Mn} at the surface, we used XPS, measuring the Mn 3s splitting energy ΔE_{3s} of the top 5 nm surface of the annealed LSMO film using the equation^{25,26}

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$$V_{Mn} = 9.67 - \frac{1.27\Delta E_{3s}}{eV} \quad (4.1)$$

The XPS result in Figure 4.4(c) shows that ΔE_{3s} is 5.1 eV, giving a V_{Mn} of 3.2, which is consistent with the EELS results.

Another method to study the Mn oxidation states is to analyze the fine structure of the EELS oxygen K-edge. In the dipole approximation, the oxygen K-edge fine structure contains information on excitations from O 1s electrons to 2p bands. Three main features are found in the EELS fine structure: a pre-peak at about 530 eV, the first main peak about 535 eV which arises from the oxygen hybridization with La 5d and Sr 3d bands, and the second main peak at about 540 eV, contributed by Mn 4sp bands.²⁷ The pre-peak has a strong contribution from the Mn 3d bands and is sensitive to Mn 3d e_g state occupancies, since the Mn 3d t_{2g} state is fully occupied. Hence, information about Mn 3d band occupancy (i.e., Mn valence) will be extracted by pre-peak analysis. As was demonstrated by Varela *et al.*, the energy separation between pre-peak and adjacent main peak, ΔE , linearly increases with the Mn valence.²⁴ This effect is attributed to the difference in chemical potential between the initial core and final states of the ejected electrons.²⁸ The oxygen K edge EELS images in Figures 4.5(a) show that ΔE stays constant from the interface to the middle part of the annealed film and then decreases linearly until the surface, showing the same trend for the Mn valence as we observed earlier with the Mn $L_{2,3}$ -edge. The variation of ΔE in the reference sample is negligible. The extracted ΔE values are shown in Figure 4.5(b), the

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reference sample and the surface region of the annealed sample have similar ΔE values of about 5.3 eV. Thus, they have almost same Mn valence. Since oxygen ions bond with La, Sr and Mn, the overall oxygen bonding is quite complicated in LSMO, so the change of oxygen K-edge fine structure is presented here merely to verify the concurrent Mn valence change.

Figure 4.5 Variations in the oxygen bonding in the annealed and reference samples. (a) EELS spectrum line scan of the oxygen K-edge, the dotted lines indicate the intensity maxima. (b) The extracted energy separation between the pre-peak and the first main peak.

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It should be noted that TEM sample preparation processes, especially the conventional Ar-ion milling scheme can leave amorphous surface layer due to high energy ion bombardment, which leads to degradation of the electron channeling along atom columns and a reduced image contrast in atomic resolution Z-contrast TEM. As the EELS of elements are sensitive to their chemical coordination, the crystalline to amorphous transformation, accompanied by modified composition during ion milling process can alter their chemical states, hence EELS. To avoid this situation, low energy ion milling in the miller with liquid nitrogen cooling stage, which was used in this work, could effectively reduce the artifacts induced from preparation processes. In addition, Mn ions with higher oxidation states are supposed to be more sensitive to electron beam degradation. Riedl *et al.* recorded EELS of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films with increasing electron dose.²⁹ They found that, as the dose was beyond the threshold for damage, the EELS O K pre-peak nearly disappeared and the intensity of the third peak was only 10% greater than the minimum following the second peak. Correspondingly, the ratio of the maximum intensity of Mn L_2 peak to L_3 peak falls from 0.6 to 0.4. Compared with the results of Riedl *et al.*, the oxygen pre-peaks in our spectra presented in Figure 4.5 (a) are stronger and the intensity of the third peak is about 60% greater than the minimum following second peak for the whole LSMO layer. Accordingly, the ratio of maximum of Mn L_2 to L_3 peaks is about 0.6. As such, we observed no evidence for electron beam induced damage. Additionally, the high-angle annular dark-field (HAADF) scanning TEM (STEM) image taken after the EELS line scans showed

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no sample damage. Therefore, we rule out electron beam damage as cause for the observed EELS fine structure modulations in our experiment.

To investigate the local cation stoichiometry, we analyzed the EELS signal of La $M_{4,5}$, Sr $M_{4,5}$, Mn $L_{2,3}$, and O K-edges and used the normalized EELS intensity to extract the elemental profiles across the LSMO films, shown in Figure 4.6. By normalizing the intensities, we obtain relative profiles for each element. As the sample was fully oxygen annealed at high temperature for 5 hours, the oxygen nonstoichiometry was removed. The experimental evidences are shown in Figure 4.6(e) and (f), which will be explained later. Figure 4.6(a) shows that the annealed sample has excess La near the film-substrate interface, after which its content reduces towards the surface. From the relative content of La and Sr shown in Figure 4.6(b), there can be no segregation between A-site cations near the interface, but the Sr content decreases somewhat near the surface. Combined with the experimental results in next section, this observation can be attributed to the migration of Sr cations towards the surface during the film growth, with a tendency to form SrO monolayer. Figure 4.6(c) and 4.6(d) show that Mn is deficient compared with La and O near the interface, and then its content increases towards the surface in the annealed sample. However, as demonstrated in Figure 4.6, the cation gradient mentioned above is absent in the reference sample, as its relative profiles of each element are all close to zero.

In analytical TEM, we need to be careful with the quantitative interpretation of the EELS signal. As was shown earlier, the limited collection angle of EELS can lead to quantification artifacts when the thickness or density of the specimen

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locally varies.³⁰ To give a complete picture of our specimen, energy-dispersive X-ray spectroscopy (EDX), a technique that is much less likely to have such artifacts is employed to provide an additional information of the elemental distribution. The detailed EDX results are given in Figure 4.6(e) and (f). The slightly wedge-shaped cross-section of the TEM specimen is reflected in the decreasing trend of the HAADF signal, and the trend is followed by the oxygen profile. This demonstrates the uniform distribution of oxygen throughout the two samples. It can also be seen that the manganese concentration is slightly below this value near the interface in the annealed sample, while this decreased Mn signal is not observed in the reference sample. Therefore, the deficiency of Mn content near the film/substrate interface in the annealed sample is demonstrated. The results are consistent with the EELS results, supporting the conclusions drawn from Figures 4.6(a-d). It can therefore be concluded that near the interface, the A-site cations (La and Sr) are in excess, while the Mn cations are deficient in the annealed sample. Thus, portional A-site cations have moved to the B-sites during the film growth to substitute Mn cations.^{16,31} As the film becomes thicker,

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Figure 4.6 Distribution of the chemical elements in the annealed and reference LSMO films. (a) Intensity difference from normalized EELS line scans between the elements La and O, (b) between Sr and La, (c) between Mn and O, (d) between Mn and La. (e) and (f) normalized Mn and O profiles measured with STEM-EDX, compared to the simultaneously acquired HAADF signal.

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the A-site/B-site cation ratio recovers to nearly nominal value. As the oxygen content is uniform throughout the film, the cation stoichiometry is suggested to dominate the observed gradient of Mn valence. With excess of A-site cations and deficiency of Mn cation near the manganite/substrate interface, the Mn valence should be higher to maintain the charge neutrality, which was confirmed in Figure 4.4. As a comparison, the mentioned cation nonstoichiometry is not observed in the reference sample grown at high oxygen pressure, thus we can conclude the oxygen vacancies during the film growth played a dominant role in modifying the cation stoichiometry.

4.3.3 Strontium Surface Segregation

The second type of cation nonstoichiometry that occurred during the film growth is the off-stoichiometric ratio between La and Sr near the film surface. This deviation of the surface chemical composition might severely affect the interface properties of manganite-based tunnel junction devices. As observed by other groups, Sr surface segregation is the most likely surface cation nonstoichiometry.^{18,32} Utilizing the surface-sensitive angle-dependent X-ray photoelectron spectroscopy (XPS) and element-sensitive Z-contrast STEM imaging with atomic resolution, we here investigate the relationship between Sr surface segregation and oxygen vacancies. Figures 4.7(a) and (b) show the XPS Sr 3d peaks of the annealed sample with normal and grazing emission of photoelectrons respectively, with the latter being more sensitive to surface composition due to the finite escape depth of photoelectrons. After the deconvolution of Sr 3d peaks, two peak doublets are found in the spectrum of the annealed sample. Based on

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Figure 4.7 Surface analysis of the annealed LSMO film. (a) Angle-dependent XPS of the annealed sample, collected with normal emission of photoelectrons, showing the Sr 3d band. (b) Angle-dependent XPS, collected with grazing emission of photoelectrons. As grazing emission of photoelectrons are more sensitive to the surface content, we can see the surface of LSMO is covered with SrO in rock-salt phase. (c) HAADF-STEM image (Z-contrast image) from the surface region of LSMO. (d) Integrated intensity profile of the HAADF-STEM image near the surface, integrated from a 10 nm wide area of the top 3 nm.

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literature,³² we assign the peaks with higher binding energy (around 135 eV) to Sr 3d in SrO rock-salt phase, and the lower binding energy (133.5 eV) to Sr 3d in perovskite. The XPS results show that the annealed sample has both surface segregated SrO phase and perovskite underneath. The increased signal for the SrO rock-salt structure in the grazing emission spectrum suggests that SrO is located at the topmost 1 nm, as the X-ray detection depth here is less than 1 nm for the used photon energy of 220.8 eV. The Z-contrast STEM image in Figure 4.7(c) shows that the topmost monolayer, indicated by the arrow, has lower intensity in comparison with the more uniform intensity of the layers below. The integrated Z-contrast intensity profile in Figure 4.7(d) shows this effect in more detail. As the contrast in the HAADF-STEM image is proportional to approximately $Z^{1.7}$ (with Z as the atomic number) and La has larger atomic number than Sr, it can be concluded that the outermost atomic layer has more Sr cations. Combined with the EELS elements profiles from Figure 4.6(b), it is concluded that Sr atoms diffuse to the top surface to neutralize the surface charge,³³ resulting in slightly decreased Sr content in the perovskite underneath, and a monolayer of SrO at the surface.

However, the thermal annealing effect might also induce Sr diffusion towards the surface, and needs to be considered as well. To verify this, the surface of the as grown LSMO film deposited under low oxygen pressure was also characterized by angle-dependent XPS. Figure 4.8(a) and (b) show the XPS Sr 3d band of the as-grown LSMO film which was grown under low oxygen pressure. Similar to the annealed sample, two peak doublets are observed, demonstrating that the SrO rock-salt phase is not developed by post-deposition annealing. Figure 4.8(c)

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and (d) present the XPS Sr 3d band of the reference sample. There is only one doublet, assigned to pure perovskite phase.³² It should be noted that the LSMO

Figure 4.8 Surfaces of LSMO film grown under low oxygen pressure before annealing and the reference sample grown under high oxygen partial pressure. (a) Angle-dependent XPS of the Sr 3d bands, with grazing emission, and (b) with normal emission of photoelectrons from the as grown sample which was grown under low oxygen pressure. (c) With grazing emission and (d) normal emission of photoelectrons from the reference sample grown under high oxygen pressure.

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samples were exposed to ambient conditions during the samples transfer from PLD chamber to XPS chamber in Singapore Synchrotron Light Source. Normally, contacting with oxidizing and reactive species in air can hinder the intrinsic characters of the sample surfaces. In addition, surface contaminations, such as carbon contaminations could also be induced. However, as mentioned earlier, the cation mobility is strongly limited by the high activation barrier in the close-packed perovskite structure; thus, although the angle dependent XPS experiments in this thesis were performed “ex-situ”, exposing sample to ambient conditions cannot supply enough thermal energy for cation diffusion, hence modify the intrinsic surface cation stoichiometry theoretically. Furthermore, from the clear difference in the XPS of all three samples, it is therefore concluded that the oxygen vacancies during the film growth dominate the observed Sr surface segregation.

4.3.4 Magnetic and Transport Properties

Electrical and ferromagnetic properties of LSMO are dominated by the double-exchange mechanism,³⁴ where the Mn e_g electrons hop between Mn^{3+} and Mn^{4+} cations when their spins are parallel. Therefore, the Mn nominal valence which represents the Mn^{3+}/Mn^{4+} ratio, which plays a crucial role in determining these properties. Figure 4.9(a) shows magnetic hysteresis loops of the annealed sample and of the reference sample, measured at 5 K. Coercivity of the annealed sample is 526 Oe, while that of the reference sample is only 98 Oe. Saturation

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magnetization of the annealed sample is 50% lower than that of reference sample which exhibits bulk values around 550 emu cm^{-3} .²² This shows that the Mn valence and composition of the manganite films grown under high oxygen pressure give

Figure 4.9 Magnetic properties of the LSMO films. (a) Magnetic hysteresis loop at 5 K. The inserted graph is a magnification of the magnetic hysteresis loop from the annealed sample, showing the multistep magnetization reversal processes. (b) $M-T$ curves. (c) $R-T$ curve. (d) Magnetoresistance plot, with applied magnetic field along the (001) plane.

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nearly nominal values, while the annealed sample maybe severely off chemical stoichiometry. Interestingly, pronounced multistep magnetization reversal processes are observed in the magnetic hysteresis loop of the annealed sample, while the reference sample displays a square-like loop. This difference may result from the inhomogeneity of the magnetic phases in the annealed sample. According to the magnetic phase diagram, LSMO is expected to be nonferromagnetic when the Mn valence is at least +3.6 (60% Mn^{4+} , 40% Mn^{3+}), and ferromagnetic when the Mn valence is below +3.5.³⁵ Therefore, it is reasonable to assume that the annealed LSMO layer near the interface is nonferromagnetic while it becomes ferromagnetic closer to the free surface. This assumption is supported by Infante *et al.*³⁶, who observed the nonferromagnetic phase at the La-enriched interface and Sr-enriched surface of (La,Ca) MnO_3 films. The existence of a nonferromagnetic phase explains the suppression of magnetization in the annealed sample, while the enhanced coercivity could then be attributed to the pinning of magnetic domains by the nonferromagnetic phase near the interface. Figures 4.9(b-d) show that Curie temperature (T_C) of the annealed sample is about 130 K and the magnetoresistance is 400% at 7 Tesla, while respective values of 290 K and 180% are found for the reference sample. Additionally, there is a magnetic transition at about 25 K in the

Figure 4.10 The resistivity vs. temperature curves of LSMO grown at oxygen pressure of 1 Pa and annealed for 5 h at 900 °C twice.

magnetization vs. temperature (M - T) curve of the annealed sample, suggesting the existence of a supplementary magnetic phase at low temperature. The differences in the resistivity vs. temperature (R - T) curves between the as-grown (with oxygen pressure of 1 Pa) and the post-annealed samples are quite dramatic, due to the existence of oxygen vacancies during film growth. Further oxygen annealing has no effect on the magnetic and electrical properties, which shows that the oxygen content achieves a chemical equilibrium state. This observation confirms the EDX results in Figure 4.6(e) and (f). As the Curie temperature of the annealed sample remains suppressed, nonstoichiometry of the cations in the film is suggested. Note

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that post annealing in oxygen for 5 h at 900 °C twice had no effect on the transport properties, which suggests that oxygen vacancies do not dominate the observed magnetic and transport properties.

4.3.5 Discussion

According to Muller *et al.* and Kourkoutis *et al.*,^{13,14} A-site cation excess can be induced by high laser fluence during PLD growth. However, they did not observe significant changes in the Mn or Ti valence states in very thin stacks of epitaxial layers. Estradé *et al.*, on the other hand, demonstrated that the Ca/La ratio and Mn valence gradually decreased from $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3/\text{STO}$ interface to free surface, which was solely dominated by stress accommodation.³⁷ In our epitaxial LSMO films, the variation of Mn valence with opposite trend across the film is evidently demonstrated, supporting our assumption that oxygen vacancies introduced during the film growth are another important cause of local cation nonstoichiometry.

The formation of oxygen vacancies during the film growth locally generated positive charges. Together with the strain tensor towards the oxygen vacancy, the oxygen octahedral can be elongated and rotated.³⁸ As a result, the available space increased for B-site cations nearest to the oxygen vacancies, which would allow accommodation of larger cations such as La and Sr of B-sites.

At the initial growth period, the substitution of Mn cations (with oxidation states of +3 or +4) by La and Sr cations (with oxidation states of +3 and +2, respectively) at B-sites could generate negative charge to neutralize the positive

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charge induced by oxygen vacancies. Meanwhile, the accommodation of large La and Sr cations at B-sites could increase the lattice constant and relieve some of the tensile strain induced by the SrTiO_3 substrate. As the growing film got thicker and thicker, the epitaxial tensile strain was abated and became insufficient to accommodate the large A-site cations at B-sites. Thus, the proportion of Mn substitution by La/Sr cations decreased. The Sr migration towards the film surface became the dominant mechanism of cation nonstoichiometry instead. The positive charge induced by oxygen vacancies near the growing surface may favor Sr segregation for electroneutrality.³³ Because there is a depletion of Mn content near the interface region, the refilling of oxygen vacancies after annealing can in fact increase the amount of negative charge and then result in larger variation of the Mn valence (to maintain local charge neutrality). As one intriguing consequence, high Mn nominal valence (+3.6) exists in the strained film near the substrate, and remains constant within a thickness of about 45 nm, beyond which it decays monotonically to 3.2 until the free surface. Therefore, it is concluded that the oxygen vacancies induced the cation nonstoichiometry, resulting in a nonmagnetic and insulating layer near the interface, which hindered the device application of such films.

Furthermore, as the magnetic properties are related to the Mn nominal valence,^{34,39} the observed variation of Mn valence in the annealed sample is expected to enhance magnetic phase separation. Earlier results showed that Mn^{4+} is in excess near the interface in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ films due to the interface reconstruction, leading to insulating and nonmagnetic phases within a thickness of

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less than 5 nm.^{40,41} However, our work showed a nonmagnetic region with excess Mn^{4+} (with Mn nominal valence of 3.6) with a thickness of about 45 nm, which is 50% of the whole sample volume. The comparison confirms that there is more than one source for the observed excess Mn^{4+} near the interface. As an extrinsic mechanism, oxygen vacancies during the film growth can also induce cation nonstoichiometry, generate interfacial dead layers, and cover the intrinsic effect from interface reconstruction. Only by carefully selecting an appropriate oxygen pressure to maintain a minimized content of the oxygen vacancies, would the interfacial dead layer be minimized.

Finally, the presence of a second cation nonstoichiometry responsible for the SrO rock-salt surface monolayer might in fact provide a new prospect for the fabrication of high performance tunnel devices. As an insulating material, SrO can serve as an extra tunnel barrier when LSMO is integrated into tunnel junctions. Meanwhile, the cation ratio in the underlying perovskite phase is also off-stoichiometric. These would account for the reduction of the Curie temperature and spin transport properties near the LSMO-barrier interface. Therefore, this observed surface cation off-stoichiometry might explain a previous observation that the transport and magnetic properties of a LSMO/STO multilayer could be improved by adding a LaMnO_3 layer between LSMO and STO.⁴² Our present work suggests that the LaMnO_3 layer in that work played the role of compensating the cation off-stoichiometry that was induced by strontium segregation.

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4.4 Concluding Remarks

In summary, the two types of cation nonstoichiometry were attributed to the formation oxygen vacancies during LSMO film growth. At the initial growth stages, near the SrTiO_3 substrate, the A-site cations (La/Sr) partially substituted Mn cations. At a later stage after most lattice strain was relieved, Sr migrated towards the film surface to form a SrO rock-salt monolayer. The resultant long-range inhomogeneity in the Mn valence in the annealed $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films along the film growth direction was demonstrated by using EELS. It was found that high Mn nominal valence (+3.6) existed in the strained film near its substrate, and remained constant within a thickness of about 45 nm, beyond which it decayed monotonically until the free surface. The suppressed magnetization and increased magnetoresistance in this epitaxial film was attributed to the nonferromagnetic phase near the SrTiO_3 - $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ interface due to this cation nonstoichiometry. The magnetic hysteresis loop of the annealed sample possessed multistep magnetization reversal processes, indicating an inhomogeneity of the magnetic phase. These results demonstrated the importance of oxygen vacancies *during the film growth* as a source of cation nonstoichiometry near the interface and surface of epitaxial thin films. With regard to tunneling devices, the two types of cation off-stoichiometry induced by oxygen vacancies in the LSMO during growth can generate an extra insulating and nonmagnetic layer near LSMO-barrier interfaces, leading to the reduction of the Curie temperature and conductivity.

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Chapter 5 Multiferroicity in Manganite/Titanate Superlattices Determined by Oxygen Pressure- Mediated Cation Defects

5.1 Introduction

Multiferroic materials with integrated electric and magnetic degrees of freedom serve as one of the most promising candidates for spintronics applications, such as high density storage devices.¹ Naturally occurring materials with a single multiferroic phase have limited application as their magnetoelectric couplings are often weak.² Therefore, artificial heterostructures consisting of ferroelectric and ferromagnetic materials have been engineered.¹ Interface engineering can be applied based on strain mediation,³ magnetic exchange bias⁴ and charge-based couplings mechanisms.⁵ In the charge-based heterostructures, the valence states of the interfacial transitional metal can be manipulated by applied electric field, resulting in tuned charge density and spin properties.^{6,7} Compared to conventional bilayer multiferroic composites, a multilayer/superlattice structure has a much higher interfacial area to volume ratio, thus the magnetoelectric coupling effect can be greatly enhanced.^{8,9} This approach has attracted intensive research recently because oxide interfaces can now be defined with atomic-scale precision due to the recent advances in growth technology.^{10,11}

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However, as the materials are shrunk to ultrathin layers in superlattices, their bulk ferroic properties are difficult to be maintained because of the size effects.^{12,13} This problem strongly limits the magnetoelectric coupling at nanoscale, hindering the application of multiferroic superlattices. The thickness-dependent ferroelectricity is controlled by the strength of interfacial bonding between ferroelectric and adjacent electrode and by the intrinsic dipole moment at the interfaces.¹⁴ For ferromagnetic ordering, saturation magnetization and ferromagnetic to paramagnetic transition temperatures are reduced by charge transfer, or by spin canting states, induced by interface reconstruction.^{15,16} Besides these intrinsic mechanisms, the physical properties are also very sensitive to extrinsic effects, such as cation nonstoichiometry—which cannot be removed by post-deposition annealing. The formation of extrinsic defects, implies local fluctuations in chemical composition. Kourkoutis *et al.* revealed that the metallic ferromagnetism at room temperature can be stabilized in a five-unit-cell-thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ layer in the pulsed laser deposited (PLD) LSMO/ SrTiO_3 superlattices when the cation defects are eliminated by optimizing the laser fluence on a ceramic target.¹⁷ Therefore, understanding how the growth conditions mediate the cation defects and the impact on the corresponding physical properties is crucial for the performance of interface engineered superlattices at the nanoscale.

Due to the chemical stability and near-lattice match with each other, ferroelectric BaTiO_3 (BTO) and ferromagnetic $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) can be engineered together to form multiferroic superlattices.¹⁸ To utilize the conventional reflected high energy electron diffraction (RHEED) for in-situ thickness

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monitoring during superlattice growth, low oxygen pressure is required to prevent significant scattering of electron beam by gas molecular in the chamber. It has also been demonstrated that BaTiO₃ (BTO) films grown at high oxygen pressure exhibit a more coarsened morphology, resulting in lattice strain relaxation and dislocations in the films.^{19,20} Thus, a relatively low oxygen pressure is preferred during the film growth. However, as oxygen vacancies may introduce cation nonstoichiometry and structural defects,²¹ which could possibly severely affect the ferroelectricity, an insight into the effect of oxygen pressure will be critical in deposition of films with good multiferroic properties. It is also crucial for the realization of magnetoelectric coupling in superlattices structures. To explore the effect of oxygen pressure, two samples were grown with different oxygen pressures, without changing other growth conditions. Oxygen nonstoichiometry was removed by annealing before the structural and properties characterizations. Microstructure analysis, including the defects types and their interactions in the two samples, was carried out by using electron microscopy at atomic resolution. Moreover, the role of these defects on the multiferroic properties, which were characterized by scanning probe microscopy and temperature-dependent ferromagnetism measurements, were investigated. The subsequent discussion will treat the underlying physical mechanisms for the defects types that are mediated by oxygen pressures, and the impact on the multiferroic properties.

5.2 Experimental

16 unit cells of La_{0.8}Sr_{0.2}MnO₃ (LSMO) and 12 unit cells of BaTiO₃ (BTO) layers were alternatively grown on TiO₂-terminated (001) SrTiO₃ (STO) substrates

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by using PLD. A KrF excimer laser (COMPex 205 Fluorine from Lambda Physik) with a wavelength of 248 nm was employed with an energy density of 1.9 J/cm^2 and repetition of 1 Hz. The target materials were made by using the conventional solid state route using stoichiometric amounts of La_2O_3 , Mn_2O_3 and SrCO_3 for LSMO, and BaO and TiO_2 for BTO respectively. Powder X-ray diffraction analysis showed that the targets were single phase without any impurity peaks. Growth temperatures of LSMO and BTO were 780°C and 680°C respectively. For Sample A, the oxygen partial pressure was 1 Pa, the two layers were alternately deposited for 16 periods. The growth was *in situ* monitored by reflected high energy electron diffraction (RHEED).²² To study the impact of cation stoichiometry and the cation defects, annealing at 780°C for 3 h in oxygen flux was carried out twice after the deposition to exclude the effect from oxygen nonstoichiometry. Magnetic properties measurements as a function of temperature were conducted after each annealing. As there were no differences in the magnetization vs. temperature curves, the elimination of oxygen nonstoichiometry was confirmed. A reference sample, Sample B, was deposited at oxygen pressure of 16 Pa, while the other growth parameters were kept the same. After high temperature oxygen annealing, there is no change in its electrical and magnetic properties, thus we can conclude most of the oxygen vacancies are eliminated during growth. The samples for TEM were prepared by grinding, dimpling and ion milling in a Gatan Precision ion polishing system (PIPS). The specimens were cleaned by oxygen plasma and then transferred to the microscope for characterization. To identify the types of cation defects, both cross sectional TEM samples with zone axes of $[010]$ and $[110]$ were prepared.

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High resolution TEM characterization was performed by using JEOL 2100F microscope with a point resolution of 0.19 nm operating at 200 kV. A Philips CM300 TEM with Gatan 2000 electron energy loss spectroscopy (EELS) detector was employed for the energy filtered TEM studies. The corresponding chemical maps are acquired by selecting the EELS of Mn L_{2,3}-edge at ~640 eV and Ti L_{2,3}-edge at ~456 eV using a slit width of 5 eV. X-ray photoelectron spectroscopy (XPS) analysis of the samples was carried out by using a VG ESCALAB 220i-XL spectrometer with an Al K α monochromatic X-ray source (1486.6 eV). Its energy resolution is 0.2 eV. Piezoresponse analysis was conducted on a Cypher AFM from Asylum Research. Conductive Pt-Ir-coated silicon cantilevers were used for PFM imaging and polarization switching studies. The local piezoresponse amplitudes during polarization switching were measured in fixed location on the thin films surface as a function of a dc switching bias. The bias was applied to the bottom electrode (the LSMO layer which is under the surface BTO) and the tip was grounded. A Quantum Design physical properties measurement system (PPMS) was used to characterize the magnetic properties. The magnetization *vs.* magnetic field (M-H) curve was measured at 5 Kelvin with the magnetic field applied in-plane, and the magnetization *vs.* temperature (M-T) curve was measured by applying a magnetic field of 1000 Oe along the in-plane direction of the films.

5.3 Results and Discussion

5.3.1 Elemental Mapping by Energy Filtered TEM

In order to demonstrate that the grown film has a well-defined layered structure with coherent interfaces, energy filtered TEM (EF-TEM) analysis was

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performed to disclose the elemental distribution of the chemically modulated layers. Spatial resolution of the EF-TEM imaging was theoretically estimated to be better than 1 nm, by taking into account the spherical and chromatic aberrations in the image-forming lenses, as well as the delocalization of inelastic scattering of electrons. Spatial drift is also considered, as it will deteriorate the spatial resolution due to long exposure time.²³

Fig. 5.1 shows conventional TEM image and the Ti and Mn chemical maps of Sample A. The thickness of each layer is estimated by the full width at half the maximum (FWHM) of the element profile peaks. It can be clearly observed from the Mn and Ti distributions that the LSMO and BTO layers (3.2 nm each) were firstly successfully grown on the STO substrate, followed by periods of LSMO (6.2 nm) and BTO (4.9 nm) with stacking unit cell ratios of 4:3, as indicated in Fig. 5.1 (d). This result approximately agrees with the estimated values from the X-ray diffraction results.²² The superlattice shows sharp, flat and well-defined interfaces between the successive LSMO and BTO layers with low concentration variation and chemical inter-diffusion below our EF-TEM resolution of about 1 nm. The chemically sharp interfaces proved that the interfacial cation diffusion could be negligible due to thermal annealing. Normally, the annealing temperature of more than 1000 °C is needed to supply enough thermal energy to jump the activation barrier for cation diffusion as the cation mobility is very limited in close-packed perovskite structure.^{24,25} However, the ultrathin layers are not entirely flat, which may contribute to the mosaic structures.

Figure 5.1 (a) Conventional TEM image of Sample A; the substrate is located at the top right corner. (b) Mn map and (c) Ti map by EF-TEM. The bright areas indicate the location of the mapped chemical elements. (d) EF-TEM intensity profiles of Mn (blue) and Ti (red).

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5.3.2 Defects Study by High Resolution TEM

The nature of the lattice defects is studied here by atomic-resolution TEM on cross-sectional superlattice samples along the [010] and [110] zone axes. Fig. 5.2 (a) shows the interface between substrate and film taken along the [010] direction. It presents perfect cubic-on-cubic epitaxial growth, with no amorphous layer. Selected area electron diffraction (SAED) pattern is shown in Fig. 5.2 (b), which was obtained from the area covering the superlattice and partial substrate. Several weak satellite spots were clearly observed adjacent to the main diffraction spots, indicating the formation of a superlattice structure.²³ Fig. 5.2 (c) and (d) are representative TEM images of the Sample A grown at low oxygen pressure and the Sample B respectively. A strong dependence of structural quality on the oxygen pressure is clearly visible. There are some boundary-like contrast and blur areas in Fig. 5.2 (c), which is due to the strong lattice distortion or structural defects, while the contrast in Fig. 5.2 (d) is much more uniform. The microstructure of Sample A is further studied to identify the defects types and interactions between them.

Fig. 5.3 shows lattice image near the central part of the Sample A. Many parts of LSMO lattices are strongly distorted, as presented in Fig. 5.3 (a). The squared areas are magnified, and the gray scale is converted into a false color representation to enhance the visibility of defects configuration.²⁶ The Burgers circuits in this study were drawn clockwise which would be closed in a perfect crystal; the Burgers vectors were determined from the start point of the loop to the

Figure 5.2 (a) HRTEM of the interface between the superlattice and the STO substrate, viewed along the $[010]$ zone axis. (b) Selected area electron diffraction (SAED) pattern covering whole superlattice and partially the substrate area, with the (000) diffraction spot blocked. (c) and (d) Representative HRTEM images of Samples A and B (the reference) respectively. The central part is LSMO, the bottom and top layers are BTO. The arrows mark the defective area.

finish point.²⁷ A pure edge dislocations with Burgers vector of $a[100]$ are identified at the interface between LSMO and BTO with extra atom plane in LSMO side, and a partial defect $a/2[\bar{1}0\bar{1}]$ is found inside the LSMO layer, as shown in Fig. 5.3 (b) and (c), respectively. The formation of the $a[100]$ pure edge dislocations can effectively relax the lattice mismatch strain energy, and the defect density increases as the strain increases.²⁸ Besides the $a[100]$ misfit

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dislocations, another type of pure edge dislocation is determined as shown in Fig. 5.3 (d). The Burgers circuit surrounding the dislocation core shows the closure vector of $a[00\bar{1}]$ along the c-axis, resulting in a lattice bending of around two degrees. This is consistent with the mosaic spread value measured by X-ray diffraction.²² In the dislocation core area, the contrast is smeared out due to the strong lattice distortion. According to the model proposed by Suzuki *et al.* and Qin *et al.*, $a < 110 >$ dislocation loops glide on the $\{101\}$ planes and dissociate near

Figure 5.3 (a) Lattice image of Sample A. The central area is the LSMO layer and the dashed lines indicate the interface between LSMO and BTO. The squared area b and c in (a) correspond to panels (b) and (c), respectively. (d) Another area in the LSMO

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the interface to yield the $a[100]$ and $a[001]$ edge dislocations, where the latter are supposed to be eliminated by mutual annihilation.^{29,30} In this study, we proposed that the appearance of the edge dislocation with Burgers vector along c-axis was introduced by $a/2 \langle 111 \rangle$ dislocations resulting from the cation nonstoichiometry.

It should be noted that, according to the Matthews-Blakeslee mechanical model, the theoretical critical thickness of BTO for free misfit dislocation is 10 nm for a lattice misfit of 3%.³¹ Sun *et al.* found that the critical thickness of BTO grown on STO (001) substrate is about 4 nm.²⁸ Thus, it is not arbitrary to assume that, when BTO film is only 5 nm thick, there should be very few nucleation sites

Figure 5.4 (a) Lattice image of Sample A along the $[010]$ zone axis. (b) Applying (100) -Fourier filtering. The pure edge dislocations with Burgers vector of $a[100]$ near the interfaces are marked. The average spacing between them is about 12.4 nm.

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for $a[100]$ defects. However, we observed distribution of $a[100]$ pure edge defects near the LSMO/BTO interface in Sample A, with an average spacing of 12.4 nm as shown in Fig. 5.4 (a) and (b). Therefore, to explain the observed high density of $a[100]$ interfacial edge dislocations, a mechanism was presented in the discussion section.

Partial dislocations with Burgers vector of $a/2[\bar{1}0\bar{1}]$ as shown in Fig. 5.3 (c) are usually accompanied by another partial dislocation, with a two-dimensional planar defect sandwiched between them.²⁹ In this planar defect area, lattice distortion and composition fluctuation are then generated. As a consequence, the presence of these defects is expected to have a strong impact on the corresponding physical properties.

Two types of planar defects were observed in the superlattices, presented separately in this section.

The first type is *Ruddlesden-Popper fault*. Previously we demonstrated that A-site cation excess could be induced at LSMO interfaces when low oxygen pressures are used during the film growth.¹⁹ Such growth conditions were used here for the deposition of the ultrathin LSMO layers, cation stoichiometry is therefore expected to occur. Fig. 5.5 (a) shows a TEM image of Sample A along the $[010]$ zone axis. At the bottom LSMO layer, a partial dislocation with a Burgers vector of $a/2[101]$ is identified. Meanwhile, a boundary-like contrast is observed starting from the dislocation and climbing along the film growth direction. This area (marked by the black square) is enlarged in Fig. 5.5 (b) and color-coded to enhance

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the visibility of the contrast variation. The dashed white lines connecting the brighter dots near boundary indicate a shift in $c/2$ along the $[001]$ direction. The white lines mark the location of the boundary and show its zig-zag character, originating from the partial dislocation. By selecting appropriate multislice simulation parameters, the simulated TEM image in Fig. 5.5 (c) and the lattice image of the boundary in LSMO side are matched. The former shows that two adjacent columns (or rows) of brighter dots indicate an extra plane of A-site cations (La or Sr); the darker dots represent the Mn B-site cations in this case. The observed boundary with the extra plane of A-site cations in the TEM image is determined to be Ruddlesden-Popper (RP) fault, which has also been reported for Sr-riched SrTiO_3 thin films.³² The existence of the RP fault is consistent with our previous finding,²¹ suggesting that this is the structural accommodation of the observed cation nonstoichiometry. The crystallographic model of the RP fault is described in Fig. 5.5 (d). When the RP fault propagates to the surface of the LSMO layer, both $(\text{La,Sr})\text{O}$ and MnO_2 -terminated surfaces are created. The resulting lattice displacement vector along the c -axis, hence RP faults

Figure 5.5 (a) A high-resolution TEM image of Sample A; the Burgers circuit is shown to identify the $a/2[101]$ partial dislocation. The area covered by the black square is enlarged in (b). The white lines mark the structural boundaries. The core area of the partial dislocation $a/2[101]$ is located at the turning point of the RP fault. (c) The multislice –based calculated through-focal HRTEM image of the RP fault with focus of 74 nm and thickness of 7 nm. (d) The crystallographic model for the propagation of RP faults in the LSMO/BTO heterostructure.

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will continue in the subsequently grown BTO layer, generating possible Ba cation excess relative to Ti cations. Furthermore, the RP fault can dissociate into other types of partial dislocations which will then produce stacking faults between them.³³

The second type of planar defects is *stacking fault*. Fig. 5.6 (a) and (b) show a TEM image taken along the [010] zone axis, and the corresponding inverse Fourier transform image using the selected reflections (101), ($\bar{1}01$), (10 $\bar{1}$) and ($\bar{1}0\bar{1}$). The partial dislocations with a Burgers vector of $a/2[\bar{1}01]$ and $a/2[10\bar{1}]$ are identified according to the glide of {101} planes. It is clearly observed that the partial dislocations originate from the interface area in the LSMO, and then propagates into the BTO layer, resulting in a stacking fault which passes through the interface. The two parallel $a/2[\bar{1}0\bar{1}]$ partial dislocations are the dissociation of the $a[\bar{1}0\bar{1}]$ edge dislocations as indicated in the following dissociation reaction equation.²⁹

$$a[\bar{1}0\bar{1}] = a/2[\bar{1}0\bar{1}] + a/2[\bar{1}0\bar{1}] \quad (1)$$

According to the Frank's rule, this dissociation reaction is energetically favorable since the $|b|^2/a^2$ value decreases from 2 to 1. Although the $\langle 110 \rangle$ { $\bar{1}\bar{1}0$ } system is regarded as the most favorable glide system in perovskite materials,³⁴ stacking faults in another glide system are also observed. Fig. 5.6 (c) and (d) show a TEM image along the [110] zone axis and the corresponding inverse Fourier transform from the selected reflections (1 $\bar{1}2$), ($\bar{1}1\bar{2}$), ($\bar{1}11$) and (1 $\bar{1}\bar{1}$). Several Frank partial dislocations with a Burgers vector of $a/3[\bar{1}11]$ are

Figure 5.6 (a) High-resolution TEM image of the LSMO and BTO layers viewed along the $[010]$ zone axis in Sample A. The Fourier transform of the lattice image is given in the inset. (b) Inverse Fourier transform image using the superstructure reflections indicated by the black circle in the inset of (a). The partial dislocations are marked. Trace of the stacking fault is shown by the dashed white line. (c) HRTEM image along zone axis $[110]$; the inset is Fourier transform of the lattice image. (d) Inverse Fourier transform image using the superstructure reflections indicated by the black circle in the inset of (c). The dashed white line shows the trace of the connected stacking faults.

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identified by the glide of $(1\bar{1}2)$ planes in Fig. 5.6 (d). The stacking fault sandwiched between them is indicated by the dotted white line. The Frank partial dislocation starts from the LSMO layer, then extends into the BTO and stops in the adjacent LSMO layer. Pairs of partial dislocations connected by stacking faults can interact with each other to generate a defect network, exemplified by the white dotted lines. The source of $a/3[\bar{1}11]$ partial dislocations could be the dissociation of $a/2[111]$ dislocations at the end of the observed RP faults.³³ For example, the following dissociation is energetically favorable:

$$a/2[\bar{1}11] = a/3[\bar{1}11] + a/6[\bar{1}11] \quad (2)$$

in which the $|b|^2/a^2$ value decreases from $3/4$ to $1/3 + 1/12 = 5/12$.

5.3.3 X-ray Photoelectron Spectroscopy

Besides the structural defects, oxygen vacancies that were incorporated during the film growth will also affect physical properties of the deposited films. Taking BTO as an example, oxygen vacancies can generate Ti^{3+} cations, which might result in degradation in ferroelectricity. To confirm the status of the Ti cations, we have performed X-ray photoelectron spectroscopy (XPS). Fig. 5.7 (a) and (b) show XPS Ti 2p spectra obtained from Sample A and Sample B. The Ti $2p_{3/2}$ peaks of both samples locate at binding energy of 458 eV which correspond to Ti^{4+} cations. A careful curve fitting shows that no shoulder peak appears at position of about 1.3 eV lower than that of Ti^{4+} cation, suggesting the absence of Ti^{3+} cations.³⁵ We

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therefore attribute the ferroelectric property difference between the two samples to their difference in the state of structural defects.

Figure 5.7 XPS spectra of Ti 2p states in (a) Sample A and (b) Sample B.

5.3.4 Local Ferroelectricity Measured by Piezoelectric Force Microscopy

To investigate ferroelectricity of the topmost BTO in the superlattice, we have adapted scanning probe microscopy to perform ferroelectric poling, piezoelectric force microscopy (PFM) mapping, and local switching spectroscopic measurements. Fig. 5.8 (a) and (b) show the topographic images of the Sample A and B, respectively. The surface of the latter is very smooth with a roughness of about 0.2 nm, while the former has a roughness of about 0.6 nm, with some nanoscale particles on its surface. A $4 \times 4 \mu\text{m}^2$ square area was first poled using +3 V DC (direct current) voltage, followed by a reversal of the polarization in the central $1 \times 1 \mu\text{m}^2$ region under -3 V. After relaxing for half an hour, the polarization was read under AC (alternating current) voltage of $V_{pp} \sim 0.3$ V. The out-of-plane

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piezoresponse phase (OPP) contrast in Sample A gradually faded away, as shown in Fig. 5.8 (c), suggesting weak or unstable ferroelectricity. In Sample B, large OPP

Figure 5.8 (a and b) Topography of Sample A and B, respectively. (c and d) PFM images of the polarization pattern scanned with an AFM tip on Sample A and B, respectively. The purple region corresponds to polarization switched downwards (with tip bias +3 V); the yellow region in the centre corresponds to polarization switched upwards (with tip bias -3 V).

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contrast was observed, as shown in Fig. 5.8 (d), indicating that ferroelectric domains with opposite polarizations have been successfully written on the topmost BTO layer in Sample B.

Besides phase signals, out-of-plane ferroelectric amplitudes were measured during polarization switching. As shown in Fig. 5.9 (a), the amplitude of the piezoresponse in Sample A is near-linearly proportional to the bias voltage, indicating nearly no remnant ferroelectricity. Fig. 5.9 (b) was measured on Sample B, showing a typical ferroelectric response during the switching process. Together with the phase information, we can evidently conclude that the BTO layer in Sample A has deteriorated ferroelectricity, while BTO in Sample B maintains robust ferroelectricity.

Figure 5.9 Out-of-plane PFM amplitude of Sample A (a) and Sample B (b).

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5.3.5 Magnetic Properties

In order to understand the interplay of the observed defects and the magnetic properties of the superlattice, magnetic measurements at low temperatures were performed. The magnetism in the superlattice arises from the LSMO layers, thus the crystallinity and composition of the LSMO dominates its measured magnetic properties. Fig. 5.10 (a) shows magnetization vs. temperature diagram. The Curie temperature of the Sample A is around 260 K, while a value of 290 K is

Figure 5.10 Magnetic properties of LSMO in superlattices. (a) Magnetization vs. temperature (M-T) curves of Sample A and B. The inset is the M-T curve of the Sample A; the ferromagnetic to nonferromagnetic transition temperature is 260 K. (b) Magnetic hysteresis loop of the Sample A and B at 5K. The inserted graph is a magnification of the magnetic hysteresis loop of Sample A, showing the magnetization reversal processes with small saturation magnetization.

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found for the Sample B. Fig. 5.10 (b) shows the magnetic hysteresis loop of both Sample A and B, measured at 5 K. The coercivity of Sample A is 190 Oe, while that of Sample B is only 98 Oe. The saturation magnetization of the Sample A is 90% lower than that of the Sample B which exhibits nearly bulk values. Previously, we demonstrated that annealed LSMO films (80 nm thick) grown at low oxygen pressures have an almost nonferromagnetic layer near the interface, becoming more ferromagnetic closer to the free surface.²¹ Then, according to this cation nonstoichiometry dominant mechanism, the saturation magnetization value is expected to decrease as the film thickness reduces, which is clearly observed in the ultrathin LSMO layers in this study.

5.3.6 Discussion

It was found that oxygen pressure during the film growth determines to a great extent the state of cation defects in the superlattices and, therefore, their multiferroic properties. These defects will still be present after post-deposition oxygen annealing, due to the very low mobility of the substitutional cations once the layers are formed. According to literatures, BTO films grown under low oxygen pressures prefer layer-by-layer growth mode, achieving high crystalline quality.^{19,20} These results and our observation are in conflict. Here, we proposed a mechanism to explain the observation. The underlying mechanism for the cation defect formation in LSMO is a concurrent effect of the oxygen vacancies and the tensile stress caused by the adjacent BTO. To neutralize the positive charge induced by the oxygen vacancies, the B-site Mn cations (with oxidation states of +3 or +4) could be substituted by La and Sr cation (the oxidation states are +3 and +2, respectively).

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Meanwhile, the A-site cation excess can increase the lattice constant of LSMO and relieve the epitaxial strain from BTO.²¹ This cation nonstoichiometry in LSMO is accommodated by the introduction of extended RP faults. As the RP faults propagate to the LSMO surface, the surface terminations at the two sides of an RP fault boundary are different, one is Mn-O₂ terminated and the other is (La,Sr)-O terminated. Subsequently, a BTO layer is deposited on this surface along the [001] direction; as the Ba-O atomic layer and Ti-O₂ atomic layer would be on the same level, indicating that the RP faults propagate into the BTO, producing A-site cations (Ba) excess relative to B-site cations (Ti). The two ends of the planar defect are $a/2 \langle 111 \rangle$ partial dislocations. To release the strain energy, some $a/2 \langle 111 \rangle$ dislocations can dissociate into Frank partial dislocations with Burgers vectors of $a/3 \langle 111 \rangle$ and $a/6 \langle 111 \rangle$, producing stacking faults with a shear vector of $a/3 \langle 111 \rangle$. In addition, a superdislocation, such as the $\langle 110 \rangle$, $\langle 001 \rangle$, $\langle 111 \rangle$ or null type, can be formed due to various arrangements of the extra lattice plane associated with the $a/2 \langle 111 \rangle$ dislocations, while the formation of $\langle 110 \rangle$ in-plane dislocation is the most effective way to release epitaxial strain.³¹ To explain the observed high density of $a[100]$ interfacial edge dislocations, we proposed that the RP faults induced $\langle 110 \rangle$ -type dislocations loops glide on the {101} planes and dissociate near the interface to yield the $a[100]$ and $a[001]$ dislocations. This explanation is supported by the model proposed by Suzuki *et al.* and Qin *et al.*^{29,30} However, according to their model, the $a[001]$ dislocations are supposed to be eliminated by mutual annihilation. We proposed that the following dislocation reaction between the $a/2 \langle 111 \rangle$ partial

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dislocations can reduce the strain energy and generate the $a[001]$ edge dislocation along c-axis direction.

$$a/2[\bar{1}\bar{1}1] + a/2[111] = a[001] \quad (5.3)$$

in which the $|b|^2/a^2$ value decreases from $3/4 + 3/4 = 3/2$ to 1.

As a result, the observed RP faults and the $a/2 < 111 >$ dislocations accommodated the cation nonstoichiometry that was induced by low oxygen pressure during the film growth. Furthermore, the interactions between defects produce extra pure edge defects to release the strain energy, such as $a[100]$ and $a[001]$ edge dislocations, or stacking faults with a shear vector of $a/3 < 111 >$ within the $< 111 > \{11\bar{2}\}$ glide system.

The suppressed ferroelectricity in Sample A is explained in terms of the local strain field, cation nonstoichiometry and charged domains induced by dislocations. Chu *et al.* visualized that the strain fields of edge type dislocations extended into $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ nano-islands and induced ferroelectric instability.³⁶ Alpay *et al.* developed a thermodynamic model based on the Landau-Devonshire formalism to study the role of dislocations in ferroelectric materials. They found that the coupling of the polarization and the strain field associated with the dislocations resulted in a strong depolarization field that suppressed the ferroelectricity over several nanometers.³⁷ This effect can be aggregated in ultrathin ferroelectric layers, such as our BTO film, since the defective area-to-volume ratio increases. By employing a negative spherical aberration imaging technique, Jia *et al.* revealed that the strain field of the $a[011]$ dislocation in the SrTiO_3 substrate

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can propagate across the interface into $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ film, leading to a strong reduction of the c – axis parameters and a decrease of local spontaneous polarization.³⁸ From the reciprocal space mapping and the detection of the $a[00\bar{1}]$ and of $a[100]$ edge dislocations, Sample A was demonstrated to have mosaic structures, leading to severe lattice bending and local strain fields around dislocations. Together with the cation nonstoichiometry (possible Ba cations excess) induced by the RP fault boundaries, the atomic ordering in a large part of our BTO film deviates from the regular perovskite structure, resulting in very weak ferroelectricity. Additionally, the cation nonstoichiometric RP faults in BTO can locally induce net negative charge since the Ba^{2+} cations replace the Ti cations (with oxidation states of +3 or +4). Then, electric fields which can couple with strain fields are built-in along the zig-zagged RP fault area. As a result, a strong depolarization field can be formed, strongly suppressing the ferroelectricity, forming ferroelectric dead layers. As the oxygen pressure increases during growth, the cation off-stoichiometry of LSMO and the RP faults can be removed due to the elimination of oxygen vacancies effect. Then the crystalline quality of subsequently grown BTO layer can be improved, resulting well-strained lattices and ferroelectricity.

The impact of defects on the ferromagnetism of the LSMO layers can also be attributed to the oxygen pressure-induced interface cation nonstoichiometry.²¹ The ferromagnetic properties of LSMO are dominated by the double exchange mechanism where the Mn e_g electrons hop between Mn^{3+} and Mn^{4+} cations when their spins are parallel.³⁹ Therefore, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio (the Mn nominal valence)

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plays a crucial role in determining the magnetic properties. According to the magnetic phase diagram and our previous finding in LSMO grown with low oxygen pressure (1 Pa),²¹ the cation nonstoichiometric LSMO has high Mn nominal valence of around +3.6, with greatly reduced magnetization.⁴⁰ In this study, the observed RP faults contain extra A-site cation planes, forming a boundary with the rock-salt structure, which is consistent with the previous finding. Then the A-site cation excess and depletion of Mn cations can generate a high Mn nominal valence state inside the LSMO layers, resulting in ferromagnetic dead layers, explaining strongly the suppressed magnetization in Sample A.

To measure the magnetoelectric coupling effect, the superlattices should be etched to isolated pillars at micron or nanometer scale, otherwise, partial BTO layers and interfaces maybe short-circuited by conductive pinholes or particulates. By applying external voltage on the surface BTO, the magnetization change can be measured by magneto-optical Kerr effect (MOKE) to determine the magnetoelectric coupling coefficient.⁷

5.4 Conclusion

LSMO (16 unit cells)/BTO (12 unit cells) superlattices were grown by using pulsed laser deposition on STO (001) substrates. For the samples grown at a low oxygen pressure with oxygen vacancies introduced during growth, an A-site cation excess is formed in LSMO, deteriorating the crystalline quality of the superlattice. This cation nonstoichiometry is accommodated by the introduction of Ruddlesden-Popper faults, which can propagate from the LSMO layer to the adjacent BTO layer, inducing possible Ba cation excess. Furthermore, stacking faults with a shear

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vector of $a/3 \langle 111 \rangle$ within the $\langle 111 \rangle \{11\bar{2}\}$ glide system, and extra $a[001]$ and $a[100]$ pure edge dislocations can be produced due to the interaction between $a/2 \langle 111 \rangle$ dislocations. Our detailed analysis demonstrates that both the ferroelectric and ferromagnetic properties are strongly suppressed due to the cation nonstoichiometry and local strain fields induced by the observed defects. Avoiding the occurrence of oxygen vacancies—by using an elevated oxygen pressure during growth—improves the cation off-stoichiometry, and results in a better crystalline quality and robust ferroelectric and ferromagnetic properties.

A mechanism was proposed to explain the role of oxygen pressure-mediated cation defects play in the formation of ferromagnetic and ferroelectric dead layers. Only after elimination of the defects by optimizing the oxygen pressures can stronger multiferroic properties and magnetoelectric coupling effects in LSMO/BTO superlattices be realized.

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Chapter 6 Conclusions and Future Work

6.1 Conclusions

To fabricate oxide devices with high performances, it is necessary to have a thorough understanding of the manner in which the film growth conditions mediate the cation stoichiometry and defects and what impact they have on the film's physical properties. The effect of laser fluence on cation stoichiometry of pulsed laser deposited thin films has been well demonstrated in the literature. This work offers a deep insight into another critical growth parameter, oxygen pressure, that can result in off-stoichiometric pulsed laser deposited $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) thin films and $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{BaTiO}_3$ (LSMO/BTO) multiferroic superlattices.

Local chemical information of the manganite thin films at nanometer scale was obtained with TEM spectroscopy, where the electron beam was focused to a diameter of around 2 nm, and slowly scanned along the thin film growth direction. The distribution of chemical elements was extracted from the normalized intensities of their EELS and energy dispersive X-ray spectrums (EDX). The A-site/B-site cation ratio is larger than one near the interface of the manganite and the SrTiO_3 (STO) substrate. Moreover, by using surface sensitive angle dependent X-ray photoelectron spectroscopy (XPS), and element-sensitive Z-contrast STEM imaging with atomic resolution, we found that the oxygen vacancies formed during the film growth induced strontium surface segregation as well, forming a SrO rock-

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salt monolayer. A mechanism based on charge neutralization and strain relaxation was proposed. At the initial growth stages near the STO substrate, the A-site cations (La/Sr) partially substituted Mn to compensate the positive charge associated with the oxygen vacancies. Meanwhile, the accommodation of large La and Sr cations in B-sites increased the lattice constant and relieved some of the tensile strain induced by the STO substrate. At a later stage after most lattice strain is relieved, the proportion of Mn substitution by La/Sr cations decreased. The Sr migration towards the film surface became the dominant mechanism of cation nonstoichiometry. The positive charge induced by the oxygen vacancies near the film surface may favor Sr segregation for electroneutrality. Sr cations migrated towards the film surface to form a SrO rock-salt monolayer. The Mn nominal valence was exacted according to the quantitative analysis of the EELS Mn $L_{2,3}$ edges and oxygen K edges. The profiles of the Mn valence were completely different in the samples grown under different oxygen pressure. It was found that high Mn nominal valence (+3.6) existed in the manganite film grown at low oxygen pressure near its substrate, and remained constant within a thickness of about 45 nm, beyond which it decayed monotonically until the free surface. The suppressed magnetization and increased magnetoresistance in this epitaxial film was attributed to the presence of the nonferromagnetic phase near the STO-LSMO interface due to this cation nonstoichiometry. The magnetic hysteresis loop of the annealed sample exhibited multistep magnetization reversal processes, indicating aggravated inhomogeneity of the magnetic phase. For the thin film grown at higher oxygen pressure, the Mn nominal valence remained constant (+3.2) and there was

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no cation stoichiometry inside the film. These results demonstrated that the presence of oxygen vacancies was responsible for cation nonstoichiometry near the interface and surface of the epitaxial thin films. The oxygen vacancies in the LSMO could generate an extra insulating and nonmagnetic ‘dead layer’ near the LSMO-barrier interfaces, leading to the reduction of the Curie temperature and conductivity, which can be used to develop tunneling devices.

Secondly, we have elucidated the impact of oxygen pressure-mediated cation defects on multiferroicity of the superlattices of LSMO and BTO. LSMO (16 unit cells)/BTO (12 unit cells) superlattices were grown by using pulsed laser deposition on STO (001) substrates. For samples grown at low oxygen pressure, it was found that an A-site cation excess was formed in LSMO, deteriorating the quality of the superlattice. This cation nonstoichiometry was accommodated by the formation of Ruddlesden-Popper faults, which propagated from LSMO to adjacent BTO layers. Furthermore, stacking faults with a shear vector of $a/3 \langle 111 \rangle$ within the $\langle 111 \rangle \{11\bar{2}\}$ glide system, and extra $a[001]$ and $a[100]$ pure edge dislocations could be produced due to the interaction between $a/2 \langle 111 \rangle$ dislocations. By using piezoelectric force microscopy and magnetic properties measurements, it was demonstrated that both the ferroelectric and ferromagnetic properties were strongly suppressed due to the presence of the defects. When the crystalline quality of the superlattices was improved due to use of higher oxygen pressure, robust ferroelectricity and ferromagnetism were achieved. Therefore, we conclude that cation defects are the major obstacle limiting the functionalities of multiferroic superlattices with ultrathin ferroic layers and that high oxygen pressure

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which prevents the formation of oxygen vacancies in the films during growth is required to achieve nearly bulk ferroic properties.

6.2 Future Work

6.2.1 The Magnetoelectric Coupling in LSMO/BTO Superlattices

Since robust ferroelectric and ferromagnetic properties were achieved by tuning the growth conditions in Chapter 5, strong magnetoelectric coupling between LSMO and BTO in superlattice structure is expected. To measure the coupling effect, we propose to use magneto-optic Kerr effect (MOKE) magnetometry that had been reported to measure the magnetoelectric effect of $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3/\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ bilayer system.¹

From the interface physics aspect, the LSMO/BTO interface can be further studied by Cs corrected STEM combined with electron energy loss spectroscopy. The valence of Mn cations and Ti cations can be mapped as a function of distance from the interface to reveal the interface reconstruction.² Moreover, spatial resolved electron energy loss spectroscopy in scanning transmission electron microscopy mode with *in situ* ferroelectric polarization switching in TEM holder can map the variation of Mn valence during the switching process. The results can directly demonstrate the origin of the magnetoelectric coupling effect at nanoscale.

6.2.2 The Functionality of Defects During Polarization Switching

It has been demonstrated that different types of defects can be generated in LSMO/BTO superlattices under low oxygen pressure. However, the functionalities of the defects have not been demonstrated. By using *in situ* TEM holder that can

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apply voltage to the sample and dark field image, the nucleation and expansion process of ferroelectric domain can be directly observed. Then the map of switching process can be related with the location of defects. Similar experiment had been presented.³

6.2.3 The Ferroelectric Tunnel Junction

In this work, room temperature ferroelectricity in ultrathin BTO films was obtained, which paved the way to the fabrication of ferroelectric tunnel junction device with tunneling electroresistance (TER) effect.⁴ Using the LSMO or SrRuO₃ as bottom electrodes, the ultrathin BTO could act as ferroelectric barrier layer for the tunnel junction. The top electrodes at nanoscale will be patterned by electron beam lithography (EBL). The ferroelectric domain can be switched by PFM and the corresponding tunneling currents will be measured by conducting atomic force microscopy.⁵ Moreover, the BTO thickness effect on ER can be systematically studied in future.

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