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Reflectivity and photoemission electron microscopy studies of magnetic heterostructures

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Reflectivity and photoemission electron microscopy studies of magnetic heterostructures

Chih-Yeh Huang

Dissertation submitted
to Benjamin M. Statler College of Engineering and Mineral Resources
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in partial fulfillment of the requirements for the degree of

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Materials Science and Engineering

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Abstract

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Chih-Yeh Huang

When a thin film thickness becomes ultrathin, the magnetic properties of the thin film can be altered, degraded or even lost. The loss of magnetism has been called the magnetic dead layer (MDL). Considering the trend for miniaturization of information storage and other devices, the MDL is a significant challenge for materials science and engineering. $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) with $x=0.3$ is an excellent model material that exhibits ferromagnetism at room temperature to study the MDL. This dissertation focuses on understanding the MDL in LSMO films on their own and the effect of this dead layer when coupling with a ferroelectric material [$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (LSMO/PZT)].

The LSMO/PZT magnetic heterostructures

Ferromagnetic-ferroelectric layers at the interface can show strong magnetoelectric coupling, allowing electrical control of magnetism or vice versa. Images of magnetic domains and interfacial Ti spins were taken at the same locations of the LSMO/PZT heterostructures by utilizing photoemission electron microscopy (PEEM). The interfacial Ti spins prefer to be perpendicular to ferromagnetic domains in the adjacent layer. Using image analysis techniques confirms the population of magnetic switching and the interfacial spins are related to the magnetization within LSMO. In other words, if the ferromagnetic layer begins to lose its magnetic order, the coupling between ferroelectric and ferromagnetic layers will also decrease or even disappear. Thus, this work suggests a magnetoelectric dead layer is about 2.8 nm for the LSMO layer. This result further emphasizes the need to enhance the magnetization in magnetic thin films.

The LSMO/STO magnetic heterostructures

The location of the magnetic reduction can have strong effects on devices for some magnetic applications. Does this reduction occur only at the surface, the interface, or throughout the material? Polarized neutron reflectometry can provide depth dependent magnetic properties. Using this method, we determined that the MDL at the surface of LSMO has a thickness of about 1.7 nm. We attribute the polar discontinuity induced charge reconstruction to interpret the suppressed magnetization at the surface. Unlike the MDL at the surface, the resultant enhanced magnetization at the interface is likely subject to oxygen vacancies. The magnetic moments originate from unpaired electrons which occupy the d orbitals on the Mn site. Oxygen vacancies result in charge accumulation on the interfacial region explained by raising densities of magnetic moments on the Mn site and the enlargement of the ratio of mixed $\text{Mn}^{2+}/\text{Mn}^{3+}$ states at the interfacial region.

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Chih-Yeh Huang

*Morgantown, WV
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Chapter 1 Introduction

1.1 Introduction

Functionalized heterostructures have several specific application areas such as magnetic field sensors, magnetic tunneling junctions and data storage devices or logic operations. [1] In commercial and engineering applications, those thinner, smaller and even faster devices would cut down consumption for energy-driven and materials usage, significantly. However, in order to understand characterization of the functionalized heterostructures, thin film deposition would be necessary to fabricate them. Thin film deposition is to grow a thin film of material onto a surface of a substrate or onto previously deposited layers of material. For instance, depositing a magnetic layer is an act of growing the magnetic thin film onto a substrate, resulting in a magnetic heterostructure. By utilizing thin-film deposition techniques, a film thickness down to a single unit (a few tenths of a nanometer) thick can be grown precisely layer by layer. For example, pulsed laser deposition (PLD) is the one of few versatile thin-film growth techniques which can be precisely used for nanoscale engineering of high-quality complex oxide materials. [2] But, when a thin film becomes too thin, the magnetic properties of the thin film can be altered, degraded or even lost. This challenge is unfavorable for device miniaturization, particularly for magnetic thin-film devices. The loss of magnetism has been called the magnetic dead layer (MDL), where the suppressed magnetization occurs at the surface or the interface, even on both regions. In some cases, MDL is made of a few atomic layers. [3-6] However, it is unclear if this loss of

magnetism is always limited to a single region of the film or might even just be evenly spread throughout it.

However, the mechanisms and depth dependence of MDLs are not fully explored yet. For example, there are many cases that have been published to explain the interplay of interfacial atomic inter-diffusion [6], oxygen vacancies [7-9], lattice strain [10, 11], charge [12] and orbital [13, 14] at the heart of the physical phenomena for unraveling the studies of MDLs. **All of above these interpretations affect magnetism. It is possible that there is more than one underlying mechanism.** But, when we change one thing, it changes lots of things, and it is hard to say what is responsible. In other words, the details of MDLs remain unclear.

With the miniaturization of information storage devices in so many current and proposed future applications, the MDL is a significant research area for materials science and engineering. It goes beyond even magnetism. Other properties also change at surfaces and interfaces. If we can understand surface magnetism, we might be able to apply some of these principles to some other systems, too. Indeed, this is my research motivation. Why my dissertation focuses on magnetism in LSMO is because it is an excellent model system. In order to grow any good film, it is important to start with a well-matched substrate or starting material. Here, we utilized SrTiO_3 , whose lattice parameters are similar to LSMO.

1.1.1 SrTiO_3 (STO)

ABO_3 perovskites are typically represented as cubic or nearly cubic shown in Figure 1-1. Each cation A is located in the corner of the perovskite structure and the position of the oxygen anions are located in the center of

the cubic faces. The cation B is located in the center of the perovskite structure. [15] In other words, the name perovskite represents any compound that has ABO_3 formula where a BO_6 octahedron structure of a transition metal as the B ion is surrounded by six oxygen ions and A cations are in the cube corners. To deposit a perovskite thin film, it is useful to start from a perovskite substrate. Thus, one commonly used single crystal perovskite due to its cheap price and close lattice match with LSMO is $SrTiO_3$ (STO), which is cubic structure with a lattice constant of 0.3905 nm. The lattice parameter of bulk ferromagnetic LSMO is 0.3876 nm. The lattice mismatch between the substrate STO and LSMO is about 0.8% with a tensile strain. [16]

Figure 1-1 ABO_3 cubic perovskite structure. [15]

1.1.2 $La_{0.7}Sr_{0.3}MnO_3$ (LSMO)

$La_{1-x}Sr_xMnO_3$ with $x=0.3$ is an excellent model material to understand MDLs. LSMO is one of the few magnetic oxide systems that exhibits ferromagnetism at room temperature shown in Figure 1-2. Many academics and industries (e.g. Intel) have suggested that this material can be used in real devices for applications such as magnetic field sensors and magnetic tunnel junctions (MTJs). An MTJ consists of at least two magnetic layers

separated by an ultrathin insulating layer as a tunneling barrier. The tunneling current is measured perpendicular to the MTJ. The tunneling current is related to the orientation of the magnetization of the two magnetic layers. For example, if the magnetizations on both of LSMO layers are in parallel, electrons will tunnel the insulating barrier more than if the magnetizations are antiparallel. In other words, two states of the tunneling resistance are low for parallel and high for antiparallel orientation, respectively. If the magnetization in LSMO and other materials is lost due to the MDL, then this will affect the efficiency of this and other devices.

1.1.3 Mixed Mn valence in LSMO and double exchange interaction

The magnetic properties of bulk $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ are shown in Figure 1-2, where lanthanum is a trivalent rare earth element and strontium is a divalent alkaline earth element, respectively. [17] The Mn oxidation state in the LSMO endpoint, LaMnO_3 (LMO), is 3^+ while the other oxidation state in the other endpoint, SrMnO_3 (SMO), is 4^+ . Both LMO and SMO are antiferromagnetic via the super exchange interaction. In the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ compound, 30% of Mn^{3+} cations convert into Mn^{4+} in order to keep the charge neutrality for the doped manganese oxides. Since $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is composed of 70% of LMO and 30% of SMO, the oxidation state of manganese is the weighted average of 3.3^+ .

Figure 1-2 Phase diagram of bulk $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. [17]

The LSMO exhibits ferromagnetism via the double exchange interaction shown in Figure 1-3. More specifically, the magnetic property of LSMO is dominant by an indirect exchange interaction between magnetic moments of unpaired electrons, indicating the Mn ions separated by an intermediate oxygen atom. In the cubic perovskite symmetry, an Mn (III) ion has four electrons on d orbitals with three electrons at the lower t_{2g} levels (triply degenerate) and one electron at the high e_g levels (doubly degenerate). Furthermore, an Mn (IV) ion has three electrons d-electrons with three electrons at the lower t_{2g} levels (triply degenerate) and no electron at the high e_g levels (doubly degenerate). Thus, an electron at the e_g levels of the Mn (III) can hop on the unoccupied states of a neighboring Mn (IV) ion. In the double exchange interaction, the highest energy electron can simultaneously hop from the Mn (III) “ e_g ” orbitals to the O “2p” orbitals and then from the O “2p” orbitals to the Mn (IV) “ e_g ” orbitals. This double exchange interaction explains the ferromagnetic and metallic properties in the doped manganese oxides. Unlike the super exchange interaction meaning two Mn ions with the

same valence separated by an oxygen atom, the double exchange interaction takes place between two Mn ions with a different number of electrons separated by an oxygen atom. More specifically for LSMO, the double exchange mechanism is a simultaneous transfer of two electrons across oxygen occurring in a system with two different oxidation states (here, Mn (III)-O-Mn (IV)). In the most outer shells (the d orbitals), all of the electron spins of Mn (III) and Mn (IV) are parallel. One spin up electron is transferred from Mn (III) through the intermediate oxygen to the Mn (IV), which can reduce the energy of the system if it is spin up and replaced by another electron from Mn (III). [18] The alignment between the spins of the different Mn causes the magnetic ordering to be ferromagnetic below the Curie temperature, T_c .

Figure 1-3 Schematic representation of the double exchange mechanism. [18] For a double exchange mechanism, a simultaneous transfer of two electrons occurs: one 'spin up' electron is transferred from the intermediate oxygen to the Mn (IV). The five-fold degenerate atomic 3d levels split into lower t_{2g} (triply degenerate) and higher e_g (doubly degenerate) levels due to crystal field splitting.

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Chapter 2 Experimental techniques

We fabricate and characterize our own samples in the Shared Research Facility at WVU and perform other valuable experiments using facilities in national labs to determine depth-dependent studies in LSMO. In Chapter 2, we will discuss the fabrication of our own samples and characterize them by utilizing synchrotron facilities. Section 2.1 is about our sample preparation and fabrication by PLD. The following section 2.2 is an introduction of synchrotron techniques, including X-ray absorption spectroscopy (XAS), X-ray magnetic circularly dichroism (XMCD), and photoemission electron microscopy (PEEM), respectively.

2.1. Experimental techniques - Fabrication

2.1.1 SrTiO₃ substrate surface preparation

The SrTiO₃ (001) substrate is a cubic ABO₃ perovskite structure, consisting of alternating SrO and TiO₂ planes along the c-axis orientation. The reason of choosing STO as a substrate is that the lattice constant of STO is 0.3905 nm with a close lattice match to LSMO as 0.3875 nm. In our lab, the commercial STO (001) substrates were purchased from CrysTec GmbH. The size for each STO substrate is 10 x 5 mm² with the thickness of 0.5 mm. In general, STO substrates exhibit mixed SrO and TiO₂ terminated planes. In order to have well controlled interfaces, clean atomically flat TiO₂ terminated STO substrates are obtained via using a series of acetone, isopropanol and deionized (DI) water and thermal annealing, similarly with Connell et al. [1] First, the substrates were cleaned by acetone, isopropanol and deionized (DI) water for 5 minutes, respectively and then were prepared by annealing at 1000 °C for 2 hours in air. Second, substrates were ultrasonically recleaned with DI water about 5 minutes at room temperature. Third, the substrates were re-annealed at 1000 °C for 2 hours in air. Since the SrO is soluble in DI water, the DI water can be effectively to chemically remove the SrO terminations. [2-4] But, TiO₂ terminations cannot be affected by DI water. Through these procedures, singly TiO₂ terminated surfaces of single crystalline STO (001) substrates were shown in Figure 2-1.

Figure 2-1 The AFM images of (a) height and (b) phase images of the treated STO (001) substrate.

2.1.2 Pulsed laser deposition

Pulsed laser deposition (PLD) is a form of physical vapor deposition. PLD is a technique of fabricating thin films by using high energy pulsed laser beam to bombard one or more targets under a certain growth pressure. The target experiences a phase transition from the solid to the vapor phase, and atoms within it are subsequently deposited onto a heated substrate. [5] PLD can be assisted with the reflection high-energy electron-diffraction (RHEED) oscillations, which provide a dynamic method of monitoring deposition rate and film quality. The principle involves variation of the electron scattering which can be monitored by integrating the primary RHEED spot intensity. A smooth surface presents an intense primary spot while a rough surface provides a weak primary spot. Each fraction of a monolayer growth corresponds to the relation of the integrated RHEED spot intensity versus the recording time during deposition. The lowest intensity for one monolayer (e.g. 50%) deposited with a minimum smoothness on the surface while the highest intensity occurs for one monolayer fully (e.g. 100%) deposited with

a maximum smoothness shown the RHEED oscillations schematically in Figure 2-2. In addition to helping rule out potential extrinsic factors affecting MDL formation, high-quality smooth films are particularly important many surface sensitive synchrotron techniques. When we have these high-quality films, we can probe their properties by using synchrotron techniques. But, understanding the fundamentals of the synchrotron techniques is necessary prior to performing the experiments. Thus, we will introduce the experimental techniques, including XAS, XMCD, and PEEM in next section.

Figure 2-2 PLD system setup (Left) and RHEED oscillation diagram (Right).

[5]

2.2 Experimental techniques - Synchrotron techniques

2.2.1 Overview

Synchrotron radiation known as relativistic cyclotron radiation or magnetobremsstrahlung radiation is the electromagnetic radiation when charged particles in vacuum are accelerated radially, meaning the acceleration direction is perpendicular to the velocity direction, causing a curved path. If the electron beam velocity approaches the speed of light, this sharply collimated emission is synchrotron radiation. On the other hand, if the charged particles are non-relativistic, meaning the speed of charged particles much lower than the speed of light, the emission is called cyclotron emission. Synchrotron radiation can be produced toward the tangential direction of the electron beam while the electron beam enters through bending magnets or undulators that is an array of periodic magnets as an insertion device. Moreover, the radiation with a characteristic polarization such as linear or circular polarization produced in the various undulators is very intense and concentrated in narrow energy bands.

This section briefly introduces few of synchrotron techniques, including X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and photoemission electron microscopy (PEEM). First, XAS is a technique to probe electron transitions, such as from 2p core levels into 3d unoccupied states in transition metals absorbed by X-rays. The absorption line shapes produced from this technique are strongly correlated to variations of the electronic configurations such as the valence of the absorbed atom. Second, since using energy-tunable and polarized X-ray sources in synchrotron facilities with an adjustable cryogenic and magnetic

field environment under an ultrahigh vacuum environment is achievable, XMCD makes a great probe for studying surface-sensitive magnetic properties on ferromagnetic thin films. Finally, PEEM is a magnetic imaging method to visualize magnetic domains, showing spatially magnetization distribution across the sample surface.

2.2.2 X-ray absorption spectroscopy (XAS)

Elemental specificity of transition metals in a wedge sample

XAS is a technique to obtain information about the elemental composition of the measured samples using the energy-dependent X-rays. Example scans are illustrated in Figure 2-3. From bottom to top of this sample, the layer thickness of Fe increases, forming a wedge. On the contrary, the layer thickness is fixed for Cu and Ni, respectively. As you go up the wedge, the Fe signal increases because of the increasing Fe layer thickness and the Ni signal from the layer underneath Fe decreases because of the limited electron escape depth of the total electron yield signal used to record the spectra. The Cu signal is approximately constant, reflecting its constant thickness. [6]

Figure 2-3 X-ray absorption spectra of a wedge sample, revealing the composition at various points along the wedge. [6]

Elemental specificity of transition metals in bulk materials

In their bulk metallic form, the first three transition metals in Figure 2-4 are magnetic (but not Cu). The area of the resonant peak is directly related to the number of 3d empty states above the Fermi level. Therefore, Fe has the most holes in the 3d subshell, where the 3d subshell is almost full for Cu based on the atomic number Z of these transition metals, as evident from the smaller peak structure for Cu. [7]

Figure 2-4. X-ray absorption spectra of 3d transition metals [7]

Chemical specificity

XAS comes from core electrons that are excited in the absorption process into empty valence states above the Fermi energy. XAS also gives information on the chemical environment of the atoms such as atomic states, which are correlated with their magnetic state. In other words, the magnetic

properties in compounds containing transition metals are typically related with the 3d valence electrons. The L edge X-ray absorption spectra of the transition metals and oxides are dominated by two main peaks separated by about 15 eV shown in Figure 2-5. The two main peaks in the spectra arise from the spin orbit interaction of the 2p core shell and the total intensity of the peaks is proportional to the number of empty 3d valence states. Thus, the highest atomic number Z is Ni with the lowest empty 3d valence states. Additionally, the metal spectra mainly show two broad peaks, reflecting the width of the empty d bands. Compared with transition metals and their oxides, they arise from different 3d valence holes in the electronic ground state, reveal various absorption profiles and shifts in L edges. [6]

Figure 2-5. L edge X-ray absorption edge spectra of Fe, Co and Ni in the form of the elemental metals and oxides. The two main structures are called the L3 (lower energy) and L2 absorption edges. [6]

Experimental modes

The most common methods are three types of XAS detection methods: transmission, fluorescence yield, and total electron yield modes present in Figure 2-6.

Figure 2-6 Modes of X-ray absorption spectra with right and left polarized X-rays: transmission mode, fluorescence yield (FY) mode, and total electron yield (TEY) mode.

In the following, I would briefly introduce these measuring modes of X-ray absorption spectroscopy.

First, the transmission mode is a bulk-sensitive probe. XAS is a technique for measuring the linear absorption coefficient $\mu(E)$. Transmission mode counts both the individual flux amounts of the X-rays with the incident flux I_0 and then the transmitted flux I , passing through the measured sample. Based

on the Beer's law, the absorption coefficient can be written as either $I/I_0 = \exp(-\mu(E)t)$ or $\mu(E)x = \ln(I_0/I)$, where t is the sample thickness.

The second one is fluorescence yield (FY) mode. The probing depth for the FY mode is about 100 nm. The variations of the absorption coefficient with energy in the absorption event can be indirectly measured by the emitted fluorescence yield I_{FY} since the strength of fluorescence yield would be proportional to the number of initially core holes generated and photoexcited by the incident X-rays. In other words, when a core electron is removed by an X-ray photon, an electron from an outer shell may fill the vacancy, further resulting in energy release in the form of an emitted X-ray photon.

Third, the last one is total electron yield (TEY) mode. The surface-sensitive technique probes the top about 5 nm depth. X-rays are absorbed through electrons photoexcited from core levels to empty states above the Fermi level. Sometimes an upper electron from the outer shell drops to fill the vacancy in the core level, generating a photon emission, called X-ray fluorescence yield. However, this energy can also be transferred to another outer electron, potentially escaping from the surface of the sample. In this case, the ejected secondary electron or so-called Auger electron will result in a net current into the sample, which is used as a probe of the absorption.

However, the main contribution to the current in the TEY signal does not raise directly from the Auger electrons, but rather from cascade of secondary inelastically scattered electrons that have sufficient energy to escape the sample, sometimes encouraged by application of a voltage to the sample. Therefore, the emitted primary Auger electrons create scattered secondary electrons which dominate the total electron yield measurement. The cascade

of total electron yield involves several scattering events dependent upon the sampling depth. For example, electrons created deep from the surface of the sample lose too much kinetic energy to overcome the work function of the sample, they then have no signal contribution to the TEY measurement.

In order to compare the TEY-XAS technique with the other widely used surface-sensitive spectroscopic technique, I will briefly mention a similar technique that is X-ray photoelectron spectroscopy (XPS). XPS is also a technique used to measure elemental and chemical specificity. XPS is based on the photoelectric effect. The emitted signals are photoelectrons from core levels. Additionally, the electrons at the core levels of each atom have elemental and characteristic binding energies. For example, if the incident X-ray photons with an energy $h\nu$ is greater than the binding energy such as the Mn 2p core levels, the X-ray photons can completely be absorbed by the core electrons of each Mn atom. These electrons can overcome the binding energy ($E_{B.E.}$) from the atoms and emit out of the surface with the kinetic energy ($E_{K.E.}$). The electrons are called photoelectrons. Thus, if the ejected core photoelectrons reach the electron energy analyzer as the detector without any energy loss, these electrons contribute to XPS peaks shown as the Mn L3 and L2 peaks due to the spin-orbital coupling, respectively. In summary, while the TEY-XAS signals mainly contribute from cascades of secondary electrons scattered by Auger electrons with a tunable X-ray photon energy, XPS peaks originate from the excited core photoelectrons with elastic scattering events by using a monochromatic X-ray photon energy such as aluminum X-ray K-alpha source (1486.7 eV). Additionally, the sampling length in angle-resolved XPS can be smaller than the sampling length of TEY-XAS (about 5 nm). Our main goal is to image spatial

distribution of magnetic domains and uncompensated Ti spins at the same locations of LSMO/PZT heterostructures through PEEM images discussed in chapter 4. That is a significant reason why we have to use synchrotron X-ray facilities instead of utilizing the widely used XPS technique.

2.2.3 X-ray magnetic circularly dichroism (XMCD)

Principle of X-ray magnetic circular dichroism

X-ray magnetic circular dichroism (XMCD) measures the difference in absorption of X-ray left and right circularly polarized light while the helicity of incident X-rays is parallel and anti-parallel to the magnetization orientation of ferromagnetic materials. For magnetized materials such as LSMO films, the absorption spectra with right and left circularly polarized X-rays would be different, having a dichroism in XMCD spectrum ($\mu_{\text{XMCD}} = \mu_{\text{RCP}} - \mu_{\text{LCP}}$) shown in Figure 2-7, reflecting the unbalanced density of empty states.

Figure 2-7 XAS with right (red) and left (green) circularly polarized X-rays at Mn L-edges and spectrum of X-ray magnetic circularly dichroism (blue) for 8.4nm LSMO films on STO substrate measured at temperature= 50K with an in-plane magnetic field parallel to the incident direction of X-rays.

The XMCD measurements are performed near absorption edges where an electron from the core level is photo-excited into the unoccupied states above the Fermi level. The concepts of XMCD spectroscopy were proposed by Schütz et al. in 1987. [8] For a magnetic material, the d shell has a spin moment given by the imbalance of filled states below the Fermi level, showing majority and minority of electronic spins. The spin-dependent X-ray absorption process can be probed through circularly polarized photons which transfer their angular momentum to the photo-excited electron present in Figure 2-8. Since the magnetic moment is opposite to the spin direction along the same axis, the majority of electrons have spin down. In other words, the direction of applied field indicates the minority electron spin below the Fermi level in the 3d valence band. By using Figure 2-8 to illustrate the result shown

in Figure 2-7, the absorption intensity in LCP is greater than the RCP at the L3 edge because the dominant unoccupied states are electron spin up. Then, mainly transition probability (62.5%) of spin up electrons is excited by left circular polarized (LCP) incident X-ray at the L3 edge while 37.5% spin up electrons are excited by right circularly polarized (RCP) incident X-ray at the L3 edge. The XMCD signal is the opposite sign at L2 edge due to the opposite sign of the spin-orbit coupling in the 2p core levels, meaning $l+s$ for L3, and $l-s$ for L2 edge, respectively. On the contrary, above the Curie temperature (T_c), there is no significant difference in XMCD for ferromagnetic materials due to the balance of density of unfilled states in spin up and spin down electrons. Here, the excitation percentages of electronic spins probed by RCP and LCP X-rays are shown as Table 1.

Figure 2-8 One-electron model applied in the 2p to 3d transition excited by RCP and LCP X-rays to illustrate XMCD effects.

Table 1 Transition probabilities of spin up and down probed by RCP and LCP at L₃ and L₂ edges of 3d transition metal atoms.

Edge	RCP	LCP
L3	37.5%, ↑	62.5%, ↑
	62.5%, ↓	37.5%, ↓
L2	75%, ↑	25%, ↑
	25%, ↓	75%, ↓

Practical methods of obtaining the XMCD

XMCD measures the difference in the absorption coefficient over an absorption edge. The difference can reveal magnetic information in the measured sample, specific to a particular element and orbital via circularly polarized X-rays with energy tunability. In order to obtain XMCD results, there are two types of applicable methods: one by reversing the sample magnetization; the other by changing the helicity of the incident circularly polarized X-rays. In other words, the XMCD measurements can be done either reversing magnetization of the sample with a fixed circular polarized X-ray or applying both of the polarized X-rays with a fixed magnetization. These measurements are typically performed at synchrotron radiation sources because of the advantages of high X-ray flux, energy-tunable X-rays, and selective polarizations. Furthermore, the XMCD experimental setups can be separated into two regimes that are soft and hard X-rays based on the energy ranges. The basic setup requirement for the soft X-ray regime should need a high-vacuum chamber (about 10^{-8} torr), X-ray optics for the monochromatic X-ray light source, a source of circularly polarized X-rays, a set of magnets for applying a field to the measured sample, a cryogenic system for controlling temperature at the sample environment in this vacuum chamber, and a mode or modes for collecting the XMCD signals.

2.2.4 Photoemission electron microscopy (PEEM)

Generally, a PEEM image is measured at a selective monochromatic X-ray edge energy, at which the greatest dichroism results in the TEY mode. Figure 2-9 shows an example of magnetic domains imaged by PEEM. Thus, the image contrast in PEEM techniques can be used as a contrast mechanism to reflect the local spatial orientation of magnetization with magnetized domains shown in Figure 2-9, using imaging techniques on the sample via left and right polarized X-rays.

PEEM is a standard technique for high spatial resolution imaging of nanometer-scale magnetic domains [10] and buried magnetic layers. [11] The first X-ray magnetic circularly polarized dichroism spectroscopy measurement was published in 1987 by Schütz et al. [8] The first imaging of ferromagnetic domains was pioneered in 1993 by Stöhr et al. [11] Also, the spatial resolution of the first PEEM paper revealing magnetic domains published in Science is about 1 μm in 1993 shown in Figure 2-10. [11] Nowadays the current PEEM has the resolution down to tens of nanometers. In other words, PEEM is an important surface-sensitive technique to monitor domains on magnetic films.

Figure 2-9 PEEM images taken by various X-ray energies on a CoPtCr magnetic recording disk. (A) XMCD contrast images of magnetic domains on a CoPtCr magnetic recording disk, recorded with applying polarized X-rays at three fixed energies in eV. (B) X-ray absorption average spectra obtained on the same illuminated area of the magnetic recording disk near the Co L edges with polarized X-rays and parallel (dashed line) and anti-parallel (solid line) alignment of photon spin and magnetization vectors, respectively. [11]

Figure 2-10 High-resolution PEEM images with patterns. Patterns such as these are often used to test the resolution of the microscope. (A) High-resolution XMCD images. (B) Image intensity averaged over most of the vertical bit height plotted as a function of the distance along the rows. The observed pattern is that of the written magnetic bits, the squares having a dimension of 10 μm by 10 μm in the first row, the bits in the second row measuring 10 μm by 2 μm , and the bits in the third row measuring 10 μm by 1 μm as the limit spatial resolution. [11]

PEEM setup

The schematic of a PEEM setup is shown in Figure 2-11. Secondary scattered electrons escaping off the sample produced by X-ray absorption events are the main source forming the PEEM image. Then, these electrons are accelerated by an external electric field in a UHV vacuum chamber and toward the microscope column. Energy and angular selection of the electrons passing through the microscope column is achieved by an aperture

in the back focal plane of the objective lens. Then, a series of electronic lenses like optical lenses are used to magnify a spatially electronic image and project these ejected electrons on a phosphor screen, showing a visible image. Therefore, PEEM with polarized X-rays is a non-destructive technique of X-ray absorption microscopy, particularly recording magnetic images on surface or even buried layers of multilayer magnetic films.

Figure 2-11 Schematic of X-ray photoelectron microscopy. The X-rays are only moderately focused in order to match the "field of view" of an electron microscope. Electrons emitted from the sample are projected with magnification onto a phosphor screen and the image can be viewed in real time at video rates. The spatial resolution is determined by the electron optics within the microscope, the size of the aperture and the operation voltage. [12]

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Chapter 3 Literature review of LSMO films on STO substrates

In this literature review, there are three sections. First, understanding other sample treatments on the STO substrates is also a necessary review although we have our own recipes mentioned in chapter 2. Thus, we will briefly introduce one of the methods as an example in section 3.1. Next, we are not only interested in understanding how to optimize PLD-grown LSMO films, but also the distinct mechanisms of the magnetic dead layers (MDL) in LSMO films in the consecutive sections.

3.1 Sample preparations of (001) STO substrates

The goal of doing substrate pretreatment here was to generate atomically flat STO substrates. In order to reduce the surface roughness on STO substrates, possessing a singly TiO_2 terminated plane on the surface was required prior to the deposition process of LSMO films. Thus, chemical processes on STO substrates are utilized in the following details. The substrates were treated with a solution mixture of NH_4F and HF in an ultrasonic vessel. Then, they were annealed at a temperature of 950°C for 75 minutes with continuous oxygen injection in a tube furnace, suggested in the literature by Ohnishi et al. [1] In this way, the atomically flat surfaces with step-and-terrace morphology have been obtained for STO by AFM images shown in Figure 3-1(a)-(d). [2]

Figure 3-1 AFM images of a STO substrate. (a) AFM image of unetched surface topography of the STO substrate. (b) AFM image of a typical STO substrate after etching with solution composed with NH_4F and HF . (c) AFM image of surface morphology of the treated STO substrate with a red line across the steps. (d) an AFM line cut across the terraces in (c). [2]

3.2 Optimized PLD-grown LSMO films

3.2.1 Oxygen partial pressures correlated with magnetic properties of LSMO films

In addition to having high quality substrates, understanding optimized growth conditions for PLD-grown LSMO films onto STO substrates is necessary. Thus, introducing the relevant investigations in the literature is essential for finding potential effects on magnetic properties of LSMO films (oxygen partial pressures and annealing temperatures etc.) In the following, we will focus on these studies in this section.

(It should be noted that there are a lot of variations in the reported optimal conditions and this is due to the fact that each PLD chamber differs a bit, resulting in small differences in gas flow and temperature. The conditions were typically optimized for their system, though the method of that optimization can vary.)

The first cited reference here is for 50 nm thick LSMO films grown on STO substrates with their optimized growth conditions. As reported by Wang et al. [2], oxygen partial pressure is an important factor for the Curie temperature transition point of the LSMO films shown in Figure 3-2. The experimental details and relationship among oxygen partial pressures and the Curie temperature were also systematically discussed. LSMO thin films were fabricated on (001) STO single crystal substrates by using a PLD with a 248 nm KrF pulsed laser. While the substrate temperature was maintained at 750 °C, the oxygen partial pressure was varied from 0.001 to 0.4 mbar (or 0.75 to 300 mTorr). After the PLD deposition of LSMO films, samples were

annealed for about 30 minutes in the PLD chamber under the same growth partial pressure.

The Curie temperature of 50 nm thick LSMO films is above 350 K for growth pressure of 0.3 mbar (225 mTorr), which is close to the bulk Curie temperature of about 369 K [3]. More specifically, there are two resultant features in this paper. First, it has been found that oxygen deficiency has an influence on the decreasing Curie temperature, but the situation is more complicated for the magnetization. For these 50 nm films, there seems to be two oxygen pressures the give strong low temperature magnetization (0.001 and 0.2 mbar), though the low pressure has a much lower transition temperature. Second, based on the highest Curie temperature, T_c shown in Figure 3-2(b), the substrate temperature of 750 °C, the post-annealing treatment onto the PLD-grown LSMO films, and the oxygen partial pressure of 0.3 mbar (225 mTorr) are the optimal thin-film fabricating conditions.

Figure 3-2 Magnetic properties of 50 nm thick LSMO on STO grown at different oxygen pressures. (a) Temperature dependence of magnetization for 50 nm thick LSMO films with different oxygen partial pressure. Note: The diamagnetic contribution (best observed by negative magnetization at high

temperature) to magnetization has been attributed to the substrate. (b) The Curie temperature, T_c with different oxygen partial pressure. [2]

The next reference shows a different perspective. When the thickness is less than 50nm, varying oxygen growth pressure would not only affect the Curie temperature, T_c but also the magnetization in LSMO films [4] . In comparison with Wang et al. (50 nm LSMO) [2] and Huijben et al. (28 nm LSMO) [4], the differences in perspectives are oxygen partial pressure and the post-annealing treatment, respectively. According to Huijben et al. [4], these observations indicate that the treatment of the post-annealing did not improve the magnetic properties. Furthermore, Huijben et al. concluded that oxygen deficiencies are responsible for the reduced magnetization, which was not seen in the previous report on thicker films. [2].

One further detail shown by Huijben et al. is the RHEED patterns of ultrathin LSMO films with thickness from 70 to 3 unit cells (28 to 1.2 nm). For the films, the growth dynamics were determined by monitoring the intensity oscillations of the reflection high-energy electron-diffraction (RHEED) patterns. The RHEED has been proven to be a very versatile technique for growth and surface studies of thin films and also been used to investigate the growth of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin films. [5-7] RHEED is a method to monitor smoothness during growth. The authors may be likely to attempt to find whether the surface morphology would affect their magnetization. (However, our group also utilizes RHEED to ensure high quality films and use X-ray reflectivity to measure LSMO thickness and roughness in a larger scale than AFM images.) Now, we go back to this paper. The systematic unit-cell-controlled growth process has been reported by Huijben et al. [4] Figure 3-3 shows the clear oscillations of the RHEED intensity recorded during the initial

growth of LSMO on STO surfaces. For Figure 3-3(a) and (b) growth at 100 and 200 mTorr, continuous layer-by-layer growth can be observed by obvious RHEED oscillations. But, the RHEED oscillations at 300 mTorr vanish dramatically due to the growth mode variations from layer-by-layer to island formation, resulting in the increase of thin-film roughness after ~10 unit cells. This result was confirmed and measured by AFM, showing aggregations of forming islands on the surface of the sample done by the other group. [2]

Figure 3-3 Surface analysis by RHEED during initial growth of LSMO on TiO_2 terminated STO (001) substrates at oxygen deposition pressures of (a) 100, (b) 200, and (c) 300 mTorr. The insets display the RHEED diffraction patterns after the growth of 70 unit cells (~28 nm) thick LSMO layers. [4]

In Huijben's work, the dynamic growth process of PLD-grown LSMO films was monitored by RHEED. RHEED oscillations are typically present in films that grow layer-by-layer with a high quality of smoothness. But, as RHEED is a measure of smoothness during growth, RHEED oscillations do not necessarily correlate with the optimized magnetic properties. Hence, temperature dependence of the magnetization was measured by a Quantum Design superconducting quantum interference device (SQUID) in the temperature range of 10 to 380 K shown in Figure 3-4. These results related

with the previous RHEED oscillations claim that oxygen growth pressure (not the thin-film surface morphology) in the 28 nm thick PLD-grown LSMO films is a significant factor for the reduction of magnetization. For example, even though the sample of LSMO films grown at 100 mTorr is grown with a smooth surface based on the RHEED oscillation, this sample has inferior magnetization. To understand this, we should remember that the oxygen deficiencies result in a main influence on the magnetic properties of LSMO films, leading to three phenomena: (i) the increase in the coercive field (the zoomed in hysteresis loop in Figure 3-4 (a)), meaning magnetic moments in the films become less sensitive to a direction change of the applied field and more energy with wide hysteresis loops will be wasted for application aspects, (ii) the reduced magnetization, and (iii) the decrease in the Curie temperature. And, the post-annealing treatment cannot improve the magnetic properties. Therefore, the optimum growth conditions were found to be at 750 °C in 200 mTorr of O₂. The following discussion will refer only to LSMO films of different thickness grown under their optimized conditions.

Figure 3-4 Magnetic properties of 28 nm thick LSMO on STO grown at different oxygen pressures. (a) Magnetic hysteresis loop measured at 10 K. The inset shows an enlargement of the loop near the origin. (b) Temperature dependence of the magnetization measured at 100 Oe. All samples were field cooled at 1 T from 360 K along the [100] direction before the measurements were performed. [4]

3.2.2 Magnetization in LSMO films of different thickness and features of MDL

The limitation of applications in magnetic films is an occurrence of the MDL while decreasing down to the critical thickness. In the following results, scientific evidence and possible mechanisms will be investigated and discussed about characterization of the MDL. As shown in Figure 3-5, the

results of different thicknesses of LSMO films have revealed that the coercive field (H_c) as well as Curie temperature (T_c) are almost constant down to the thickness of 13 unit cells (5.2 nm). In other words, the coercive field H_c is increasing from the 8 to 3 unit cells shown in Figure 3-5(a). They concluded that the so-called magnetic dead-layer thickness is about 3.2 nm, lower than the result (~ 4.0 nm) for the LSMO films on STO reported by M. Angeloni et al. [8] In short, **these features of the MDL in magnetometry include the suppressed saturation magnetization, the increased coercive field H_c , and the reduced Curie temperature** relatively lower than room temperature shown in Figure 3-5(a) and (b), respectively.

Figure 3-5 Ferromagnetic properties of ultrathin LSMO films on STO. (a) Magnetic hysteresis loops measured at 10 K. (b) Layer-thickness dependence on the coercive field H_c and the Curie temperature T_c . [4]

3.3 Distinct mechanisms of the MDL in LSMO films

3.3.1 Charge redistribution at the interface

To further explore the microscopic details of the MDL, J.-S Lee et. al. took X-ray absorption spectroscopy (XAS) measurements with total electron yield (TEY), which is a surface sensitive technique that probes about 4-10 nm (or about 10-25 unit cells LSMO films). [9] The XAS measurements are photo-excited transitions at the Mn 2p edges, meaning 2p to 3d transitions were recorded between 640 and 665 eV. Due to the spin-orbit coupling effects, the Mn 2p core levels split into two broad peaks, which are the L_3 ($2p_{3/2}$) edge at lower photo energy and the L_2 ($2p_{1/2}$) at higher photon energy. As can be determined by comparing with reference spectra, the peak shapes and chemical shifts are very sensitive to the 3d ground state configuration as well as the crystal-field interactions, which can be used to study the 3d occupation states of the transition-metal ions. [10] As a reminder, the average Mn valence of the bulk LSMO is 3.3^+ as mentioned in Chapter 1. Here, the mixed-valence of LSMO films with various thickness could be observed by the XAS at the Mn $L_{2,3}$ -edges and shown in Figure 3-6. It was observed that the interfaces with STO had relatively more Mn^{3+} . For example, the thick LSMO film (90 unit cells) at the Mn L_3 -edge on the surface is closer to Mn^{4+} . On the hand, the average Mn valence of our thin LSMO film (4 unit cells) is near Mn^{3+} . This implies that the LSMO films has an inhomogeneous distribution of the Mn valence, related to the degraded magnetization. A similar charge transfer is observed at the recently popular polar interface of $LaAlO_3/SrTiO_3$. Similarly, the charge redistribution observed at the $LaAlO_3/SrTiO_3$ interface may be likely due to localized oxygen vacancies. [11]

Figure 3-6 Thickness dependent XAS on LSMO. The A and B positions are identified by Mn³⁺ and Mn⁴⁺, respectively. [9]

3.4 Summary

In the prior reviewed literature, oxygen incorporation affects the Curie temperature and surface morphology during the growth of epitaxial LSMO films. The substrate temperature (750 °C) and oxygen pressure (200 mTorr) are the optimal growth conditions, indicating smooth surface morphologies, ferromagnetic properties and the Curie temperature above room temperature. **But, each PLD system may still have a little difference with their own optimized growth parameters.** Based on their individual thin-film growth recipes, LSMO films of different thickness on the STO substrates can further be systematically investigated to understand the MDL. The critical thickness of the MDL may be 3.2 or 4 nm. It depends on the individual

research group's optimal growth conditions. However, the mechanisms causing the MDL are in debate. **Correlations of charge redistribution, oxygen vacancies, strain as well as orbital ordering are likely at the heart of the physical phenomena for causing magnetic dead layer.**

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Chapter 4 Imaging interfacial ferromagnetic and ferroelectric domains in magnetoelectric $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ heterostructures

Photoemission electron microscopy (PEEM) was discussed as a non-destructive technique of X-ray absorption microscopy, particularly useful for visualizing magnetic images on surface or even buried heterostructures at the interface. Based on this perspective, PEEM can be used to image both interfacial ferromagnetic and ferroelectric domains in the same locations of coupled $[\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (LSMO/PZT)] heterostructures. The LSMO/PZT heterostructures are called multiferroics. Multiferroics have at least two of the following properties—ferroelectricity, ferromagnetism, and ferroelasticity in the same phase. The term is usually used to describe the magnetoelectric multiferroics. The most promising among the magnetoelectric multiferroics are systems that have both properties of ferroelectricity and ferromagnetism. The magnetoelectric multiferroics have a coupling of magnetic and electric fields, causing a magnetization (polarization) proportional to an electric (magnetic) field. In other words, this allows the possibility to control one by the other. Thus, these LSMO/PZT heterostructures may provide potential applications such as next generation bits for data storage.

Strong magnetoelectric coupling between magnetization and ferroelectric polarization occurs at the LSMO/PZT interface. As a consequence, if the ferromagnetic LSMO layer starts to lose its magnetization (such as by reducing the LSMO thickness), the interfacial magnetoelectricity will decrease. We discovered that below a certain magnetic layer thickness (sometimes called the magnetic dead layer), we also lost the

uncompensated interfacial spin (a signature of interfacial coupling), suggesting a simultaneous magnetoelectric dead layer. **Thus, not only was the work the first ever observation of the uncompensated spin at a magnetoelectric interface, but we also discovered the thickness limits for this coupling.** Note that prior work in the Holcomb group [1] found that thinner films would better support interfacial magnetoelectric coupling, but this work shows that there is some limit to how thin will still work. This chapter will be separated by three sections in the following. Section 4.1 will start from an introduction of multiferroics. Section 4.2 is about sample preparation of LSMO/PZT heterostructures by using pulsed laser deposition. Since single-phase multiferroic materials are rare in nature and their magnetoelectric responses are either relatively weak or occurs at temperatures too low for practical applications, multiferroics in composites are fabricated instead. This approach promises an independent optimization of the ferroelectric and ferromagnetic films, which make them available for technological applications. Last but not least, results and discussion are presented in section 4.3 to illustrate our first observations by PEEM: (1) imaging magnetic and ferroelectric domains in the same locations of LSMO/PZT heterostructures; (2) uncompensated Ti spins at the LSMO/PZT interface and the perpendicular orientation of the interfacial Ti spins; (3) determining the magnetoelectric dead layer thickness via quantitative data analysis on PEEM images.

4.1 Multiferroics

Based on magnetic, electric and mechanical properties, multiferroics are defined as a single-phase material or composite materials that contain more than one of the primary ferroic properties, exhibiting hysteresis loops. We will focus on magnetoelectric multiferroics shown in Figure 4-1, as they have a great interest for potential device applications which allow us to control the ferroelectricity by using an applied magnetic field or to manipulate the ferromagnetism by using an applied electric field. [2] Single-phase magnetoelectric multiferroics, simultaneously having both ferromagnetic and ferroelectric properties in the same material, are indeed rare in nature. Some examples of single-phase multiferroic materials are some of the rare earth manganites perovskite oxides. BiMnO_3 is a single-phase magnetoelectric multiferroic material which undergoes ferroelectric (FE) and ferromagnetic (FM) transitions when cooled below 500 K (T_c^E) and 100 K (T_c^M), respectively. [3,4] Notably, the ferromagnetic transition temperature, T_c^M is below the room temperature. It is useful to understand the fundamental requirements of ferroelectric, ferromagnetic and magnetoelectric multiferroics in the following introduction.

Figure 4-1 Multiferroics combine the properties of ferroelectrics and magnets. In the ideal case, the magnetization of a ferromagnet in a magnetic field displays the usual hysteresis (blue), and ferroelectrics have a similar response to an electric field (yellow). If we manage to create multiferroics that are simultaneously ferromagnetic and ferroelectric (green), then there is potential to have a magnetic response to an electric field, or, vice versa, the modification of polarization by magnetic field. [2]

Requirements of ferroelectric, ferromagnetic, and magnetoelectric multiferroics

Single-phase magnetoelectric multiferroics are rare and have significant drawbacks such as weak magnetoelectric coupling and low transition temperatures [3,4]. But, knowing the requirements of ferroelectric, ferromagnetic, and magnetoelectric multiferroics in theoretical descriptions is still essential prior to new research fields in multiferroics in next subsection.

Symmetry governs physics, in particular a broken symmetry leads to a phase transition. [5] Shown in Figure 4-2, ferroelectric materials typically possess a time reversal symmetry, but exhibit a broken symmetry in space inversion. On the other hand, ferromagnetic materials typically possess a

space inversion symmetry, but a broken symmetry in time reversal. So, in order for both ferroelectric and ferromagnetic orders coexist, one of them has to occur from an unusual means. Since composite multiferroic thin films made up of a magnetic and ferroelectric layer are to be synthesized and tuned the coupling in labs, we will continue to present **fundamental properties of LSMO/PZT** and **new research fields in multiferroics**, particularly for introducing reasons why we choose these heterostructures in this work.

Figure 4-2 Time reversal and spatial inversion symmetry in ferroics. [5]

a. Ferromagnets. The local magnetic moment $\mathbf{m}$ may be represented classically by a charge that dynamically traces an orbit, as indicated by the arrowheads. A spatial inversion produces no change, not time reversal switches the orbit and thus $\mathbf{m}$. **b. Ferroelectrics.** The local dipole moment $\mathbf{p}$ may be represented by a positive charge that lies asymmetrically within a crystallographic unit cell that has no net charge. There is no net time dependence, but spatial inversion reverses $\mathbf{p}$. **c. Multiferroics** that are both ferromagnetic and ferroelectric possess neither symmetry.

Fundamental properties of $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$

$\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) is a ferroelectric (FE) material presenting electrical polarization changes under a spontaneous phenomenon or by applying an external electric field. More specifically, the ferroelectric tetragonal phase in PZT crystalline structure at 80 mol% PbTiO_3 reveals spatial displacement of the B-site cations resulting in a net pointing-up spontaneous electrical polarization, P along the out-of-plane direction shown in Figure 4-3 as the green region while the temperature is below the critical temperature (about $T_c^E=723$ K). [6] On the hand, if when the temperature is above T_c^E as the light yellow area in Figure 4-3, the Zr and Ti cations are symmetrically located at the center position of the paraelectric cubic phase, meaning there is no net electrical polarization present. In other words, the changes in PZT structure and displacement of B-site cations produce electrical polarization illustrated in ferroelectric materials. It is worth mentioning that the T_c^E of PZT in ferroelectric tetragonal phase is greatly above room temperature, useful for practical applications. All ferroelectrics (including PZT) are also piezoelectric materials, which can generate a voltage difference through structural deformations in crystals, and vice versa. Applications of piezoelectric devices could have numerous examples in our daily lives such as activating LEDs on children's shoes by walking, delicate and sensitive stage and position controllers in a microscope operated by pressing and energy-harvesting highways and walkways through utilizing PZT or other relevant materials into these designs and products. The PZT lattice parameters for in-plane and out-of-plane are 3.935 and 4.135 Å, respectively.

Figure 4-3 Phase diagram of $Pb(Zr_{1-x}Ti_x)O_3$ structure [6]

New research fields in multiferroics

Most single-phase multiferroic materials - materials that show spontaneous magnetization and polarization simultaneously at ambient conditions - exhibit multiferroicity only at low temperature. [3,4,7,8] Alternatively, composite multiferroics can be fabricated instead by pulsed laser deposition or other growth techniques. [1,9-12] This composite approach promises an independent optimization of the ferroelectric and ferromagnetic properties and thus a chance to tailor the functionality of the thin film stack within a broader range of the physical parameters. The recent advances in the preparation and characterization of well-defined thin oxide films have enabled to a new research strategy in the field of multiferroicity, building upon layer stacks of ferromagnetic and ferroelectric thin films. [10] In recent work on two-phase multiferroic materials, Lu et al. reported an electrical modulation of magnetization in a $\text{BaTiO}_3/\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ bilayer by switching the ferroelectric BaTiO_3 polarization directions. [11] Our group studied the interfacial Mn valence on the related system of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO)/ $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (PZT) heterostructures (Zhou et al.) to investigate the magnetoelectric effect. **The leading source of magnetoelectric coupling at the interface may likely arise from the screening of ferroelectric surface charge.** [1] $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ is a significant ferroelectric material with a ferroelectric Curie temperature above room temperature. Hence, ferromagnetic LSMO and ferroelectric PZT films are good selections to study interfacial magnetoelectricity in LSMO/PZT heterostructures. Next, section 4-2 will introduce sample preparation before presenting results and discussion in section 4-3, focused on imaging ferromagnetic and ferroelectric domains in the same locations of LSMO/PZT heterostructures.

4.2 Experimental details

PLD-grown wedged samples were used to study thickness-dependent ferromagnetic LSMO layers on top of flat ferroelectric PZT layers. Wedges causing small thickness variation across the film can be made by use of a programmable shutter during growth. The advantage of the wedged samples is to reduce amount of preparing multiple flat samples and time due to mounting them onto a sample holder, which should be placed into a low-temperature and high-vacuum chamber at the PEEM beamline in synchrotron facilities. The growth parameters were calibrated by X-ray diffraction, surface roughness in atomic force microscopy, and the layer by layer oscillations observed with reflection high energy electron diffraction (RHEED). [1] During the growth, the oxygen growth pressure in the chamber was set as 100mTorr, as determined to be optimal. The heating temperature on the SrTiO_3 (001) substrate was set as 685°C for LSMO and 620°C for PZT, respectively. The laser intensity was 1 J/cm² at 10 Hz for LSMO and 15 Hz for PZT. Based on these growth conditions, multilayers of wedged top LSMO (0-10nm)/flat PZT (180nm)/flat LSMO buffer (5nm) grown on STO were further systematically investigated by TEM shown in Figure 4-4, the Mn and Ti L-edge XAS and XMCD spectra in Figure 4-5, and the photoemission electron microscopy (PEEM) images in Figure 4-6. Similar LSMO/PZT/LSMO multilayers have been utilized to study ferroelectric capacitors [13] and strain-driven exchange bias. [14] An interface may indicate a few unit cells of the films, increasing the probing difficulty and limiting experimental approaches that will work to study these systems.

Cross-section transmission electron microscopy is a powerful technique (yet destructive due to cutting samples) for showing structural characteristics in bulk [15,16] and interfaces. [17] Shown in Figure 4-4, cross-section scanning transmission electron microscopy can probe elemental specificity between layer-by-layer interfaces. The purpose of spatially scanning elemental maps can illustrate whether there is atomic diffusion observed at the interfaces. The STEM image was taken by our collaborators at North Carolina State University by a probe corrected FEI Titan 60-300 STEM equipped with a high brightness field emission gun (X-FEG) and a Super-X energy dispersive X-ray (EDX) spectrometer. The atomic resolution EDX maps of the cations are shown on the side where Pb (pink), Mn (green), and Ti (red) elements are presented with different colors. [12] Thus, the lack of color mixing from this EDX mapping indicates that the interface shows no observable atomic diffusion.

Figure 4-4 Atomic resolution EDX maps of the cations are shown on the side where Ti (red), Mn (green), and Pb (pink) elements are presented in color. [12]

4.3 Results and discussion

XAS and PEEM images

Interfacial research on multilayer perovskite (ABO_3) materials can also be investigated through synchrotron-based X-ray absorption spectroscopy (XAS), which is a non-destructive and powerful technique. We will focus on the Ti and Mn L-edges to understand the ferroelectric, magnetic and interfacial properties.

As presented in Figure 4-5(a), the Auger electrons and secondary electrons were generated by specific incident X-ray energies and those yielded electrons would be further collected, analyzed and shown as images. Illustrated in Figure 4-5(b), the X-ray photons were absorbed by electrons localized in 2p core levels, having transitions from the $2p_{1/2}$ and $2p_{3/2}$ levels to unoccupied 3d levels due to the spin-orbital coupling that is L+S and L-S where $L=1$ and $S=1/2$, respectively. Thus, the lower energy value is labeled L_3 edge. On the contrary, the higher energy should be L_2 edge marked in Figure 4-5(c) as well. Both of Ti and Mn L-edges X-ray absorption spectra are demonstrated in Figure 4-5(c). Owing to various energy splitting between 2p and 3d states in Ti and Mn L-edges, their characteristic absorption peaks could be measured at specific ranges via tunable incident X-ray energies. However, there are two peaks originating from each 2p core level to unoccupied e_g and t_{2g} states in common d^0 orbitals at the L-edge of Ti. That is why there are more than two peaks shown in Ti L-edges labeled as L_{3A} , L_{3B} , L_{2A} , L_{2B} , respectively. Thanks to the probing length of the TEY-XAS technique of about 5-10nm, the intensity of total electron yields even originating from the buried layers such as PZT behind LSMO films can be

detectable within the detecting range. Therefore, we could measure two different absorption edges located on the same spot of the sample by adjustable incident X-ray energies with two helical polarizations shown in Figure 4-5(c).

Through changing directions of circularly polarized light, the difference taken from the two XAS results and then divided by the sum of the two XAS was shown in Figure 4-5(d) as Mn XMCD spectra with LSMO films as a function of thickness. Those data were taken at beamline 6.3.1 at the Advanced Light Source. This surface-sensitive TEY-XAS technique via varying left and right circularly polarized X-rays shows that the thicker LSMO film (5.2nm) exhibits obvious dichroism at Mn L-edges on average, equivalently probing empty density of states for 3d spin-up (magnetic moment down) and spin-down (magnetic moment up) electrons in terms of the relative strength of Mn magnetic moments.

Figure 4-5 (a) Scheme illustrates the creation of Auger and secondary electrons due to incident X-rays. Note: Exponential curve represents the percentage of the signal originating from a given depth within the sample. As shown by the exponential decay, when the top layer is thicker, a smaller percentage of the interface and layer 2 signal will complete the journey involving more scattering events and escape the sample to the detector. It should be noted that the measurement spot size is much smaller than the wedge region, so each spot measured will present a specific thickness (not varying). (b) Illustration of absorption L-edge (2p to 3d transition) showing two energies due to spin-orbit splitting and thus two peaks are expected. (c) The spectral L-edges for both Ti and Mn are shown, each exhibiting an L_3 and L_2 peak or multiple peaks in the case of Ti. (d) The dichroism asymmetry is created by taking the difference in the spectra with reversed magnetic field or light polarization over the sum of these spectra. This dichroism decreases as the magnetic layer thickness approaches the magnetic dead layer. [12]

The magnetic sensitivity of Mn PEEM images

In order to get electrons out of the sample and get a PEEM signal, the energies of incident radiation should be greater than the work function of the materials and binding energies. The spatial distributions of escaped electron intensities varying at tunable incident X-ray energies and polarizations can be collected and analyzed as a PEEM image. So, both measuring local spectra from buried layers or imaging PEEM at selective energies and polarizations are valuable methods for understanding and visualizing interfacial magnetic domain orderings of bilayers and tri-layers such as FM/AFM bilayers related with interfacial uncompensated spins and

exchange bias and FM/non-magnetic FM/(NM) heterostructures, correlated with magnetic tunnel junctions at interfaces. [18,19]

To image a magnetic material, XAS with left and right circularly polarized X-rays will be sensitive to the net magnetic moments parallel and anti-parallel to the incident X-ray direction. The electron yield intensities at absorption edges would be slightly different depending on whether they are taken with left or right circularly polarized light. As shown in Figure 4-6, the plots of the XMCD asymmetry versus incident X-ray energy show strong dichroism at L_3 and L_2 absorption edges. However, PZT is a ferroelectric material instead of a ferromagnetic material. Since ferroelectrics are not typically ferromagnetic, the XAS spectra for Ti probed by circular polarized X-rays would normally be the same, indicating no magnetic dichroism in XMCD spectrum. **Thus, any unusual dichroism result observed by left and right circularly polarized light on the non-ferromagnetic element absorption edge such as Ti of PZT layers has to be due to uncompensated magnetism, due to the proximity of the magnetic layer (which does not contain Ti).** [20] Note that Ti does not normally exhibit net magnetization. In order to understand magnetic properties at interfaces, PEEM images of Mn and Ti in Figure 4-6 were measured at beamline 11.0.1 at the Advanced Light Source. Images on the left side of Figure 4-6 belong to 3.6nm LSMO and the figures on the right side are 2.8nm LSMO grown on top of a flat PZT layer. Note that the magnetic “dead” layer thickness for LSMO is 3.2 nm (in between these two thicknesses). For each thickness, those pixel-by-pixel Mn and Ti images were obtained with incident LCP and RCP X-rays at the same locations. The incident angle from the normal of the incident X-ray radiation was 60 degrees

from the direction normal to the surface and these cryo-PEEM measurements were executed at $T=105\text{K}$, to increase the magnetic signal.

Imaging electron yield intensity in PEEM images of Mn with LCP and RCP light are presented in Figure 4-6(a) to (d) for the 3.6 and 2.8 nm LSMO films, respectively. At first, we focus on the PEEM images for the 3.6 nm LSMO. Note that the spatial intensity contrasts marked inside the purple circles in Figure 4-6(a) and (c) are reversed and switched by two different X-ray polarizations. **This reversal is the signature of a net magnetization signal in PEEM.**

By using the two different polarized light (the LCP and RCP), the intensity reversal in pixels in the same location are due to magnetic domains in the spatial distribution. More specifically, we can notice that the directions of the ferromagnetic domains are fixed in the spatial distribution. The exciting thing here is we can visualize and identify the spatially magnetic domains in the same locations of the LSMO/PZT heterostructures via the intensity reversals for the PEEM images. In order to image the spatial distribution of magnetic domains, the scale bar in electron yield intensity (0-255) is with three false colors. In other words, directions of ferromagnetic domains parallel to the incident X-ray direction as a high intensity (yellow, 170-255), anti-parallel as a low intensity (blue, 0-85), and perpendicular as an electron yield signal between the high and low intensities (green, 85-170) are depending on which circular polarization of light we are using.

Thus, after comparing images taken from RCP and LCP X-ray polarizations together, the switched contrast in pixels are due to magnetic domains. As shown in Figure 4-6(b) and (d), the 2.8nm thick LSMO layer

shows less contrast which is consistent for this thickness below the critical magnetic dead layer resulting in a degraded magnetization on magnetic films. [22] The Mn asymmetry images which are treated by $(\frac{I_{LCP}-I_{RCP}}{I_{LCP}+I_{RCP}})$ on each pixel-by-pixel with LCP and RCP images are shown in Figure 4-6(e) and (f), showing the magnetization projection along the incident X-ray direction. Thus, the blue areas show domains areas pointing to the left direction; on the contrary, the red areas show domains area point into the right direction. The fact that much of the asymmetry image is white or light in color (indicating small change with polarization) does not necessarily indicate that most of the film is nonmagnetic, since domains perpendicular to the incident X-rays will not reverse intensity. [12] To fully map the magnetic domains, one would want to rotate the sample by 90 degrees and repeat that discussed images; however, mapping was not the goal of this work.

The magnetic sensitivity of Ti PEEM images with uncompensated magnetic moments

Presented in Figure 4-6(g)-(j), the images of PZT domains in the buried layer exhibit considerably less resolution and more statistical noise than the images of the magnetic domains on the covering LSMO layer. As the electrons from the PZT layer have to travel through the full thickness of the LSMO layer to make it out of the sample, fewer of electrons will arrive at the detector. [12] Thus, the Ti asymmetry images are important to quantify the weak reversal signals with switching X-ray circular polarization. The weak but significant contrast in intensity with LCP and RCP Ti L-edge images originates from uncompensated magnetic spins at the interface of FM/FE bilayers.

As PEEM imaging can be sensitive to sample roughness, it is important to verify that the signal is not just due to interface roughness. To average the sum of RCP and LCP images shown in Figure 4-6 (m) and (n) can demonstrate whether or not the weak intensity contrast may come from surface roughness or dust particles. Typically, the images are normally uniform white unlike those asymmetry images instead of other two colors, red or blue as an uneven surface. The few red spots on the images are dust particles. Since they are not ferromagnetic materials, the illumination electron intensity would cancel with each other in asymmetry images. On the other hand, those dust particles or particulates as the non-magnetic would be highlight and marked in the chemical images. Therefore, there is no significant correlation with small roughness proven by the Ti chemical image. The weak intensity contrast with Ti LCP and RCP images is uncompensated magnetic spins at the LSMO/PZT interface. [12]

Now that we have determined that our interfacial contrast is real and due to net magnetization at the interface, correlations between the Mn and Ti images can inform as to how the layers correspond to each other. The interfacial magnetic directions for Mn and Ti atoms by varying LSMO thickness from 3.6 to 2.0 nm are first unveiled in Figure 4-6(o), where a_{Mn} is the Mn asymmetry and a_{Ti} is the Ti asymmetry magnitudes in average for each pixel extracted at the same sample location, respectively. Let us set the vector $\mathbf{a} = (a_{\text{Mn}}, a_{\text{Ti}})$, where the magnitude and angle of the vector $\mathbf{a}$ can be interpreted as a measure for the relation of the Mn and Ti asymmetries for each image pixel. [12] For example, when the vector $\mathbf{a} = (a_{\text{Mn}}, a_{\text{Ti}})$ is along either the horizontal or vertical axes, the only one element is significantly marked, corresponding to the largest contrast in Mn (Ti) asymmetry (parallel

(+) and anti-parallel (-) domain directions) and the nearly zero intensity change in Ti (Mn) asymmetry (perpendicular domain directions) to the incident left circularly polarized (LCP) X-ray direction, respectively. This situation would correspond to the uncompensated spins being perpendicular to the magnetic directions. Note that there is a slight preference for when one of the asymmetries are large, the other is small, which indicates a preference for perpendicular coupling. As expected, the average magnitude of a_{Mn} significantly decreases for the LSMO thickness from 3.6 nm to 2.8 and 2.0 nm, which are thinner than reported magnetic dead layers, suppressions of magnetic ordering domains [21].

Thus, through pixel-by-pixel comparisons of Mn and Ti asymmetry images and the statistical analysis plotted in Figure 4-6(o), the aligning direction of the coupling of Mn domains and Ti spins in spatial distributions prefers to be perpendicular. This work is not only the first observation of uncompensated spin at a ferroelectric/ferromagnetic interface, but also the first observation of a preference for perpendicular coupling of uncompensated spin to the magnetization of the adjacent magnetic films in the LSMO/PZT heterostructures.

Figure 4-6 PEEM images of Mn and Ti L-edges showing magnetic and uncompensated spin directions. This figure illustrates (a-f) Mn and (g-l) Ti images. The asymmetry $a=(LCP-RCP)/(LCP+RCP)$ is shown in all asymmetry images (e, f, k, and l).

Note: (i) The colored arrows indicate the magnetic direction to which the LCP and RCP colors correspond. The left columns of images were all taken at the same sample location and the same scale, for a LSMO thickness of 3.6 nm. The right columns of images were all taken at a different sample location from the left column, where the LSMO thickness was 2.8nm and the switching was significantly reduced.

(ii) The image (m) and (n) show the Ti chemical contrast for different thickness of LSMO. The image (o) is a polar plot relating the Mn and Ti asymmetries for different thickness of LSMO. The anisotropy of the asymmetry polar plot indicates a preferred perpendicular orientation between the Mn ferromagnetic direction and the Ti interfacial spins. [12]

Statistical analysis on PEEM images

From the Figure 4-6 (o), this polar plot reveals that the Mn (Ti) asymmetry is the largest while the asymmetry of Ti (Mn) is small. This indicates that the uncompensated Ti spins at the interface are perpendicular to magnetic domains in LSMO. In addition to indicating the perpendicular orientation of the interfacial spins, the Mn asymmetry significantly decreases due to having the suppressed magnetization when the LSMO thickness decreases from 3.6 nm to 2.8 nm. In order to further analyze whether the drop in magnetization affects the interfacial spins, we compared the Mn and Ti

signals as we changed the thickness of the top LSMO layer. There was previously no method utilized in PEEM literature to quantify the amount of switching, so we developed one. It was needed in order to verify that the interfacial contrast we observed was not just from noise. While we tried a lot of other methods, our most useful approach is shown in Figure 4-7, showing a scatterplot of pixel intensities from a LCP image of the Mn L-edge for 5.2 nm LSMO versus the change in intensity with a RCP image. While nearly one million pixels were analyzed for each thickness, only random subset of 100,000 pixels is shown in Figure 4-7 to make the graph easier to view and interpret for the reader. Blue dots represent the average change for all pixels, including all pixels beyond the random selection. With the blue average dots, a clear V shape is visible. The result can be better understood by considering a few examples. If the magnetic domains are ferromagnetic domains aligned along the incident X-ray direction, blue (low) and yellow (high) intensity should reverse, resulting in the |LCP-RCP Intensities| with a large difference. On the other hand, the green (medium and perpendicular) domains will maintain a similar contrast observed in the middle range. Since the center of the x-axis is 127, the slope of a line going from (0, 255) to (127,0) is -2; Likewise, the second half of the V shape has a slope of 2. In short, the ideal slope is +2 and -2 which are indicative of strong contrast switching and a slope of 0 would be no systematic switching. [12] For a thicker 5.2 nm LSMO, this shows the value close to the ideal slope, but not perfect due to noise. As one moves to thinner films, the magnitude of the slope for the Mn ferromagnetic domain images decreases, as would be expected as we approach the magnetic dead layer.

Figure 4-7 Scatterplot of a random selection of pixel intensities from a left circularly polarized (LCP) image of the Mn L-edge for 5.2 nm LSMO versus the change in intensity with a right circularly polarized light. [12]

Blue dots show the average change in intensity for every pixel for each LCP intensity. The red fit shows the best fit to the data given that it should be centered at $255/2$. In previous discussions of these types of images in the literature, people only discussed the low intensity images that switched to high intensity with polarization switch (shown by blue box), the high intensity images that changed to low (the yellow box) and the medium intensities that stayed the same (the green box). Thus, all points outside of these colored boxes would have been ignored as “outliers” which cuts out a significant portion of the data! Our new approach of using the slope is more thorough.

There is a similar trend of the pixel intensity change is seen in the Ti data with decreasing the LSMO thickness shown in Figure 4-8. If the measurement of the interfacial Ti uncompensated spins were strongly influenced by passing through a thicker top LSMO layer, the opposite trend would be expected, as it would be harder for yielded electrons traveling from the interface through a thicker LSMO layer. However, thicker LSMO yields a higher fit slope and thus more uncompensated Ti spins at the interface. On the other hand, while the LSMO layer on top of the PZT layer approaches its magnetic dead layer about 2.8 nm, interfacial uncompensated Ti spins are induced less in PZT. The right-hand side of the y axis of Figure 4-8 shows another method for determining switching, beside the slope method. Basically, we took histograms the frequency of the difference of the absolute value of LCP image intensity – RCP image intensity shown in Figure 4-9. We looked at what percentage of our domains fell above a difference of $255/3 = 85$. This method produced very similar results to our slope method.

Having observed very similar trends with two very different analysis methods, we conclude that the reduction in the magnetism in magnetic thin films also causes a reduction in the interfacial coupling leading to uncompensated Ti spins. As stated previously, we had determined in other work that thinner films would have stronger magnetoelectric coupling due to having a larger percentage of this interface, though this work says that we either have to deal with a limit to this improvement, or we need to figure out how to stop the reduction in magnetization in thin films.

Figure 4-8 LSMO thickness dependent slope from Figure 4-7 and percentage switching for dichroism images from both the Mn and Ti L-edges. [12]

Figure 4-9 (a) Histograms of $|LCP - RCP \text{ Intensities}|$ in bins of 5 for 5.2 nm LSMO measured on the Mn edge and (b) 3.6 nm LSMO measured on the Ti edge. [12]

Summary

According to comparisons of PEEM images and statistical analysis in LSMO/PZT heterostructures, we have listed three first observations in the following: (1) We present the first observation of uncompensated spins at a ferromagnetic/ferroelectric interface. Similar uncompensated spin at ferromagnetic/antiferromagnetic interfaces has long been studied to understand exchange bias coupling at the interface. Although Ti is not a normally magnetic element, this work observes that magnetism can be induced at the interface between LSMO and PZT layers, forming the nonzero Ti circular dichroism measured by PEEM images. (2) We present the first observation of uncompensated spin with a preference for perpendicular coupling to ferromagnetic domains in a oxide system. (3) We have the first observation of a magnetoelectric dead layer. According to combinations of PEEM images and statistical analysis, the magnetoelectric dead layer occurs for about 2.8 nm LSMO. Additionally, we developed a method to quantify contrast switching between two images, that could be applied well beyond PEEM images. The V shape method reveals the amounts of uncompensated Ti spins induced by thickness-dependent LSMO layer. The perfect slope is +2 and -2 which are indicative of strong contrast switching. The deviations from the perfect slope is due to a weak contrast switching.

The presence of a magnetic dead layer is supposed to cause a degradation of ferromagnetism in average, usually expected to occur at the interface and/or surface. Another possibility is that there is no specific layer or layer of lost or reduced magnetization, but the whole film is uniformly lost. This uniform loss seems less likely given how common it is for surface properties to different from bulk material properties. However, the magnetic

dead layer is not fully explored in LSMO or most materials. In order to understand more about where is the magnetic dead “layer”, polarized neutron reflectivity will be performed in LSMO and introduced in chapter 5.

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Chapter 5 Probing magnetic depth profile of the LSMO film

By imaging ferromagnetic domains and ferroelectric uncompensated spins in the previous chapter, we found that the “magnetoelectric dead layer” in the LSMO/PZT system occurs when LSMO films are thinner than 2.8 nm and occurs simultaneously with the ferromagnetic dead layer. In other words, if the ferromagnetic layer begins to lose its magnetic order, the coupling between the ferroelectric and magnetic layers will also decrease or even disappear. Thus, we are left with a new problem—how do we prevent the magnetic dead layer, which will also improve the efficiency of some purely magnetic applications. It would be helpful to understand where this loss in magnetism is occurring—only at the surface or throughout the material? The location of this magnetic loss can have strong effects on its influences on devices and our ability to prevent it. In order to understand where is the “ferromagnetic dead layer” in the LSMO film, we eliminate the ferroelectric layer and investigate the magnetic properties of the LSMO film deposited on a (001) STO substrate.

The main goal in this chapter is that probing the magnetization depth profile at surface and interface through the LSMO film is achievable, as will be intensively discussed below. Section 5.1 is associated with the sample preparation and section 5.2 discusses X-ray reflectivity (XRR), a complementary probe with the polarized neutron reflectivity (PNR). Probing the magnetic depth profile in the LSMO film through polarized neutron reflectometry will be introduced in the following two sections, respectively. Section 5.3 includes the theoretical basics of polarized neutron reflectometry. Finally, section 5.4 discusses the PNR results in the LSMO film, including

why the ferromagnetic dead layer(s) may occur and the magnetization profile across the LSMO/STO interface by the PNR measurement.

5.1 Experimental details

Sample preparation

In order to achieve a high-quality interface of the LSMO/STO heterostructures as well as this well-defined chemical and magnetic depth profiling measured by polarized neutron reflectivity, some prior treatment of the substrate on which we grow LSMO is necessary. The (001) SrTiO_3 substrate consists of alternating SrO and TiO_2 planes along the c -axis orientation. Since the surface termination plane of SrTiO_3 would affect the sequence of the PLD-grown film, singly terminated SrTiO_3 substrate is a necessary requirement before growing LSMO onto the substrate in order to obtain a smooth interface. Because TiO_2 terminated SrTiO_3 with the lowest surface energy was predicted to be energetically favorable to affect the stability and properties of the epitaxial film on the perovskite substrate [1], we use the SrTiO_3 substrate with a well-controlled TiO_2 terminated surface for our studies. In order to have the atomically flat SrTiO_3 substrate, chemical and thermal treatments on the SrTiO_3 substrate were necessary. The (001) SrTiO_3 single crystalline substrate was first ultrasonically cleaned into acetone, isopropanol, and deionized water for 5 minutes and then thermally treated at $1100^\circ\text{C} \times 2$ hours. After cooling down to room temperature, the substrate was ultrasonically cleaned into deionized water for 5 mins and again annealed at $1100^\circ\text{C} \times 2$ hours. Finally, a singly TiO_2 terminated SrTiO_3 (001) substrate was obtained. After the above procedure, the substrate was

placed into the epitaxial growth chamber of pulsed laser deposition (PLD; KrF excimer laser, $\lambda=248$ nm) with an energy density of 3.1 J/cm^2 . The substrate temperature was maintained at 750°C during the growth. The PLD-grown LSMO film was deposited on the SrTiO_3 substrate under oxygen partial pressure at 100 mTorr. After finishing this LSMO epitaxial film thickness up to 17 nm as expected, the oxygen partial pressure was raised from 100 mTorr to 450 mTorr during cooling to room temperature. Once a high-quality sample is produced, we need to characterize our sample. The top priority is to find the sample thickness and surface roughness of the LSMO/STO heterostructures. Hence, X-ray reflectivity (XRR) can be used in order to access the above results.

5.2 X-ray reflectivity

Generally speaking, XRR is a probe to determine chemical characterization via the interaction between incident X-rays and electron clouds of the atoms in the materials. XRR was performed to reveal chemical depth profile of the LSMO film. XRR probes the laterally average electron density contrast along the surface normal, which is different for the STO substrate versus the LSMO thin film. In order to further probe characteristics of this PLD-grown LSMO film on the (001) STO substrate, XRR was measured by Bruker Discover D8 reflectometer at the WVU Shared Research Facilities. The collected XRR data were fitted and analyzed by using GenX software. [2] Sample information was obtained from XRR, mainly including the film thickness, surface roughness and interfacial roughness between the LSMO film and the STO substrate. X-ray reflectivity

(XRR) was highly recommended to be performed prior to polarized neutron reflectivity (PNR). There are at least two reasons that explain why we should measure XRR to support PNR measurements of the LSMO film. The first reason is that XRR can be a complementary probe used to provide initial given parameters in order to estimate and constrain the simulation in the PNR data. The second is that we can execute X-ray reflectivity to evaluate the film roughness and film thickness at WVU prior to performing the advanced PNR measurement in NIST. Regarding the data collection time for one sample, the whole XRR data collection should take about two hours while the entire PNR data collection should take about two days. In order to obtain the standard PNR results, both of the LSMO film and the STO substrate should be less than about 1 nm in roughness for this specular neutron optics setup. In the other words, if the film smoothness is without any validation by XRR in advance, this may indicate risks in failure for the PNR measurement due to mostly specular reflected neutrons replaced by diffuse reflection, which means that a neutron beam is scattered at many angles rather than at just one angle as in the case of specular reflection. Thus, XRR can be a necessary probe prior to the PNR measurement. Also, the specular reflectivity geometry of XRR is essentially identical to that of neutron reflectivity except that, as uncharged particles in neutrons and photons in X-rays. The XRR result of the LSMO/STO heterostructures will be further illustrated in the following.

XRR study for chemical characterization of the LSMO film

The film thickness, roughness, and scattering length density (electron density) profile can be obtained through X-ray reflectivity (XRR). Since the scattering length density (SLD) is a measure of the scattering power of a

material, the scattering power arises from the interaction between incident X-rays and the electron clouds of the atoms in the material. For X-rays, the higher electron density of a material has the higher critical angle. With the higher electron density, more intensity is scattered at higher angles. Thus, this scattering means electron density in the material. However, the specular scattering intensity can be described by the Born approximation while the specular scattering X-ray intensity is much less than the incident X-ray intensity.

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{d\rho(z)}{dz} \exp(iq_z z) dz \right|^2 \quad (5.1)$$

This specular scattering intensity $I(q_z)$ is presented by the absolute square of the Fourier transformation of the derivative of the scattering length density and divided by q_z^4 . Also, the measurement in the x-axis can be expressed in terms of a scattering wave vector $q_z = 4\pi \sin(\theta)/\lambda$ in reciprocal space because there is a non-zero scattering vector q along the surface normal. The XRR result with a simulated agreement is shown in Figure 5-1. The inset plot is the XRR normalized by the Fresnel reflectivity ($R_F = 16\pi^2/q_z^4$) in order to highlight these oscillation fringes due to the self-interference of the X-ray simultaneously reflected from the surface and interface of the LSMO film, particularly at high angles. The resultant SLD depth profile $\rho(z)$ versus z in real space is shown in Figure 5-2 via simulations in GenX. The simulated XRR result for the 17 nm LSMO film was obtained by using the two-slab model which is common in these films [3]: one slab is a bulk region of about 15.8 nm and the other slab is at surface region is 1.2 nm, respectively. Therefore, XRR is a surface-sensitive X-ray scattering technique to probe

the lateral average electron density contrast in the z direction. Even without the PNR results, XRR has provided us a significant information. The surface of the LSMO film shown in Figure 5-2 has a reduced SLD value likely associated with the magnetic dead layer, indicating the suppressed magnetization. Unfortunately, XRR cannot quantify and probe the magnetic depth profile along the surface normal. However, this can be accomplished by doing reflectivity with neutrons.

Figure 5-1 X-ray reflectivity of the about 17nm LSMO film on a (001) STO substrate, having a good simulated agreement with the two-slab model. Upper inset: X-ray reflectivity normalized by the Fresnel reflectivity to highlight the oscillations at higher angles.

Figure 5-2 X-ray scattering depth profile obtained from the best simulated result in Figure 5-1.

5.3 Theoretical basics of polarized neutron reflectometry

While X-ray reflectometry probes the laterally averaged electron density along the vertical direction of sample surface as illustrated in section 5.2, polarized neutron reflectometry not only extracts the chemical depth profile but also the magnetic depth profile of ferromagnetic materials. Neutrons are insignificantly attenuated and highly penetrating in most cases, the magnetic information at interfaces can be probed through the magnetic interactions of the spin-dependent neutrons and ferromagnetic materials. By measuring and simulating a set of spin-up and spin-down polarized neutron reflectivity, we can extract a depth-dependent magnetization profile of the LSMO film on the (001) STO substrate from the above PNR data collections. Thus, exploring the magnetization $M(z)$ depth profile through the LSMO film measured by the PNR is possible. However, introducing the mechanism of neutron-matter interactions is useful prior to presenting analyzed results. In this introduction of neutron reflectometry, I will mostly follow two articles. The first one is “Application of polarized neutron reflectometry to studies of artificially structured magnetic materials” by Fitzsimmons and Majkrzak in *Modern Techniques for Characterizing Magnetic Materials*. [4] The second one is “Neutron reflectometry” by Fermon, Ott, and Menelle in *X-ray and Neutron Reflectivity*. [5] As discussed below, the theoretical basics of polarized neutron reflectometry will be consecutively introduced in section 5.3 and results and discussion in section 5.4.

Neutron-matter interactions

For neutrons, there are two main interactions with matter. One strong interaction is with the nuclei and the other interaction is with the magnetic moments created by unpaired electrons of magnetized materials via a neutron magnetic dipole - electron magnetic dipole interaction.

Magnetic interaction

For magnetized materials, the internal magnetic induction field created by the unpaired electrons of the magnetic atoms contains two terms, the spin part and the orbital part given by:

$$B = \frac{\mu_0}{4\pi} \left\{ \nabla \times \left[\frac{\mu_e \times R}{|R|^3} \right] - e \frac{v_e \times R}{|R|^3} \right\} \quad (5.2)$$

, where $\mu_e = -2\mu_B\sigma$ is the magnetic moment of the electron, μ_B is the Bohr magneton, σ is the Pauli matrices, and v_e is the speed of the electron.

The neutron magnetic moment with a negative value is equal to

$$\mu_n = -1.913\mu_N \quad (5.3)$$

$$\mu_N = \frac{e\hbar}{2m_p} \quad (5.4)$$

, where μ_N is the nuclear magneton and m_p is the mass of a proton.

The potential energy of a neutron magnetic dipole in the internal magnetic induction field B_{ind} is given by

$$V_m = -\mu_n \cdot B_{ind} \quad (5.5)$$

Reflection on a non-magnetic medium

Reflection occurs when a wave propagation hits a plane boundary between two different media. Reflection of wave propagation can be classified as specular and diffuse reflection. Here, the reflection is the mirror-like reflection of waves, meaning that the incident angle equals the reflected angle known as specular reflection. The theory and experimental setup of polarized neutron reflectometry is almost analogous to X-ray reflectometry (XRR) except using a magnetic moment of an uncharged particle. Both are non-destructive methods. Nevertheless, there are still a few differences which will be introduced in the following. In general, reflectometry is a sensitive technique to probe the depth-dependent index of refraction. For light, the refractive index depends on a given wavelength. For example, we can find the index of refraction for two media using Snell's law. The incident angle of the incoming light is equal to the specular reflected angle of the reflecting light. Total reflection (100% reflectivity) can occur in the medium with the larger refractive index. The critical angle can be determined while the refracted beam is perpendicular to the surface normal. According to the specular scattering geometry shown in Figure 5-3, the wavevector transfer has a non-zero component perpendicular to sample surface. In contrast to X-rays, neutrons are scattered by nuclei rather than electron clouds. In this case, the Schrodinger equation is typically written as

$$\left[\frac{\hbar}{2m_n} \frac{\partial^2}{\partial z^2} + V(z) \right] \Psi(z) = E \Psi(z) \quad (5.6)$$

, where z is the vertical coordinate, the m_n is the neutron mass, and $V(z)$ is the nuclear scattering potential. The wave function $\Psi(z)$ and its derivative should be continuous at $Z=0$, the interface between vacuum and the medium. The nuclear scattering potential is

$$V(z) = \frac{2\pi\hbar^2}{m_n} \rho(z) \quad (5.7)$$

, where the $\rho(z)$ is the nuclear scattering length density (nSLD). The scattering potential $V(z)$ is proportional to nSLD. Thus, the nSLD is a function of depth along the surface normal because the neutron scattering vector q_z has a non-zero component along the surface normal shown in Figure 5-3.

Figure 5-3 Specular reflectivity geometry.

Figure 5-4 Potential energy $V(z)$ versus z between the vacuum and the medium, corresponding to Index of refraction for neutron.

$$\frac{\hbar^2 k_{vacuum}^2}{2m_n} = \frac{\hbar^2 k_{medium}^2}{2m_n} + V(z) \quad (5.8)$$

As illustrated in Figure 5-4, the index of refraction in the medium for a neutron can be written as

$$n = \frac{c}{v} = \frac{\lambda_{vacuum}}{\lambda_{medium}} = \frac{k_{medium}}{k_{vacuum}} = \sqrt{1 - \frac{2m_n \cdot V}{\hbar^2 k_{vacuum}^2}} = \sqrt{1 - \frac{\lambda^2}{\pi} \rho} = \sqrt{1 - \frac{4\pi}{k_{vacuum}^2} \rho} \quad (5.9)$$

$$n = \sqrt{1 - \frac{\lambda^2}{\pi} \rho} = \sqrt{1 - \theta_c^2} \quad (5.10)$$

$$\theta_c = \sqrt{\frac{\rho}{\pi}} \lambda \quad (5.11)$$

The quantity $1-n$ is on the order of 10^{-5} and thus n can be approximated as

$$n = \sqrt{1 - \frac{\lambda^2}{\pi} \rho} = \sqrt{1 - \theta_c^2} \approx 1 - \frac{1}{2} \theta_c^2 = 1 - \frac{1}{2} \frac{\lambda^2}{\pi} \rho \quad (5.12)$$

Since the critical angle is very small ($\sin \theta_c = \theta_c$), the corresponding scattering vector is approximately

$$\theta_c = \sqrt{\frac{\rho}{\pi}} \lambda \quad (5.13)$$

$$q_c = \frac{4\pi \sin \theta_c}{\lambda} = \frac{4\pi \theta_c}{\lambda} = \frac{4\pi}{\lambda} \sqrt{\frac{\rho}{\pi}} \lambda = \sqrt{16\pi\rho} \quad (5.14)$$

, where the critical angle of total reflection for neutron can be determined by knowing the wavelength of neutron (4.75 Å) and the ρ is the nuclear SLD (nSLD) in Å⁻². For example, the nSLD of SrTiO₃ for neutron is 3.54x10⁻⁶ Å⁻² and the LSMO is 3.69 x10⁻⁶ Å⁻². Thus, neutron reflectometry will merely yield structural information to determine the ferromagnetic LSMO film thickness and roughness measured by unpolarized neutrons. However, regarding the magnetic depth profile of the ferromagnetic LSMO film, polarized neutron reflectometry will be introduced on a magnetic medium.

Reflection on a magnetic medium

When the magnetic scattering interaction between the magnetic moment of a spin 1/2 neutron and ferromagnetic materials becomes very significant, the modified potential will be:

$$V(z) = V_{nuc}(z) + V_{mag}(z) = \frac{2\pi\hbar^2}{m_n} \rho(z) - \mu_n \cdot B_{ind}(z) \quad (5.15)$$

$$B = \mu_0 (H_{ext} + M(z)) = B_0 + B_{ind}(z) \quad (5.16)$$

Figure 5-5 The variations of potential energy $V(z)$ modulated by magnetic moments of polarized neutrons corresponding with the magnetization of the magnetic induction vector B inside the ferromagnetic materials.

Note: H_{ext} is the external applied field, μ_n is the magnetic moment of a neutron, and M is the magnetization of the material.

The potential energy is the dot product of the two vectors shown in Figure 5-6: the magnetic moment μ_n of a neutron and the magnetic induction B_{ind} of the magnetic sample. Moreover, the magnetic moment of a neutron μ_n is a negative value. Thus, this modified potential $V(z)$ will increase while the direction of neutron magnetic moment is parallel to the magnetization of ferromagnetic materials shown in Figure 5-6. Therefore, the refractive index of a ferromagnetic material such as LSMO for spin-dependent neutrons can be expressed as equation (5.18) in terms of the potential V , which is not only

dependent on the nuclear composition but the magnetic moment of a neutron relative to the magnetization.

As shown in Figure 5-6 below, the ferromagnetic LSMO film with its nuclear SLD and magnetization M should obtain two different indices of refraction for polarized neutrons due to the potential changes. To put it in another way, the neutron spin is antiparallel to the magnetization M corresponding to a higher potential energy and a larger critical scattering vector q_c along the z direction. Unpolarized neutrons, on the other hand, will simply see an average index of refraction halfway between the spin-up and spin-down cases. Thus, we can use the difference between a spin-up polarized and a spin-down polarized reflectivity to extract a depth-dependent magnetization profile of our LSMO films on (001) STO substrates.

$$V = \frac{2\pi\hbar^2}{m_n}(\rho_{nSLD} \pm \rho_{mSLD}) \quad (5.17)$$

$$n_{\pm} = \sqrt{1 - \frac{2m_n \cdot V}{\hbar^2 k_{vacuum}^2}} = \sqrt{1 - \frac{\lambda^2}{\pi}(\rho_{nSLD} \pm \rho_{mSLD})} \quad (5.18)$$

$$q_{c,\pm} = \frac{4\pi \sin \theta_{c,\pm}}{\lambda} = \sqrt{16\pi(\rho_{nSLD} \pm \rho_{mSLD})} \quad (5.19)$$

Figure 5-6 Schematic diagram of magnetic interaction between magnetized LSMO films and magnetic moments μ_n of **spin up** and **spin down** polarized neutrons.

PNR apparatus in NIST Center for Neutron Research

For this PNR measurement, we used the NG-1 Polarized Beam Reflectometer in NIST center for Neutron Research. The LSMO sample was cooled down to 5 K in field of 0.7 Tesla in order to achieve the saturated magnetization before executing the PNR experiment. The schematic beamline is shown in Figure 5-7. On the upstream side of the sample is the incident polarizer arm, which houses a monochromator, supermirror polarizer, and spin flipper. The neutron optics in this beamline uses a pyrolytic graphic monochromator to intercept the polychromatic cold neutron beam (3-30 Å) by and reflects a monochromator beam with the wavelength $\lambda = 4.75$ Å. Keeping on the upstream, there is a Fe/Si supermirror in order to filter out neutron beams of a specific spin state. Hence, the purpose of a Fe/Si supermirror is used to only transmit **spin up neutron beams** toward our sample while the **spin down neutrons** will be reflected out of the beamline. The magnetic moment μ_n of **spin up** polarized neutrons is parallel to the applied magnetic field direction (the H field) shown in Figure 5-7.

After passing through the supermirror, the aluminum coil spin flipper (Mezei spin flipper) can flip the neutron beams from spin up state to spin down state if the magnetic field is produced by applying electrical current through these aluminum coils. Therefore, this method allows us to select either spin up or spin down neutrons as the incident beam toward the specimen. The sample is side-mounted with a cryostat inside the aluminum tube and an external cryogen-free superconducting magnet.

On the downstream side of the sample is detector arm, housing a spin flipper, supermirror analyzer, and helium-3 detector. Like the supermirror polarizer on the upstream, the supermirror analyzer transmits only **spin-up** neutrons. Thus, the downstream assembly allows experimental settings to label and distinguish all four polarization sections (+ +, - -, + -, and - +) by adjusting the on/off states of these spin flippers, treating on the spin states of incoming and reflected neutrons. Since this instrument utilizes highly collimated incident and scattered beams, achieving a high degree of neutron polarization is not difficult. Typically, the beam polarization is greater than 95%, and polarization corrections to the data are minor. [6]

Figure 5-7 Elements of the NG1 Polarized Neutron Reflectometer [6]

The $R_z^{++}(q_z)$ and $R_z^{--}(q_z)$ specular reflectivity of polarized neutron beams (non-spin flip, NSF) can be described in terms of nuclear scattering length

density ($\rho_{nSLD}(z)$) and magnetic scattering length density ($\rho_{mSLD}(z)$) by the Born approximation for magnetized materials. [4]

$$R_z^{++}(q_z) \propto \left| \int [\rho_{nSLD}(z) + \rho_{mSLD}(z) \cos \phi] \exp(iq_z z) dz \right|^2 \quad (5.20)$$

$$R_z^{--}(q_z) \propto \left| \int [\rho_{nSLD}(z) - \rho_{mSLD}(z) \cos \phi] \exp(iq_z z) dz \right|^2 \quad (5.21)$$

, where ϕ is the angle of the magnetization M of the specimen and the applied external magnetic field H . The $++$ ($--$) sign denotes the magnetic moments of both incident and reflected neutron beams parallel (anti-parallel) to the applied magnetic field, corresponding to reflectivity $R_z^{++}(q_z)$ ($R_z^{--}(q_z)$). By fitting the data, we can obtain $\rho_{nSLD}(z)$ and $\rho_{mSLD}(z)$, simultaneously.

The non-spin flip specular reflectivity is determined by the laterally averaged neutron scattering length density depth profile called $\rho(z)$ perpendicular to the surface normal. For a ferromagnetic material such as LSMO thin films, the $\rho(z)$ contains nuclear and magnetic scattering length density shown in equation 5.22. And $M(z)$ is the magnetization depth profile with the units of kA/m.

$$\rho^{\pm\pm}(z) = \rho_{nSLD}(z) \pm \rho_{mSLD}(z) = \rho_{nSLD}(z) \pm CM(z) \quad (5.22)$$

$$\rho_{mSLD}(z) = 2.853 \times 10^{-9} M(z) \quad (5.23)$$

Thus, the magnetic depth profile of LSMO films from the surface to the interface can be performed and extracted via the PNR experiment in NIST Center for Neutron Research (NCNR) and further data analysis. More specifically, the Ref1D and Reductus programs were used for the PNR data reduction and analysis discussed in section 5.4. [7]

5.4 Results and discussion

PNR diagnosis on LSMO magnetization

A 17 nm thick $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film on a (001) SrTiO_3 substrate was used for the PNR study. The polarized neutron reflectivity was measured by using a polarized beam reflectometer at the NIST Center for Neutron Research. This LSMO sample was cooled down from room temperature to 5 K under an applied in-plane magnetic field of 0.7 Tesla to saturate the magnetization and then the PNR measurement was performed with neutrons with wavelength $\lambda = 4.75 \text{ \AA}$. The PNR results in Figure 5-8 are plotted in reciprocal space. According to equations 5.20 and 5.21, the chemical $\rho_{\text{nSLD}}(z)$ and magnetization depth profile $M(z)$ versus z along the surface normal can be simultaneously obtained and plotted as real space via measuring and further analyzing the R_z^{++} and R_z^{--} -data. The nuclear SLD profile initially given parameters obtained from the X-ray SLD profiles and the magnetization depth profile was obtained by using DREAM fit algorithms minimized the chi-square in the Refl1D software. [7] Thus, the simulated results of the nuclear SLD and magnetization are plotted in Figure 5-9 and listed in Table 5.1.

Similar to fitting the X-ray reflectivity data, the data best fit to a multi-layered model. There are three slabs corresponding to various magnetization depth profiles in the film: the interfacial layer between LSMO and STO, the intermediate layer between the interfacial layer and surface layer, and the surface layer between the intermediate layer and air, respectively. Unlike bulk magnetometry, some interesting changes in the magnetization across the thickness of the sample can be determined by obtaining the magnetization depth profile. For example, that thickness

average magnetization, $M_{ave}=340$ (19) kA/m, can be determined for the LSMO sample:

$$M_{ave} = \frac{1}{t} \int_0^t M(z) dz \quad (5.24)$$

, where t is the thickness of the LSMO film from the interface to the surface.

The difference between the nuclear and magnetic scattering profiles illustrates that the magnetism decreases before the surface of the sample is reached, as emphasized with the red and blue vertical lines in Figure 5-9. Based upon the determined magnetization profile, the magnetic dead layer, meaning the degraded magnetization region of about 1.7(3) nm, occurs on the surface region in good agreement with the XRR measurement in Figure 5-2. The magnetic depth profile suggests a few interesting questions. For example, the location of the dead layer brings up the question: why does magnetic layer occur at the surface of the magnetic thin film? Additionally, the magnetization increases near the interface—why? I will discuss possible explanations and related literature in the following.

Figure 5-8 Polarized neutron reflectivity of LSMO films grown at 100mTorr. The ++ (--) sign denotes the magnetic moments of neutron beams parallel (anti-parallel) to the applied in-plane magnetic field, corresponding to reflectivity R_z^{++} (R_z^{-}).

Figure 5-9 Analysis of polarized neutron reflectivity of the 100mTorr LSMO film on STO (a) obtained nuclear scattering length density and (b) magnetization depth profiles.

Table 5.1 List of parameters obtained from the PNR measurement.

Characterizations of the 100mTorr LSMO films	Total thickness (Å)	Thickness at interface (Å)	Thickness at intermediate (Å)	Thickness at surface (Å)
	166.83 +/- 10.79	56 .02 +/- 4.35	94.11 +/- 3.65	16.70 +/- 2.79
Mean magnetization	total M (kA/m)	M (interface) (kA/m)	M (intermediate) (kA/m)	M (surface) (kA/m)
	340 (19)	461 (4)	306 (5)	94 (7)

Interesting Question 1: Surface magnetization

Why does a magnetic dead layer occur at the surface?

What is magnetization? In classical electromagnetism, magnetization or magnetic polarization is a vector field that express the density of permanent or induced magnetic dipole moments in a magnetic material. Apparently, in the film there is a reduced magnetization (density of magnetic moments) on the surface region (reduced magnetization is common in many thin films systems). The magnetic moments originate from unpaired electrons which occupy the d orbitals on the Mn site of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskite structure. According to the above briefly depictions, characterization of Mn valence are strongly correlated with magnetization in this magnetic material. Hence, we can expect the lower density of magnetic moments indicates that there are fewer unpaired electrons occupied the e_g state of the d orbitals on the Mn site for the surface region, consistent with our recent study of the depth-dependent electron distribution in these heterostructures. [8] Thus, we can expect that the Mn valence located on the top slab should be possess a relatively higher valence in average than the Mn valence 3.3^+ of the bulk LSMO, which we have observed. [8] The next question is “why does the Mn

valence have a higher Mn valence on the surface and the reduced interfacial Mn valence?” As discussed below, the hypothesis is a model called charge reconstruction to illustrate the existence of a polar discontinuity at the LSMO/STO interface.

Polar discontinuity (shown in the center of Figure 5-10) occurs in systems which consist of alternate signed charges in the atomic planes on one layer (LSMO here) and neutral planes in the other (STO here). The existence of a polar discontinuity at the LSMO/STO interface causes a buildup of electric field. The internal voltage will diverge with increasing the thickness, an unphysical phenomenon called polar catastrophe (shown in the left side of Figure 5-10).

However, charge reconstruction (shown in the right side of Figure 5-10) not only can be introduced to avoid the unphysical phenomenon but also to illustrate why the magnetic dead layer occurs at the surface in terms of the Mn valence. In order to prevent this violation of material boundary conditions, the extra $0.35e^-$ transfers from the top MnO_2 layer (the increment of the Mn valence at the surface) to the bottom MnO_2 layer (the decrement of the Mn valence at the interface). With the charge reconstruction, it will result in the increased Mn valence at the surface, meaning there is a deteriorated magnetization (density of magnetic moments) on the surface region. More specifically, the experiment-resolved Mn valence on the surface is 3.7^+ in agreement with the calculated value 3.65^+ via the charge reconstruction model. [8] In other words, this raising change in Mn valence on the surface region reveals the decreasing amounts of unpaired electrons on the d orbitals of the Mn sites. Thus, the degraded density of magnetic moments

(magnetization) on the surface region is likely subject to the charge reconstruction mechanism.

In the other words, the bottom MnO_2 layer at the interface via the charge reconstruction results in accumulating or doping electrons to the interface and the reduced interfacial Mn valence. So, the charge redistribution leads to the interfacial region with the reduced Mn valence in the LSMO film. [9-12] However, the charge reconstruction is not sufficient to explain the increased magnetization at the interface. The hypothesis in the charge reconstruction constrains that the Mn valence at the rest of the LSMO layers is unchanged except the top and bottom layers.

Figure 5-10 Schematic diagrams of polar catastrophe (left), polar discontinuity (center) and charge reconstruction (right) of the LSMO/STO heterostructures.

However, is the polar discontinuity model correct? In order to understand Mn valence studies for relevant experimental results, I need to cite two of our results from R. Trappen et. al. shown in Figure 5-11 and 5-12, respectively. [8] From the Figure 5-11, the expected bulk Mn valence for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is 3.3 shown as the horizontal dashed line. Above 4 u.c., the Mn valence probed by FY-XAS (the bulk-sensitive technique) wavers around 3.3 for the films. On the other hand, the Mn valence probed by TEY-XAS (the surface-sensitive technique) is greater than 3.3. But, the two modes get a similar Mn valence with decreasing the film thickness approaching to the interface of LSMO/STO heterostructures.

In order to explain the variations of layer-resolved Mn valence, the depth-dependent fit was created by combining both surface and bulk sensitive valence measurements and assuming a smooth transition of the valence layer by layer. The result of the plane-resolved Mn valence is obtained and shown in Figure 5-12 after modeling both of FY-XAS and TEY-XAS data originated from Figure 5-11. The main point from the paper shows that while the Mn valence at the surface is about 3.8^+ due to the charge reconstruction, the Mn valence at the interface is about 2.7^+ less than 2.95^+ expected by the polar discontinuity model. In other words, it indicates that there are additional charge accumulations to adjacent Mn sites at the interface, meaning the reduction of Mn oxidation state. The likely mechanism is oxygen vacancies, which may also enhance the interfacial magnetization. Hence, in order to further the cause, we will continue to discuss the interesting question 2. Why is the magnetization enhanced at the interfacial layer?

Figure 5-11 Mn valence determined by TEY-XAS (red solid points) and FY-XAS (black square points) measurements. Four fits by using depth-dependent models where the surface and interface valence vary (solid lines) and do not vary (dashed lines) with thickness-dependent LSMO films. The horizontal dashed line indicates the expected Mn valence for the bulk LSMO is 3.3. [8]

Figure 5-12 Plane-resolved Mn valence for thickness of 1-8 u.c. LSMO. For example, the black square point refers to the valence of a monolayer u.c. LSMO film. The red round points indicate while the higher valence is at the surface, the lower valence at the interface. The horizontal black dashed line

indicates the expected bulk Mn valence of 3.3. With increasing the film thickness along the expected tendency (the blue dashed line), to explain the interfacial enhanced magnetization. [8]

Interesting Question 2: Interfacial magnetization

Why is the magnetization enhanced at the interfacial layer?

Although there is still ongoing debate to understand the interfacial magnetization in LSMO/STO heterostructures, different mechanisms have been reported to support the observed cases of either the enhanced or suppressed magnetization at the interface, including polar discontinuity induced charge redistribution [13-16], stoichiometry differences from the bulk LSMO such as oxygen vacancies [8,17] and the interfacial oxygen octahedral behavior in LSMO/STO heterostructures. [18]

From the charge redistribution model shown in Figure 5-10, the reduced Mn valence at the interface and the increased Mn valence at the surface might be not enough to comprehensively illustrate this roughly 5-6 nm thick region of enhanced interfacial magnetization. In fact, the above discussed polar discontinuity model constrains that the Mn valence is on average 3.3^+ , as is bulk LSMO. However, the Mn valence indeed changes along the growth direction. [8]

Here, there are two possible explanations associated with the interfacial magnetization profile. First of all, there is one of possible explanations associated with “oxygen missing”, formally called oxygen vacancies. The question is how to explore the characterization of oxygen vacancies at the interfacial region.

Presumably, if we can have the direct observation of the Mn^{2+} peak at the interfacial region about 5-6 nm via TEY-XAS results, the enlargement of charge accumulations can vary the average Mn valence from the mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ to $\text{Mn}^{2+}/\text{Mn}^{3+}$ observed at the interface. In order to prove the perspective, the TEY-XAS results with different thickness in LSMO films are shown in Figure 5-13. The growth conditions of these thickness dependent LSMO samples are the same as the 17 nm LSMO sample measured by the PNR result. We can notice that the yellow blocks and black dashed line indicate the Mn^{2+} oxidation states significantly begin to be observed at the interfacial region about 5.2 nm that is consistent with the PNR result, presenting the 5.6 nm thick located at the interfacial region with the enhanced magnetization.

Figure 5-13 TEY-XAS with different LSMO film thickness on (001) STO substrates grown at an oxygen partial pressure of 100 mTorr.

Next, in order to better understand the correlation of the enhanced magnetization at the interface and oxygen vacancies, the 17 nm LSMO films grown at a series of deposited oxygen partial pressure are shown in Figure 5-14. Conventionally, oxygen vacancies can be seen as electron donors, which mean to decrease the number of the holes and increase the ratio of Mn^{3+} in LSMO. This will impair the double exchange between Mn^{3+} and Mn^{4+} , leading to the degraded magnetization in average shown in Figure 5-14 while the deposited oxygen partial pressure decreases to 25 mTorr. This also indicates the modification of Mn valence states due to the direct coupling between Mn ions and oxygen vacancies [19]

Nevertheless, the oxygen vacancy effect can also play a very important role on the enhanced magnetization in perovskite films with the decrease of the oxygen partial pressure such as LaMnO_3 , a parent material of the doped perovskite manganites. [20] Similarly, increasing the oxygen vacancy concentrations in the LSMO films can raise the saturation magnetization shown in Figure 5-14. The saturation magnetization of the 17 nm LSMO films significantly increased with the decrease of the deposited oxygen partial pressure when the pressure was less than 25 mTorr. Since double-exchange interaction is responsible for their ferromagnetism, the $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratio can influence the strength of the magnetization. With raising the amount of the Mn^{2+} states induced by the increase of the density of oxygen vacancies, resulting in the enhancement of the double exchange interaction. Therefore, the saturation magnetization increases with changing the oxygen vacancy concentrations. Any off-stoichiometry of the LSMO (such as formations of oxygen vacancies) would likely be subject to a different depth profile of the Mn valence, resulting in charge accumulation on the interface region.

Raising densities of magnetic moments on the Mn site originates from forming the enlargement of the ratio of mixed $\text{Mn}^{2+}/\text{Mn}^{3+}$ states at the interfacial region in average, and the interfacial enhanced magnetization observed by polarized neutron reflectivity.

Figure 5-14 The saturation magnetization M_s of the 17 nm LSMO films with the various deposited oxygen partial pressure measured by PPMS, Quantum Design.

Another alternate reason is associated with “oxygen tilting” instead of oxygen missing. For example, Li et. al. imaged the MnO_6 octahedral tilt across LSMO/STO interface by scanning transmission electron microscopy to understand increased interfacial magnetization shown in Figure 5-15. [18] The evolution of the oxygen octahedral tilt angle increases nonlinearly and reaches a saturated value of 6.8 degrees after 9 unit cells (3.6 nm) of LSMO. In addition, the sample from the cited literature were grown at an oxygen pressure of 200 mTorr instead of 100 mTorr in our studies. Therefore, these

films have similar growth conditions, and the properties of strongly correlated materials like LSMO can be very sensitive to these growth conditions (particularly the oxygen growth pressure). This approach may give us an additional insight to investigate the relevant characterization of structural and magnetic parameters: interfacial magnetism and oxygen octahedral tilting angle from interface to surface. We have recently started a collaboration with a transmission electron microscopy group (James LeBeau) to further explore this possibility.

Figure 5-15 Line profiles of octahedral tilting angles along the $[110]$ zone axis and c-axis lattice parameter across the interface. [18]

Summary

Utilizing PNR, the layer-by-layer magnetization was quantitatively determined in the LSMO thin film grown on a (001) STO substrate. A surface region of suppressed magnetization with a thickness of about 1.7 nm was measured by X-ray reflectivity (XRR) and polarized neutron reflectivity (PNR). On the other hand, the magnetization near the interface with the substrate was enhanced.

The phenomena for these changes from the bulk magnetization can be further illustrated by the following possible mechanisms. Polar discontinuity induced charge reconstruction leads in the inferior surface magnetization. On the contrary, the increased magnetization profile at the interfacial region can be likely subject to oxygen vacancies. If oxygen vacancies occur at the LSMO/STO interface, obtaining a degraded magnetization profile from the interface to surface, we also can fabricate other LSMO films grown at lower oxygen pressures and therefore more oxygen vacancies for PNR studies to further understand their magnetic properties. Oxygen octahedral tilt could be an additional research orientation to understand the correlation of structural and magnetic parameters at the interface, as we are beginning to explore.

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Chapter 6 Future research

Direct observation of interfacial coupling and magnetism in [La_{0.7}Sr_{0.3}MnO₃/BaTiO₃ (LSMO/BTO)] heterostructures probed by neutrons and X-rays

In our lab, we not only study LSMO/PZT and LSMO/STO heterostructures but also LSMO/BTO heterostructures. The two materials form a magnetic and ferroelectric interface. Since the oxygen growth partial pressure on the heterostructures has a strong correlation with numbers of oxygen vacancies, it will also affect the magnetization in LSMO/BTO heterostructures. Ferroelectric screening effects by oxygen vacancies have been observed to alter the interfacial Mn valence correlated with the interfacial magnetism. In short, the interfacial Mn valence can be different by changing the polarization in ferroelectric materials and likely associated with studies of oxygen vacancies. Fabricating and characterizing the LSMO/BTO heterostructures at the coupling interface can further understand the interfacial magnetism controlled by electricity in potential applications.

However, in my opinions, our goals are to build up a systematic insight or methodology in order to understand characteristics in perovskite heterostructures. Thus, we likely can combine two distinct experimental methods together by neutrons and X-rays in this future research. For example, we can explore the magnetization depth profile of the LSMO/BTO heterostructure by using polarized neutron reflectivity and probe the uncompensated Ti spins at the interface between LSMO and BTO layers. And then, Statistical analysis on the PEEM techniques about studies of ferroelectric control of oxygen vacancies is necessary. In other words, we

can study the influences of oxygen vacancies and how they will affect magnetic properties across the whole sample.

Structural characterization in the heterostructures

In addition to having the research orientation, structural properties of the LSMO/BTO heterostructure are important to understand the heterostructures. We have developed other relevant techniques for understanding the structural characterization. For example, we have built up standard instructions for experimental measurements at WVU Shared Research Facility: lattice parameters and strain effects in LSMO/BTO heterostructures can be revealed by reciprocal space map (RSM) and the built-in codes for RSM plots. The XRR simulation for the LSMO/BTO heterostructures can be accessible to obtain their thickness and roughness, respectively.

Temperature dependence of magnetic dead layer in the LSMO thin film by using polarized neutron reflectometry

Using polarized neutron reflectometry has been used to study the interfacial magnetism and magnetic dead layer via modeling the LSMO thin film measured at the temperature, $T=5$ K. However, if the thickness of this magnetic dead layer in the LSMO film may be possible temperature dependent, it may imply that the extended MDL would occur within the LSMO film with increasing the temperature. Thus, a series of temperature dependent PNR results in the LSMO film will be a significant in order to quantitatively obtain the effective magnetic thickness in the LSMO film in the future research.