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TITLE Defect Analysis and Microstructural Effects on the Surface Exchange Properties

of La_{0.7} Sr_{0.3}MnO_{3-δ} (LSM) Epitaxial Thin Films

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Abstract

 $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM) is a perovskite oxide material that possesses many interesting electromagnetic and electrochemical properties, making it desirable as magnetic tunnel junction (MTJ) and solid oxide fuel cell (SOFC) electrodes. Applications of LSM are strongly influenced by the presence of epitaxial strain and extended defects. The primary focus of this thesis are: (1) to characterize the crystal structure of and the extended defects in epitaxial LSM thin films under strain; and (2) to correlate microstructure (such as strain and defects) with the surface exchange properties of $(110)_{pc}$ LSM surfaces. Towards that end, LSM thin films with well controlled thickness, geometry, stoichiometry, surface morphology and microstructure were deposited by pulsed laser deposition (PLD). X-ray diffraction (XRD) and electron channeling contrast imaging (ECCI) were used to study the crystal structure and extended defects. The electronic conductivity and oxygen surface exchange properties were determined by electrical conductivity relaxation (ECR). The results suggest that the crystal structure of $(110)_{pc}$ - oriented LSM is strongly dependent on strain, being monoclinic under in-plane tensile strain, and orthorhombic under in-plane compressive strain. Structural modifications in LSM thin films induce extended defects, such as anti-phase boundaries (APB) related to MnO₆ octahedra tilting in LSM films on SrTiO₃, and coherent domain boundaries related to the orthorhombic structure in LSM films on $NdGaO_3$. In addition, a strong correlation between microstructure and the oxygen surface exchange properties of $(110)_{pc}$ LSM was discovered. Tensile strain enhances surface exchange coefficient (k_{chem}) and lowers the activation energy (E_a) , while compressive strain increases E_a . Extended dislocations generated during strain relaxation enhance the oxygen surface exchange kinetics (k_{chem}) by up to 25 times on $(110)_{pc}$ LSM on STO. In addition, coherent domain boundaries in LSM film on NGO enhance k_{chem} by 1 order of magnitude. Overall, microstructure (strain and defects) can change k_{chem} up to two orders of magnitude on $(110)_{pc}$ surface of LSM. These findings offer direct experimental insights into the "microstructure - property" relationship of doped lanthanum manganites. They open up windows for improving the surface reaction kinetics of LSM electrodes via defect engineering and microstructure control in solid oxide fuel cell cathodes.

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Miaolei Yan September 1, 2015 Pittsburgh, PA

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CHAPTER I

Introduction

1.1 Motivation

Materials microstructures, such as epitaxial strain and extended defects, can significantly impact their functional properties and performance, enabling new devices and physical phenomena with improved properties by up to several orders of magnitude.^{1–4} Recent developments in atomically controlled growth have been shown to be crucial in engineering strain and defects in epitaxial oxide heterostructures. For functional oxide thin films, the electronic,^{5,6} magnetic,^{7,8}, ferroelectric^{1,2} and electrochemical^{9–11} properties are strongly dependent on epitaxial strain at the film-substrate interface. In addition, commonly observed defects in thin films, such as dislocations,^{12,13} grain boundaries,^{14,15} twin boundaries,¹⁶ and antiphase boundaries,¹⁷ can severely impact the functional properties. Thus, strain and defect analysis and defect engineering of functional materials are topics of great research interest.

 $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM) is a perovskite oxide material which possesses many interesting electromagnetic and electrochemical properties. It exhibits room temperature ferromagnetism, colossal magnetoresistance, and its electronic conductivity shows nearly 100% spin polarization.^{18–20} This makes LSM thin films desirable as magnetic tunnel junction (MTJ) electrodes, where the (110)_{pc} orientation (pc denotes pseudocubic notation) is preferred due to a strong uniaxial anisotropy and an ability to eliminate interfacial charge transfer.²¹ In addition, LSM is commonly used as cathode material for solid oxide fuel cells (SOFCs) due to its high activity towards oxygen reduction reaction at elevated temperatures.^{22,23} Unfortunately, upon lowering the operation temperature of SOFCs, LSM cathode polarization increases exponentially and accounts for the majority of total cell losses.²⁴ At the fundamental level, this is due to the sluggish kinetics of oxygen reduction reaction (ORR) on cathode surface.^{25,26} Understanding the effects of microstructure (such as strain and extended defects) on the surface exchange properties of LSM provides unique opportunities to overcome this limitation and to achieve more efficient SOFC cathodes. Previous studies primarily focused on the (100)_{pc} orientation of LSM using thin film electrodes.^{9,15,27} Although recent studies have suggested that the (110)_{pc} surface exhibits the higher activity towards oxygen exchange reaction compared with other low index orientations.²⁸

Specifically, this thesis aims at addressing the following questions relating strain and defect engineering to oxygen surface exchange properties in LSM thin film electrodes:

- 1. What are the crystal structures of epitaxial $(110)_{pc}$ LSM thin films under tensile and compressive strain induced by the film-substrate lattice mismatch?
- 2. What are the resulting defect types and their distributions and how to characterize defects nondestructively on the mesoscale in epitaxial oxide thin films?
- 3. What are the effects of epitaxial strain and extended defects (such as dislocations and coherent domain boundaries) on the surface exchange properties of $(110)_{pc}$ LSM thin film electrodes?

Answers to these questions will offer direct experimental insights into the "microstructure - property" relationship of LSM. They would also open up windows for improving SOFC cathode performance by improving the the surface reaction kinetics of LSM electrodes via orientation, strain and defect engineering. This is the basic motivation for the research work conducted in this thesis.

1.2 Research narrative

Understanding and optimizing the oxygen reduction reaction (ORR) kinetics on LSM cathode is one of the key challenges to developing efficient and stable energy conversion fuel cells. Materials engineering through microstructure control has offered promises in this direction. As mentioned before, the physical and electrochemical properties of LSM can be strongly influenced by epitaxial strain and extended defects.^{7,8,21,29} For example, the electronic band gap, the surface electronic density of states,⁶ and the oxygen surface exchange properties⁹ of LSM thin films are strongly dependent on strain. In addition, grain boundaries in LSM thin film electrodes exhibit oxygen reaction kinetics that are several orders of magnitude higher than native LSM grains.^{15,30} Thus, understanding the effects of strain and extended defects is important towards achieving more efficient LSM functional devices, including better cathodes for SOFCs.

Thin film electrodes are excellent proxies to study the correlation between microstructure and oxygen exchange properties of LSM material. As will be discussed in **Chapter II**, actual fuel cell cathodes contain complex microstructures, including pores, different surface orientations, different surface morphologies, dislocations, grain boundaries and triple phase boundaries.^{31–33} They can exhibit different catalytic properties and mask the intrinsic material response.^{23,34} In comparison, thin film electrodes offer unique advantages in controlling the microstructure and extended defects at the solid-gas interface.^{27,35} The use of thin film electrodes also facilitates the understanding of oxygen reduction reactions by improving the accuracy of transport measurements and assisting in the identification of fundamental reaction mechanisms and pathways.^{36,37}

This thesis aims at investigating the effects of epitaxial strain (both tensile and compressive) and extended defects (such as dislocations and coherent domain boundaries) on the oxygen reduction reaction kinetics of $(110)_{pc}$ - oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ thin film electrodes. The LSM $(110)_{pc}$ orientation was selected since it exhibits higher ORR activity compared with other low index orientations.²⁸ Epitaxial LSM thin films were deposited on $(110)_{c}$ - SrTiO₃ and $(100)_{o}$ - NdGaO₃ single crystal substrates to induce tensile and compressive strain, respectively (where c and o represent cubic and orthorhombic notations, and $(100)_{o}$ is equivalent to $(110)_{pc}$). The crystal structure and extended defect populations in these films were characterized by X-ray diffraction (XRD) and related techniques, electron channeling contrast imaging (ECCI), and transmission electron microscopy (TEM). Special focus was placed on characterization of surface-penetrating dislocations, antiphase boundaries and other coherent domain boundaries. Strain status and defect content were then correlated to the surface exchange properties measured on well controlled LSM (110)_{pc} thin film surfaces. The results highlight the importance of strain and defect engineering in modifying the electrochemical properties of complex oxides.

1.3 Hypotheses

The overall hypothesis in this study is that epitaxial strain and extended defects (including dislocations and coherent domain boundaries) affect the oxygen surface exchange properties $(k_{chem} \text{ and } E_a)$ of LSM. The detailed hypotheses are as follows:

- 1. Epitaxial strain induced by film-substrate lattice mismatch can modify both the MnO_6 octahedral rotations and the crystal structure of epitaxial LSM thin films. Modifications to the MnO_6 octahedral rotations can result in anti-phase boundaries (APBs), while changes in the crystal structure can induce the formation of domain boundaries.
- 2. Strain relaxation through dislocation generation in LSM thin films is a kinetically governed process. Post-deposition annealing and controlled cooling can be used to control the relaxation status and dislocation generation and propagation in LSM thin films. Also, fully relaxed LSM thin films exhibit higher dislocation density than coherently strained films.
- 3. Epitaxial strain increases/decreases the oxygen surface exchange coefficient (k_{chem}) and the activation energy (E_a) of $(110)_p c$ LSM surface. Tensile strain and compressive strain likely have different effects.
- 4. Extended defects, such as surface penetrating dislocations and coherent domain boundaries, can affect the local oxygen exchange kinetics on (110) LSM surfaces. Higher densities of extended defects result in faster k_{chem} values on $(110)_p c$ LSM surfaces.

1.4 Approach

To correlate strain and defects with material surface properties, a method to consistently control strain, characterize defects and measure the surface properties must be established. Towards that end, high quality, epitaxial LSM thin films were deposited by pulsed laser deposition (PLD) onto lattice mismatched perovskite single crystal substrates in order to induce epitaxial strain. The crystal structures of as deposited thin films were characterized by X-ray diffraction (XRD) and reciprocal space mapping (RSM); their thickness and growth rate by X-ray reflectivity (XRR); their surface morphology by atomic force microscopy (AFM); their defect content and defect distribution on the meso- and atomic-scale by X-ray rocking curve (RC), electron channeling contrast imaging (ECCI), and transmission electron microscopy (TEM). Finally, the oxygen surface exchange properties of well characterized LSM thin film electrodes were measured by electrical conductivity relaxation (ECR).

1.5 Organization

This document is organized into the following parts: **Chapter I** introduces the objectives, hypotheses and experimental approaches of the overall study. **Chapter II** summarizes the recent progress on understanding the behaviors of common SOFC cathode materials, and outlines the remaining challenges in determination of the "structure-property" relationship. **Chapter III** describes the experimental techniques and conditions used for data collection. In the results sections, **Chapter IV** details the discovery and characterization of antiphase boundaries (APBs) related to MnO₆ octahedral rotations in (110)_{pc} LSM thin films grown on (110)_c SrTiO₃. **Chapter V** reports the evolution of crystal structure distortions and dislocation generation during strain relaxation of LSM thin films on (110)_{pc} LSM thin films on (100)_o NdGaO₃. **Chapter VII** correlates the effects of epitaxial strain and extended defects (dislocations and coherent domain boundaries) with the oxygen surface exchange properties of LSM (110)_{pc} surfaces. Finally, **Chapter VIII** summarizes the conclusions of this thesis and outlines the importance of microstructure control in designing better functional oxide materials for fuel cell applications.

CHAPTER II

Background

2.1 Chapter overview

This chapter summarizes the relevant literature in the field of SOFC cathode research and defect analysis techniques in thin films. Section 2.2 provides a general background of solid oxide fuel cell cathodes and $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3-\delta}$ (LSM) material. Section 2.3 summarizes the experimental determination of the oxygen transport kinetics on common cathode materials, and highlight the advantages of thin film model electrodes. Section 2.4 details the understanding of oxygen reduction reaction mechanisms and pathways. Section 2.5 highlights the effects of surface orientation, strain and extended defects on the oxygen transport properties of cathode materials. Finally, Section 2.6 summarizes the experimental methods for defect characterization in thin films.

2.2 Solid oxide fuel cell (SOFC) cathode

2.2.1 SOFCs and cathode reactions

Solid oxide fuel cells (SOFCs) are electrochemical devices that directly convert chemical energy stored in fuel to electrical energy through an electrochemical process. Their name is derived from the fact that all components use solid-state materials, typically mixed conducting transition metal oxides that conduct oxide ions at elevated temperature.³¹ SOFCs have been regarded as attractive clean energy solutions to address the world's increasing demand for energy consumption. Compared with traditional energy technologies, the major advantages of SOFCs include: high energy conversion efficiency, ability to oxidize various fuel types (hydrogen, hydrocarbons and even carbon), and quiet operation.^{31,32,38} A schematic of a solid oxide fuel cell (SOFC) during operation is shown in **Figure 2.1**. The fuel cell has three functional components: a porous cathode layer where oxygen reduction happens, a porous anode layer where fuel oxidation happens, and a dense electrolyte layer that separates the two and conducts oxygen ions. Electrons transfer through the outside circuit to complete the reaction cycle, producing useful work along the way.



Figure 2.1: Schematic of the solid oxide fuel cell (SOFC) during operation. Hydrogen fuel (blue spheres) on the anode side and oxygen gas (red spheres) on the cathode side are separated by a dense electrolyte layer that conducts O^{2-} . Electrons transfer through the outside circuit for electricity generation.

Traditional SOFCs operate with perovskite structured $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) cathodes at temperatures between 800 – 1000 °C.^{38,39} Intensive research efforts have been directed at lowering the SOFC operation temperature to 500 – 800 °C, where they are referred to as intermediate temperature solid oxide fuel cells (IT-SOFCs).^{26,40} Operation in this temperature range reduces cost by replacing the expensive chromium oxides or chromium-based metal alloy interconnects with much cheaper steel-based alloys.^{25,35} Lower operation temperatures also significantly reduce mechanical failures due to thermal stress and materials interdiffusion.^{26,34,41}

Unfortunately, since many of the electrochemical reactions that the fuel cells rely on are thermally activated, SOFC performance (including output power and current density) suffers an exponential decrease at lower operation temperature.²³ The kinetics of reactions that are sensitive to operation temperature include: oxygen ionic transport across the electrolyte layer, fuel oxidation in the anode layer, and oxygen reduction reaction (ORR) in the cathode layer. Recent studies have identified that, at intermediate temperature, 80% of total fuel cell efficiency loss is due to cathode polarization caused by the sluggish ORR kinetics.²⁴ Therefore, optimizing the ORR kinetics in SOFC cathodes is one of the key challenges to improving the energy conversion efficient of SOFCs.^{23,25,26}

The overall electrochemical reaction governing the cathode performance is known as the oxygen reduction reaction (ORR). In this reaction, oxygen molecules in the gas phase $(O_2(g))$ are reduced to oxide ions (O^{2-}) and then incorporated into the lattice, usually via oxygen vacancies $(V_o^{..})$. For anion deficient oxides, the ORR equation is given below, using the Kröger-Vink notation, where $V_o^{..}$ is the oxygen vacancy, O_o^* is the lattice oxygen, and $h^{.}$ is an electron hole:

$$\frac{1}{2}O_2(g) + V_o^{"} \to O_o^* + 2h^{"}$$
(2.1)

Owing to the complex nature of the reaction and the aggressive SOFC operating conditions, the exact ORR mechanism, including its many reaction substeps, pathways, and intermediate species, are only beginning to be understood.^{23,27,34,40} This thesis focuses on the material factors governing the ORR kinetics on LSM cathode surfaces. It aims at making quantitative correlations between microstructure, defects, and surface properties of the perovskite $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM). By doing so, it aims to enhance the understanding of "structure - property" relationships for oxide materials in SOFC applications. Towards this end, defect analysis using nondestructive techniques were carried out for LSM thin films. The effects of epitaxial strain and extended defects on the oxygen reduction properties are discussed, as are methods to quantify and control defects.

2.2.2 Cathode material: $La_{1-x}Sr_{x}MnO_{3\pm\delta}$ (LSM)

Strontium doped lanthanum manganate ($La_{1-x}Sr_xMnO_{3-\delta}$, or LSM) has long been used as state of the art cathode material in high temperature solid oxide fuel cells (800 –

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1000 °C).^{26,42} At such temperatures, LSM exhibits excellent catalytic properties towards oxygen reduction, has high electronic conductivity, and possesses a matching thermal expansion coefficient with the electrolyte material yttria-stablized zirconia (YSZ).^{22,43} Even though the performance of LSM falls short at intermediate temperature to mixed ionic and electronic conductors (MIEC), such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF)⁴⁴ or $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF),⁴⁵ it is still a material of great interest to research community. In addition, $La_{1-x}Sr_xMnO_{3-\delta}$ is also a room temperature ferromagnet with a high Curie temperature, exhibits colossal magnetoresistance, and 100% spin polarization.^{19,20} These properties make LSM an important material in spintronic devices, such as magnetic tunnel junctions.



Figure 2.2: Schematics showing: (a) the ABO₃ perovskite structure of LSM, where the blue dotted lines represent oxygen octahedral, and the red, green and blue spheres represent O^{2-} , La^{3+}/Sr^{2+} , and $Mn^{3+/4+}$ ions, respectively; (b) the interconnectivity of oxygen octahedra allows the diffusion of oxygen vacancies.

 $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3\pm\delta}$ adopts a perovskite ABO₃ structure. The larger La³⁺ and Sr²⁺ ions assume the A site, which has an oxygen coordination number of 12; and the smaller Mn^{3+/4+} assumes the B site with an oxygen coordination number of 6. A schematic of the ABO₃ perovskite structure is shown in **Figure 2.2** (a). The red, green, and blue spheres represent O^{2-} , $\text{La}^{3+}/\text{Sr}^{2+}$, and $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions, respectively. The blue dotted lines represent the oxygen octahedra formed by connecting oxygen ions at face centered positions. **Figure 2.2** (b) shows the schematic of a network of connected oxygen octahedra in neighboring pseudocubic unit cells, with O^{2-} occupying each corner position. The white cube represents an oxygen vacancy (V_{o}^{\sim}) , which can diffuse along the edges of the octahedra (e.g. along the red lines) via a hopping mechanism, once enough thermal energy is provided. Oxygen vacancy diffusion is a crucial step in the oxygen reduction reaction (ORR), as both ionic conduction and surface exchange reactions rely on the transport of oxygen vacancies.²⁷



Figure 2.3: Structural phase diagram of $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3\pm\delta}$ (LSM) as a function of Sr^{2+} doping and pO_2 , showing the monoclinic $(P2_1/c)$, orthorhombic (Pbnm) and rhombohedral $(R\bar{3}c)$ phases. Figure by Mitchell et al.¹⁹

The structural phase diagram of LSM as a function of Sr^{2+} doping and pO₂ is shown in **Figure 2.3**.¹⁹ Three different phases, a monoclinic $(P2_1/c)$, an orthorhombic (Pbnm)and a rhombohedral $(R\bar{3}c)$ phase can exist. The differences among them lie in the different oxygen octahedra rotations.⁴⁶ La_{0.7}Sr_{0.3}MnO_{3±δ}, the composition used in this study, adopts the rhombohedral $R\bar{3}c$ phase with lattice parameters of $a_r = 5.506$ Å and $c_r =$ 13.3564 Å (using a hexagonal setting for $R\bar{3}c$),⁴⁷ and has $a^-a^-a^-$ Mn-O octahedral rotations.⁴⁶ La_{0.7}Sr_{0.3}MnO_{3±δ} can also be approximated as pseudocubic (pc) with $a_{pc} = 3.873$ Å, because the r-angle is only 60.43°.^{47,48}

According to Mizusaki et al., $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3\pm\delta}$ with $x \leq 0.5$ exhibits p-type conductivity.⁴⁹ The predominant electronic conduction mechanism is electron hole hopping on the $e_g \uparrow$ level of the manganese ion.⁴⁹ The temperature dependent electronic conductivity follows **Equation** 7.3, where E_a represents the activation energy and σ_0 is a preexponential factor determined by experiments.

$$\sigma \cdot T = \sigma_0 \cdot exp(-E_a/kT) \tag{2.2}$$



Figure 2.4: Electronic conductivity of $La_{1-x}Sr_xMnO_{3+\delta}$ as a function of temperature and Sr^{2+} doping at $pO_2=1$ bar. Figure by Mizusaki et al.⁴⁹

Doping LaMnO₃ with Sr^{2+} can significantly enhance the electronic conductivity. Figure 2.4 plots the conductivity of $La_{1-x}Sr_xMnO_{3\pm\delta}$ as a function of Sr^{2+} level and temperature at $pO_2=1$ bar.⁴⁹ It can be concluded that the electronic conductivity increases with Sr^{2+} level untill a maximum value of 50% Sr^{2+} . In addition to enhancing conductivity, Sr^{2+} doping also improves the chemical compatibility between LSM cathode and yttria stabilized zirconia (YSZ) electrolyte.⁵⁰ It has been reported that at high temperature, LaMnO₃ reacts with YSZ to form insulating phases such as $La_2Zr_2O_7$.^{51,52} This reaction can be suppressed by adding a small amount of Sr^{2+} . At higher levels of substitution, (> 30 mol.%) Sr^{2+} from LSM tend to react with YSZ to form $SrZrO_3$. Thus, 30 mol.% Sr^{2+} was determined to be the optimum doping level for rendering both higher conductivity and high chemical compatibility with electrolyte material.⁵³

The defect chemistry of LSM depends critically on Sr^{2+} doping, temperature, and oxygen pressure. Unlike other perovskites, doping of Sr^{2+} under 50 mol.% does not introduce anion vacancies, but is compensated by electron holes localized on the manganese ions. This is



Figure 2.5: Oxygen nonstoichiometry of ${\rm La_{0.7}Sr_{0.3}MnO_{3\,\pm\,\delta}}$ as a function of pO₂ and temperature. Figure by Mizusaki et al. 54

expressed in Equation 2.3.

$$MnO_2 + SrO \xrightarrow{LaMnO_3} Sr'_{La} + Mn'_{Mn} + 3O_o^{\times}$$
 (2.3)

The oxygen stoichiometry of $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$ as a function of pO₂ and temperature was measured by Mizusaki et al.⁵⁴ and is shown in **Figure 2.5**. Unlike other perovskite oxides, LSM only exhibits oxygen deficient nonstoichiometry at very low pO₂. It is an oxygen excess material at intermediate to high pO₂, having cation vacancies. The oxygen content per formula written as (3+d) ranges from a maximum value of 3.03 to a minimum of 2.88, before decomposition happens at very low pressure.⁵⁴ Under normal fuel cell operating conditions, LSM is expected to be cation deficient to compensate for the oxygen excess nonstoichiometry, which favors the oxidation of Mn³⁺ to Mn⁴⁺. Decreasing pO₂ and increasing temperature results in an increase in the oxygen vacancy concentration (or a decrease in the cation vacancy population). The vacancy formation energy in LSM is typically between 3 and 4 eV,²⁷ depending on the composition. This high barrier to vacancy formation results in low vacancy concentration ($[V_o^{-}]$) compared with other cathode materials such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) or $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF). For example, at 750 °C and pO₂=1 bar, $[V_o^{-}]$ in LSM is reported to be less than 10 parts per billion,⁵⁵ while $[V_{o}^{\circ}]$ in LSCF and BSCF are orders of magnitude higher.²⁷



2.2.3 Cathode microstructures

Figure 2.6: Three dimensional reconstruction of a LSM/YSZ composite cathode using focused ion beam (FIB) and electron backscatter diffraction (EBSD), showing the complicated microstructure inside. In phase map (a), yellow, green and black regions represent LSM, YSZ, and pore phases, respectively. In orientation map (b), different colors represent grains with different orientations. Images by Dillon et al.³³

LSM is a good electronic conductor but a poor ionic conductor at high temperature. For example, the electronic and ionic conductivity values of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ are $\sigma_e = 200$ S/cm and $\sigma_i = 4 \times 10^{-8}$ S/cm at 800 °C, respectively.⁵⁶ In comparison, YSZ has an ionic conductivity of 0.043 S/cm and negligible electronic conductivity at 800 °C.⁵⁷ Thus, LSM and yttria stablized zirconia (YSZ) are often mixed together to form composite cathodes, to take advantage of the high electronic and ionic conductivity of each component material.^{58,59} In such fuel cell cathodes, micron sized pores are also introduced to increase the contact area between oxygen gas and reactive cathode surfaces.⁵⁸ Thus, a well prepared, homogenous composite cathode consists of a interconnected network of micron-sized pores, LSM and YSZ. Such porous LSM/YSZ composite cathodes exhibit significantly reduced activation polarization and increased power density.^{56,58,59} Figure 2.6 shows the 3D microstructure of a LSM/YSZ composite cathode reconstructed from focused ion beam (FIB) and electron backscatter diffraction (EBSD) techniques.³³ The yellow, green and black phases in (a) represent LSM, YSZ, and pores, respectively. The different colors in (b) represent grains with different orientations. The results suggest that microstructures inside porous composite cathodes are extremely complicated. There exists a distribution of different grain sizes and grain boundaries, different orientations of surfaces and interfaces, different geometry and length of triple phase boundaries (TPB), different porosity and connectivity of pores, etc. These microstructures are often difficult to control, as sample processing parameters (such as starting powder characteristics, calcination temperature and sintering temperature) can heavily influence the final cathode microstructure.⁵⁹

The transport kinetics and ORR mechanisms inside composite electrodes depend critically on the electrode microstructure.^{23,58,60–62} In LSM/YSZ cathode, it has been reported that the charge transfer polarization is a function of the LSM/YSZ mass ratio, the grain size, and the thickness of the cathode layer.⁶³ In addition, the length of the triple phase boundaries (TPB) and the pore surface area can significantly change the overall polarization.⁶⁴ Similar microstructural influences on electrode performance have also been observed on the anode side. It has been demonstrated by creating highly porous microstructure inside Ni-YSZ anode, unusually high power density (> 1 W/cm²) at low temperature (600 °C) can be achieved for YSZ based fuel cells.⁶⁰ Another example of using microstructure modification to improve electrode performance involves the process of infiltration. Infiltration refers to adding solution based electrochemical catalysts such as LSM, ^{65–67} LSC, ⁶⁸ or a mixture of LSM and YSZ, ⁶⁹ into a backbone of existing cathode/electrolyte porous structure. As a result, the infiltrated cathode exhibits significantly improved reactivity towards ORR and better long term stability compared with untreated cathodes.⁷⁰

2.3 Measurement of oxygen transport kinetics

The measurement of oxygen transport kinetics has been a major research focus towards understanding cathode behavior. Quantitive analysis of the diffusion coefficient (D) and the oxygen surface exchange coefficient (k) have been made on porous composite materials, dense ceramic samples, ^{22,71–73} and model thin film electrodes. ^{15,28,55}

2.3.1 Oxygen surface exchange and bulk diffusion

Oxygen transport through oxide electrodes consists of two serial processes: the oxygen exchange process across the solid-gas interface, and the ionic diffusion process through the bulk electrode. The bulk diffusion kinetics are characterized by the diffusion coefficient, D, which is defined as the constant of proportionality between diffusion flux and the negative gradient of concentration in Fick's first law. This is shown in **Equation 2.4**, where J denotes the flux density and c the concentration of oxygen. For acceptor doped oxides, the atomistic expression of D is well established^{74,75}.

$$J = -D \times \frac{\partial c}{\partial x} \tag{2.4}$$

The surface exchange kinetics is characterized by the surface exchange coefficient, k, which is defined by the exchange flux of the dynamic equilibrium between oxygen in the gas phase and oxygen in the solid.⁷⁵ This is shown in **Equation 2.5**, where z represent position, a denotes the film thickness, k denotes the surface exchange coefficient, c(a) denotes the concentration of oxygen at film surface, and c_{∞} represent the equilibrium concentration at infinite time after the step change in pO₂, respectively.⁷⁶

$$J(a) = -D \left. \frac{\partial c}{\partial z} \right|_{z=a} = k[c(a) - c_{\infty}]$$
(2.5)

The values of D and k can be extracted by several different experimental techniques, each producing a conceptually different transport parameter.^{22,55,74,77} For example, in electrochemical impedance spectroscopy (EIS) experiments, an outer electrical potential gradient is applied as driving force, while the internal ionic current is balanced by the outer electronic current.^{78,79} This produces an electrical conductance surface rate constant k^q . In isotope exchange depth profile (IEDP) experiments, a tracer composition gradient is applied and the ionic flux of the tracer (¹⁸ O_2^*) is counterbalanced by the ionic flux of the counter-isotope (O_2).^{71,72} This produces a tracer surface exchange coefficient k^* . In an electrical conductivity relaxation (ECR) measurement, a change in the oxygen pressure results in a chemical composition gradient, which produces a chemical surface exchange coefficient k_{chem} .^{9,28} In addition to these three major techniques, other transport kinetics characterization methods exist. One example is the chemical strain method, which studies the oxygen surface exchange kinetics in oxide materials in the form of epitaxial thin films by analyzing subtle cell parameter variations induced by changes in the oxygen stoichiometry of the material.^{80,81} Similar curvature relaxation experiments were also designed, which monitors the transient curvature of thin film electrodes reacting to oxygen partial pressure step changes.^{82,83}



Figure 2.7: *h*-plane plot, or $\log_{10}(k^*)$ against $\log_{10}(D^*)$, for $\operatorname{La}_{1-x}\operatorname{Sr}_{x}\operatorname{Mn}_{1-y}\operatorname{Co}_{y}\operatorname{O}_{3\pm\delta}$ bulk samples measured by De Souza et al.⁷¹

One interesting observation in the measurement of D and k is the correlation between the two parameters. Figure 2.7 shows the h-plane plot, or a plot of $\log_{10}(k^*)$ against $\log_{10}(D^*)$, of all the D^* and k^* data obtained for the $\operatorname{La}_{1-x}\operatorname{Sr}_x\operatorname{Mn}_{1-y}\operatorname{Co}_y\operatorname{O}_{3\pm\delta}$ polycrystalline electrodes by IEDP experiments.⁷¹ This type of plot removes temperature as a variable and provides a means of comparing data from many different materials. The plot clearly confirms that the diffusion coefficient (D) and the oxygen surface exchange coefficient (k) are correlated within these measurements. The correlation implies that a similar parameter, such as the concentration of oxygen vacancies, plays a major role in the rate limiting step for both the surface exchange and bulk diffusion processes.⁷¹

The relative contribution from the surface exchange and bulk diffusion processes to the overall response depends on how the electrode thickness compares with the material characteristic length (L_c) . L_c is defined by the ratio of diffusion coefficient D and the surface exchange coefficient k of a given composition $(L_c = D/k)$. Mathematically, L_c represents the sample thickness where oxygen transport is equally determined by bulk diffusion and surface exchange.⁸⁴ For a given material thickness (L), three regimes are important: (1) when $L >> L_c$, bulk diffusion is rate-limiting and D can be determined; (2) when $L \ll L_c$, surface exchange becomes rate-limiting and k can be experimentally determined; (3) when $L \approx L_c$, the sample is in a mixed controlled regime, where D and k must be determined simultaneously. The mixed regime is where most transport on bulk electrodes are measured. However, uncertainties surround the measured values in the mixed controlled regime. Most notably, the error in surface exchange coefficient k can vary up to one order of magnitude.⁸⁵ The values of L_c is on the order of 100 µm for LSC⁸⁶ and LSCF⁸⁷. The L_c derived for LSM span from a few nanometers^{22,72} to 30 µm,⁵⁵ depending on the experimental method, temperature, pressure, and possibly microstructure. In the absence of certainty over the true L_c value, one should make physical measurements as a function of thickness (or other appropriate characteristic dimensions) to determine which process dominates for a specific type of sample.²⁸

2.3.2 Interpretation of surface exchange measurement

Current studies on SOFC cathodes focus on the measurement of surface exchange coefficients (k_{chem} , k^* and k^q). Using the techniques mentioned above, a variety of compositions have been measured, including LSM,^{72,88,89} LSCF^{77,87}, BSCF^{90,91}, LNO^{92,93}, and PBCO⁹⁴. Figure 2.8 plots the experimental values of k^* and k^q collected on bulk and thin film La_{0.8}Sr_{0.2}MnO_{3 - δ} electrodes.^{15,30,56,72,88} Up to 7 orders of magnitude differences in k values have been measured on nominally the same composition, due to variations in experimental condition, sample processing, and material microstructures. Reasons for such large discrepancies are discussed below.

It is worth noting that interpretation of the measurement depends on the type of experimental technique. For example, the k values determined between electrical (k^q) and tracer experiments (k^*) are roughly equivalent $(k_q \approx k^*)$, while they are related to the chemical experiment (k_{chem}) with a thermodynamic factor (w_o) following the equation:

$$k_a \approx k^* = k_{chem}/w_o \tag{2.6}$$



Figure 2.8: Values of k^* and k^q collected on bulk and thin film $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ electrodes. ^{15,30,56,72,88} The "pc", "tf", "g", and "gb" represent polycrystalline, thin films, surface exchange on grains and surface exchange on grain boundaries.

where

$$w_o = \frac{1}{2} \cdot \frac{\partial \ln p O_2}{\partial \ln c_o} \tag{2.7}$$

 c_0 represents the oxygen ion concentration and w_o depends on the experimental condition.

Other than the difference in measurement techniques, the oxygen exchange rate constant of a given SOFC cathode material is also sensitive to the following factors:

- 1. External experimental conditions, such as temperate, oxygen partial pressure $(pO_2)^{55}$ and applied bias voltage (for impedance measurements).³⁶
- Geometrical parameters, such as the density of triple phase boundary (TPB), surface area, porosity, electrode thickness, and exact distribution of all phases, inside a porous composite cathode.^{34,79}
- 3. Intrinsic materials parameters, such as composition (doping level, impurities), microstructure (strain, ^{10,95} grain size, ^{28,96} and grain boundary ^{14,15,30}) and surface/interface properties (surface roughness, ⁷⁷ orientation and segregated species ⁹⁷). ³⁴

Due to the sensitivity of surface exchange kinetics to a variety of intrinsic and extrinsic factors, it is desirable to control as many of them as possible experimentally, to allow

for accurate measurement and meaningful interpretation of transport data. The following section discusses the advantages and limitations of using thin film electrodes to achieve this purpose.

2.3.3 Advantages of thin film electrodes

Despite that porous composite cathodes exhibit excellent performance and are used in actual fuel cells, such electrodes make poor candidates for studying the fundamental aspects of oxygen reduction reaction. The efficiencies in many energy conversion technologies are fundamentally limited by losses that occur at the level of electrons and atoms at surfaces and interfaces of solid materials. Controlling the solid - gas interface, including its morphology, crystallinity, microstructure, chemical composition and defects becomes crucial to accurately study the ORR mechanism.²⁷ As mentioned in **Section 2.2.3**, porous composite cathodes contain complex microstructural features that are difficult to control but can significantly influence the ORR mechanism and kinetics.^{33,58,59} This renders quantitative analysis of intrinsic materials properties very challenging in porous cathodes, and introduces large degrees of inconsistency to the measurement results.²³

Compared with porous electrodes, dense thin films electrodes with well defined microstructure and geometry are better candidates for investigating the mechanism of oxygen reduction reactions and intrinsic material properties.^{28,36,37,88,89} The advantages of thin film electrodes include:

1. High quality thin film samples are excellent proxies to bulk materials. It has been demonstrated that well prepared thin films can possess physical and chemical properties close to those of single crystals, 35,89,98 while sample preparation is much less time consuming. Generally, k measurements on thin film electrodes are comparable to data from bulk samples obtained via the same technique. 87,92,93 Exceptions were also reported, such as the case of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}^{77}$ and $\text{PrBaCo}_2\text{O}_{5+x}$, 94 where k on as deposited thin films were several hundred times lower than on bulk samples. In the case of LSC, this discrepancy was associated with the change in oxygen vacancy content and the number of surface defects, which are very sensitive to sample annealing.

- 2. Thin film electrodes have a well defined geometry and thickness, which greatly simplifies the transport model and allows for straightforward interpretation of kinetics parameters, such as k and D.^{77,99} For example, by varying thin film thickness, the dominant electrode response can be changed from surface exchange dominant, or diffusion dominant, or mixed controlled. In addition, thin film deposition combined with photolithography can yield patterned electrode films on dense electrolyte layers, which possess precisely controlled triple phase boundary geometries and lengths.^{79,100}
- 3. Thin film model electrodes facilitate mechanistic studies of the oxygen reduction reaction, due to their simpler geometry and better controlled microstructure compared with porous electroes.^{36,79,101} Recently, much success has been achieved on improving the mechanistic understanding of the ORR, by applying impedance spectroscopy techniques on thin film electrodes.^{36,79,87,90} These studies provide valuable insights to the fundamental aspects of ORR on different cathode materials.
- 4. Thin film deposition allows for facile control over surfaces, interfaces and microstructure of electrode materials.³⁵ Controlled studies make it possible to isolate the effects of individual variables on the overall oxygen transport properties. This has been demonstrated on surface orientation,^{28,98} epitaxial strain,^{9,10} extended defects,^{14,30} grain sizes,^{96,102} chemical segregation,^{5,103} and secondary phase evolution¹⁰⁴ using thin films. Such studies offer the possibility to experimentally correlate individual surface and microstructural features to electrochemical properties, and would eventually offer promise to performance optimization in actual SOFCs.

There are, however, limitations and challenges associated with thin film electrodes. Because thin film electrodes are typically dense and uniform, they lack the ability to study the effects of pores on cathode performance. In addition, since surface exchange measurements are very sensitive to microstructure and processing parameters,⁷⁷ it is important to fully characterize the films' structure, surface, and microstructure. Despite such limitations, the advantages of thin film model electrodes are many and they continue to serve as excellent candidates for quantitative analysis and for mechanistic studies of oxygen reduction reaction at cathode surface.

2.4 Oxygen reduction reaction (ORR) mechanism

The oxygen reduction reaction (ORR) refers to the overall electrochemical reaction in which diatomic molecular oxygen ($O_2(g)$) in the gas phase are reduced into oxide ions (O^{2-}) and incorporated into the cathode solids, as represented by **Equation 2.1**. A schematic representation of the overall oxygen reduction reaction is shown in **Figure 2.9**. The ORR is a complicated process that consists of many reaction substeps, including: O_2 adsorption, $O_{2,ads}$ dissociation, charge transfer, adatom surface diffusion, vacancy migration, and oxygen incorporation into the lattice. These reaction substeps involve intermediate species such as O_2 , $O_{2,ads}$, $O_{-2,ads}$, O, O^- , O^{2-} , O_2^{2-} , O_o^* , $V_o^{..}$, and e^- (or $h^.$). Achieving a mechanistic understanding of the oxygen reduction reaction is important, yet challenging.²³ This section aims at summarizing the progress to date.



Figure 2.9: Schematic showing the oxygen reduction reaction (ORR) at cathode surface, including intermediate species and reaction substeps such as adsorption, dissociation, charge transfer, vacancy migration and oxygen incorporation.

2.4.1 Oxygen surface exchange pathways

As illustrated in in **Figure 2.10**, two basic pathways exist for the oxygen reduction reaction on LSM: (a) the triple phase boundary (TPB) path includes surface diffusion of oxygen species and oxide ion incorporation at the triple phase boundaries; and (b) the bulk path is based on oxygen incorporation and bulk diffusion in LSM. Traditional knowledge believes that due to its poor oxygen ionic conductivity ($\sigma_i = 4 \times 10^{-8}$ S/cm at 800 °C), oxygen transport on the surface of LSM is mostly localized to regions near the TPBs (**Figure 2.10**a),



Figure 2.10: Schematic of different oxygen transport pathways in SOFC cathode: (a) TPB path commonly modeled on poor ionic conductors like LSM, and (b) bulk path through the cathode layer, typically used on MIECs (such as LSCF or LSC). Red circles in (a) indicates location of TPBs.

where criteria for gas contact, charge transfer and high ionic diffusivity are simultaneously satisfied.¹⁰⁵ Recent studies have shown that this is not necessarily the case, as oxygen reduction through the bulk path (**Figure** 2.10b) is also viable for LSM.^{23,37} Particularly, impedance studies on LSM microelectrodes revealed that the TPB surface path carries most of the current in the lower temperature region (below ca. $700 \,^{\circ}$ C), while at high temperatures (above ca. $700 \,^{\circ}$ C) the bulk path is dominating.^{79,88} And the significance of each reduction path also depends on the microstructure of the columnar LSM films which can be changed by varying deposition parameters or by annealing.⁷⁹

In addition to basic reaction paths, a third path, the oxygen incorporation near extended defect regions, can exist in the SOFC cathode material. Recent studies on LSM thin film electrodes demonstrated that surface exchange and diffusion along grain boundaries are orders of magnitude higher than across native grains.^{15,30} Computational studies suggested that, in such cases, the overall transport process is determined by the slow (rate-limiting) bulk diffusion from the grain boundaries into the grains.^{106,107} Overall, the determination of which reaction pathway is dominant depends critically on experimental conditions (temperature, pO_2), material properties (composition, microstructure, defect populations, etc.) and details of processing and operating history.²³ Though this discussion focused on the ORR, similar arguments hold for surface exchange.

2.4.2 The rate-determining step (rds)

In a chemical reaction consisting of multiple paths and reaction steps, the rate-determining step (rds) is the kinetically slowest reaction step of the overall fastest reaction pathway.¹⁰⁸ The oxygen surface exchange reaction consists of many substeps, such as oxygen adsorption, dissociation, surface migration, incorporation, etc., which involve different intermediate species with various activation energies. Determining the rds allows us to recognize which (surface) defects and possibly defect mobilities are the key for the fast oxygen exchange, providing better guidance to improve SOFC cathodes.^{23,27}

Co et al. concluded that on a dense LSM layer deposited on YSZ, the rds is the dissociation of $O_{2,ads}$ at low currents, and the first electron-transfer step, reducing $O_{2,ads}$ to $O_{2,ads}^-$, at high currents.¹⁰¹ However, at porous LSM/YSZ cathodes, the reaction mechanism is more difficult to deduce because the electrode morphology impacts significantly on the measured kinetic and mechanistic parameters. In another study, Jiang et al. identified three reaction steps for oxygen reduction on the LSM electrode, including: surface dissociative adsorption and diffusion, charge transfer and oxygen ion migration into the zirconia electrolyte phase.⁴⁴ The reaction is controlled by the dissociative adsorption and diffusion at LSM electrode surface at low temperatures and the oxygen ion migration/diffusion into zirconia electrolyte at high temperatures.⁴⁴ Similar conclusions were reported on powder samples¹⁰⁹ and thin film⁸⁸ electrodes.

Computational simulations have become complementary to experiments to study the rds of the surface exchange reaction. Using *ab initio* calculations, Kuklja et al. provided a free energy profile for possible reaction pathways for oxygen incorporation on the MnO₂ (001) termination of LaMnO₃, as illustrated in **Figure 2.11**.²⁷ The black line shows the electronic energy profile (ΔH), and the red line corresponds to a semi-quantitative free energy profile (ΔG), including the effect of the overall negative reaction entropy ΔS_{ox}^0 . The rds could be deduced from the free energy profile shown in **Figure 2.11**. Processes with positive activation energies include the dissociation of adsorbed oxygen molecules (ca. 0.6 eV), the migration of surface $V_o^{...}$ (ca. 0.7 eV), and the formation of vacancies on the surface (ca. 3.0 eV, not shown). The authors predicted that at low pO_2 , the oxygen dissociation



Figure 2.11: One of the possible reaction pathways for oxygen incorporation on the $MnO_2(001)$ termination of the LaMnO₃ perovskite. Figure adapted from ²⁷

step would become the bottleneck, with a small activation energy. While at high pO_2 , the rds is the formation and approach of surface $V_o^{..}$ to essentially immobile O_{ad}^{-} , with a high activation energy. Thus both the vacancy concentration and mobility are predicted to be decisive.

2.5 Effects of surface and microstructure on oxygen surface exchange

2.5.1 Effects of surface orientation

Surface orientation is known to influence the electrochemical and photoelectrochemical properties of many functional oxide materials. For example, the ability of oxide materials to split water into hydrogen and oxygen gas depends on surface orientation and surface termination.^{110,111} The oxygen exchange kinetics of $SrTiO_3$ single crystal also depends on surface orientation.¹¹² The surface exchange rate is fastest on (111), slower on (100) and slowest on (110) surfaces, while they exhibit different activation energies. Similar orientation dependency of surface exchange has been observed on YSZ single crystal¹¹³ and LSM thin films.²⁸ As illustrated in **Figure 2.12**, Yan et al. used epitaxial thin films with well controlled crystallinity and surface roughness to determine the orientation relationship of k_{chem}

for different surfaces. At 800 °C, the surface reactivity was to be (110) > (111) > (100), with four times difference between the highest and lowest k_{chem} values. The activation energies (0.8 - 1.2 eV) were found to vary with orientation as labeled in the figure.²⁸



Figure 2.12: Oxygen surface exchange coefficient (k_{chem}) measured on LSM thin films of different orientation. The data from left to right correspond to (100), (110) and (111) LSM surfaces of the pseudocubic notation. Data from Yan et al.²⁸

The effect of anisotropic oxygen transport is more pronounced in layered perovskite oxides.¹¹⁴ One example is the use of Ruddlesden-Popper (RP) phase $La_2NiO_{4+\delta}$ (LNO) due to its excellent electrochemical properties and mixed electronic and ionic conductivity. LNO adopts a K_2NiF_4 structure, consisting of alternating layers of perovskite (ABO₃) and rock salt (AO) stacking along the [001]_{tetragonal} direction. Several studies have aimed at quantifying the oxygen surface exchange kinetics on different LNO orientations.^{98,115} Measurements on LNO single crystal and thin films have consistently shown that both the oxygen surface exchange rate and the diffusion rate are much higher along ab-plane than along the c-direction. The extent of the anisotropy effects range between 4-10 times¹¹⁵ to two orders of magnitude.⁹⁸

It is likely that the orientation dependence of electrochemical properties are correlated with the different surface composition and surface termination. For example, the (100) surface of LSM has either La,Sr-O or Mn-O₂ termination, while the (110) surface is terminated by either O₂ or the highly polar, oxygen deficient La,Sr-Mn-O. Differences in the surface chemical composition can result in the exposure of certain transition metal electrons, rendering more active oxygen reduction kinetics for certain orientations. DFT based calculations have suggested that the dissociative adsorption of O₂ molecules from the gas phase is energetically favorable on Mn ions in LaMnO₃.^{116–118} Other studies have suggested that the MnO₂ termination has higher oxygen vacancy concentration than the La–O termination, which is depleted with oxygen vacancy.¹¹⁹ In the absence of experimental data, it is unclear which termination is more stable under fuel cell operation conditions (high temperature, high pO_2 , cubic unit cell). A few studies have predicted that the stable termination is MnO₂ in pure LaMnO₃, but Sr₂⁺ doping stabilizes the La,Sr–O termination under typical operational conditions of a cathode in solid oxide fuel cells.^{27,116,118} In addition, the Sr surface segregation tendency, oxygen adatom coverage, surface vacancy population, and surface diffusion length may all vary with surface orientation.²⁸

2.5.2 Effects of epitaxial strain



Figure 2.13: Schematic of a perovskite epitaxial thin film deposited on perovskite substrate under tensile (left) and compressive (right) strain. Figure adapted from ref.³⁵

Epitaxial strain impacts the electronic,^{5,6} magnetic,^{7,8}, ferroelectric^{1,2} and electrochemical^{9–11} properties of functional oxide materials. For LSM thin films, it has been demonstrated that the Curie temperature,⁸ the magnetic domain structure⁷ and the easy magnetization axis²¹ are heavily influenced by strain. In addition, for epitaxial LSM thin film, tensile strain has been shown to enhance the density of states near the Fermi level compared with compressive strain.⁶ Epitaxial strain can be introduced to thin films during deposition on a substrate with proper lattice mismatch. **Figure 2.13**³⁵ shows how tensile (left) and compressive (right) strain are introduced into perovskite thin films by film-substrate lattice mismatch.

Strain has been used to improve the catalytic properties of both anodes and cathodes in proton exchange membrane fuel cells. Adzic et al.¹²⁰ developed a catalyst based on



Figure 2.14: Models of pseudomorphic monolayers of Pt on three different substrates inducing compressive strain on Ru(0001) and Pd(111), and expansive (tensile) strain on Au(111).¹²⁰

a Pt monolayer deposited onto metal nanoparticles. The lattice mismatch between the Pt monolayer at the surface and the metal nanoparticle cores induces either tensile or compressive strain, as illustrated in **Figure 2.14**. As prepared co-catalysts exhibit improved activities towards ORR and fuel oxidation reactions, due to a shift of the electronic band structure of platinum induced by the strain.¹²¹



Figure 2.15: Arrhenius plots of tracer surface exchange coefficients (k^*) and diffusion coefficient (D^*) of $La_{0.8}Sr_{0.2}CoO_{3-\delta}$. (Image adapted from Kubicek et al.¹⁰) Blue and red dotted lines represent data on LSC thin films under tensile and compressive strain, respectively. Black solid lines represent data on bulk LSC.²²

The effects of epitaxial strain on the surface ORR kinetics of perovskite oxides is still yet to be fully understood. Recent theoretical studies have predicted that biaxial tensile strain can reduce the energy barrier for oxygen vacancy formation, migration and oxygen adsorption, thus favoring faster ORR kinetics on a variety of perovskite oxides.^{11,122} Experimental studies using epitaxial thin films of mixed electronic and ionic conducting (MIEC) materials have corroborated this prediction. Using scanning tunneling microscopy, Jalili et al.⁶ discovered that tensile strain facilitates oxygen vacancy formation on the LSM thin film surface. For $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC) thin film electrodes, it was found that the LSC/STO surface under tensile strain exhibited faster surface exchange (≈ 4 times) and diffusion (≈ 10 times) kinetics than the compressively strained LSC/LAO surface.¹⁰The results measured by IEDP are plotted in **Figure 2.15**, where k^* and D_* represent the oxygen surface exchange coefficient and the tracer diffusion coefficient, respectively. For $La_2NiO_{4+\delta}$ (LNO) thin film electrodes, Lee et al.⁹⁵ observed that volumetric strain increases surface exchange coefficients by approximately 30 times at 550 °C. As shown in **Figure 2.16**, previous studies on LSM thin film electrodes observed that the k_{chem} values of the LSM/STO surface under biaxial tensile strain is larger by more than an order of magnitude than the LSM/NGO surface under compressive strain.⁹ Interestingly, the same study also reported that strained (both tensile and compressive) surfaces exhibit increased activation energy (1.5 eV) for surface exchange compared with strain relaxed, defect populated surfaces (0.75 eV). This is in contradiction with the trend that tensile strain reduces the vacancy formation and migration barrier.



Figure 2.16: Effects of strain on the k_{chem} values of LSM: (a) 50 nm and (b) 600 nm thin films. Data for films on STO (NGO) are in closed (open) markers and apparent activation energies (E_a marked in images) were fitted with solid (dashed) lines.⁹

2.5.3 Effects of extended defects

Extended defects, such as dislocations, grain boundaries, twin boundaries, and antiphase boundaries, are commonly observed in thin films 16,17,123 and bulk materials. 12,124 They

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introduce distortions of local crystal planes (strain), and can have associated segregation of oxygen vacancies, cations, and/or secondary phases.^{125–127} The presence of defects can have significant impact on the electronic,^{12,128,129} magnetic,^{17,130} ferroelectric,^{1,13,131} and electrochemical properties.^{14,15} Thus, defect analysis and defect engineering of functional materials are topics of great research interest.

The presence of dislocations can significantly change the electronic, 12,128,129 magnetic, 17 and ferroelectric properties 13,131 of materials. In metals, dislocations act as fast diffusion pathways, having diffusion coefficients higher by several orders of magnitude than the bulk. 132,133 In GaN thin films, dislocations increase non-radiative recombination and reduce electronic conductivity, thus lowering the device efficiency of LED devices. 128 In SrTiO₃ single crystals, dislocations show switching abilities between non-metallic and metallic electronic conduction by the application of an electric field, thus enabling memristor devices. 12,134 These switching behaviors are generally believed to be associated with oxygen ion transport along nanoscale filamentary paths around dislocation cores. 12

Structurally, the regions near dislocations are subject to local lattice distortions (strain). Although dislocation cores are only a few angstroms wide, the associated strain fields are often significant and long-range, typically extending over tens of nanometers in ionic oxides.^{13,123,131} Simulations have predicted that the formation energy for oxygen vacancies decrease around dislocations, leading to a surplus of oxygen vacancies near dislocation cores.^{125,127,135,136} The higher concentration of oxygen vacancies, however, does not significantly enhance mobility of oxide ions near dislocations. Instead, a higher migration barrier for oxide ions diffusion was predicted in SrTiO₃¹³⁶ and CeO₂.¹³⁷ This is contrary to the fast diffusion kinetics near dislocations in metals, and is attributed to the segregation of charged defects near dislocation cores. Transmission electron microscopy (TEM) based experiments revealed that strain fields around dislocations also change the local chemical composition. In SrTiO₃, enriched Ti⁴⁺ and depleted Sr²⁺ contents have been observed around dislocations. As such, the dislocation cores are electrostatically charged because of the segregated point defects. Guo et al.¹²⁵ concluded that dislocation networks act as double Schottky barriers, which block charge carrier transport.

Grain boundaries (GB) often exhibit different electronic and ionic conductivities than



Figure 2.17: Sketches of the three reaction pathways for oxygen reduction on cathode materials: (a) triple phase boundary (TPB) path, (b) grain boundary (GB) path and (c) bulk path. The TPB path is limited to porous composite cathodes. The GB and bulk paths are limited to dense thin film electrodes. The red color indicates the active regions for oxygen adsorption and ionic conduction. Schematic adopted from Saranya et al.³⁰

native crystal grains. In CeO_2 samples, due to accumulation of charged species near grain boundaries, there exists a space charge effect, which strongly affects the electrical conductivity. If the grain size approaches a nanometer scale, the electronic component of the conductivity becomes more significant and the dominating charge carriers are changed from ions to electrons.^{138,139} Similar space charge effects have been reported in Fe-doped SrTiO₃ mixed conductor, where the overall grain boundary conductivity is almost purely electronic.^{140,141} Interestingly, the inverse situation occurs in highly textured thin films of YSZ, where a decrease in grain size results in the enhancement of the ionic conductivity, reaching 0.6 S/cm at 800 °C.¹⁴² High ionic conductivity near grain boundaries can act as fast reaction pathways and thus change the mechanisms of oxygen bulk transport. This has been demonstrated by theoretical models in mixed conducting oxides.^{106,107,143}



Figure 2.18: Arrhenius plot of (a) surface exchange coefficients and (b) diffusion coefficients of LSM native grains and grain boundaries. Image adapted from Navickas et al.¹⁵

In terms of oxygen reduction kinetics, Lee et al.¹²⁶ reported that the grain boundaries of gadolinia-doped ceria (GDC) thin film exhibits faster oxygen surface exchange kinetics than GDC grain surfaces. This phenomena is attributed to the segregation of dopants and oxygen vacancies near grain boundaries. A similar trend was observed by Sase et al.⁹⁶ on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) electrodes, who reported that smaller grain sizes (higher grain boundary populations) facilitate gas adsorption and reduce electrode resistance. In another study, by combining electrochemical strain microscopy and scanning transmission electron microscopy, Kumar et al.¹⁴ also discovered that the small angle grain boundaries (SAGB) exhibit higher electrochemical activity in LSC thin films. Most notably, recently Navickas et al.¹⁵ observed that in LSM thin film electrodes, D and k values of the grain boundaries are three orders of magnitude faster than those of LSM grains. Figure 2.18 plots the values of D and k measured by isotope exchange depth profile (IEDP) technique, where the subscript "gb" represent grain boundary.



Figure 2.19: (a) Orientation-contrast SEM images showing the twin pattern; (b) scanning force microscopy (SFM) topographic image; and (c) current map acquired by conductive SFM at V = -1.4 V of a 40 nm thick $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ film deposited on SrTiO₃. Figure by Barcells et al.¹⁶

The effect of twin walls on the electronic, magnetic and electrochemical properties of oxide materials are only beginning to be understood. It has been predicted that the ferroelastic $(100)_o$ twin walls of the orthorhombic CaTiO₃ (*Pbnm*) possess a more stable binding with oxygen vacancies, thus effectively trapping oxygen vacancies within twin walls.¹⁴⁴ This is attributed to changes in the electrostatics and strain within the twin wall. Experimental evidence have recently revealed that the $(100)_{pc}$ twin walls of La_{0.7}Sr_{0.3}MnO_{3 - δ} thin films on STO exhibit higher electronic conductivity and more robust magnetic interactions than defect free regions.¹⁶ The change in electronic conductivity is illustrated in **Figure 2.19**, which shows the correlation between twin patterns, surface topography and conductivity maps in LSM film. The twin boundary effect is attributed to the compressive strain localized within an approximately 1 nm slab centered at the twin walls, promoting stronger Mn 3d - O 2p orbital overlapping leading to a broader bandwidth and enhanced magnetic interactions. The effects of twin walls on the electrochemical properties are unknown. One can hypothesize that, due to a higher concentration of oxygen vacancies and the presence of local strain, twin boundaries could act as higher oxygen transport pathways.

In summary, the surface and microstructure (such as epitaxial strain and extended defects) can significantly change the intrinsic properties of functional oxide materials, including the oxygen reduction reaction kinetics in perovskite oxides.^{1,2,15,28} This thesis aims at investigating the effects of epitaxial strain (both tensile and compressive) and extended defects (such as dislocations and planar domain boundaries) on the ORR kinetics of $(110)_{pc}$ oriented La_{0.7}Sr_{0.3}MnO_{3- δ} thin film electrodes. As suggested by Yan et al.²⁸ the LSM $(110)_{pc}$ surface exhibits the highest ORR activity compared with other low index orientations. Films were deposited onto $(110)_{cubic}$ - SrTiO₃ substrates (tensile strain) and $(100)_{orthorhombic}$ - NdGaO₃ substrates (compressive strain). In addition, the defect contents and distributions in these thin films were characterized, with a focus on surface-penetrating dislocations and 2D planar boundaries. The surface exchange properties on well controlled thin films with varying strain status and defects content are compared with each other. The results highlight the effects of strain and defect engineering to affect the electrochemical properties of complex oxides.

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2.6 Defect analysis techniques in epitaxial thin films

Extended defects, such as dislocations, grain boundaries, twin boundaries, and antiphase boundaries, are commonly observed in thin films^{13,16,17,123} and bulk materials.^{12,124} They introduce angular distortions and/or structural distortions to local crystal planes via strain, and are sometimes associated with segregation of charged species, such as oxygen vacancies and cations species.^{125–127} As discussed in Section 2.5, extended defects can significantly impact the functional properties of thin film and bulk materials. As such, it is important to characterize defect distributions over large length scales.

This section reviews the common defect analysis techniques used in epitaxial thin film research, including: transmission electron microscopy (TEM), X-ray rocking curve (RC), and electron channeling contrast imaging (ECCI). TEM provides high resolution analysis capabilities of defect structure on the nanometer scale, although sample preparation is destructive.^{16,48} RC measures mosaic spread in epitaxial thin films caused by defects. It provides average defect information in the bulk over millimeter length scales, but is not suited to isolate or map individual defects.¹⁴⁵ Complementary to the other techniques, ECCI offers both spatial mapping and quantitative analysis capabilities of extended defects on the mesoscale in a nondestructive fashiion.^{146,147} It is worth noting that, with a signal collection depth between tens to hundreds of nanometers, ECCI is only sensitive to extended defects or near surface defects.¹⁴⁷

2.6.1 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a powerful characterization technique that reveals defect structures on the nanometer scale. High-resolution TEM and related techniques provide capabilities of both direct imaging and quantitative analysis of strain fields and angular rotations around defects.^{16,148} It is commonly adopted in thin film research to characterize misfit dislocations (MDs),¹³ threading dislocations (TDs),^{48,145} antiphase boundaries (APBs),¹⁴⁹ and twin walls (TWs).¹⁶ Examples for each defect analysis in TEM is given below. It is worth noting that sample preparation is destructive and that TEM is not ideally suited for analysis of mesoscale defects.



Figure 2.20: Cross-section HRTEM image showing a misfit dislocation (MD) at the film-substrate interface. Strain contrasts around the dislocation core are visible as gradual distortions of lattice positions. Image by Chu et al.¹³

Misfit dislocations (MD) at the film-substrate interface have been studied by TEM. **Figure 2.20** shows a high resolution TEM image of an edge-type MD in a (001)-oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin film grown on $SrTiO_3$.¹³ The associated Burgers vector was determined to be $\mathbf{b} = a[100]$. Quantitative analysis of the lattice positions reveal that strain fields near the dislocation core extend predominantly into the film region of approximately 4 nm in height and 8 nm in width. The strain fields around the misfit dislocation core have a strong effect on suppressing the polarization and piezoelectric properties of the film, leading to interfacial dead layers with severely degraded ferroelectric properties.^{131,150}



Figure 2.21: Dark field TEM images of threading dislocations in (a) cross-section and (b) plan view geometry in a GaN thin film grown on sapphire substrate. Images by Heying et al.¹⁴⁵

The contrast and distributions of threading dislocations (TDs) in semiconductor 145 and oxide 151,152 thin films have been studied with TEM. Figure 2.21 shows dark field TEM

images of TD in a (001)-oriented GaN thin film deposited on sapphire substrate.¹⁴⁵ The diffraction conditions are (a) $\mathbf{g} = (002)$ and (b) $\mathbf{g} = (100)$. In the cross section image (a), the threading dislocations have a line vector that is perpendicular to the film surface. Their density is sufficiently high that strain contrasts from adjacent dislocations begin to overlap. In the plan view image (b), TDs intersecting the surface exhibit bright-to-dark spot contrasts characteristic of the tensile and compressive strain field. The TD density is estimated to be about $2.5 \times 10^{10} \text{cm}^{-2}$ from the plan view image. More importantly, the TDs form small angle grain boundaries, which introduce a subgrain structure to the thin film with a mean subgrain size between $0.3 - 0.5 \mu \text{m}$. Using $\mathbf{g} \cdot \mathbf{b}$ analysis and dislocation invisibility criteria, it was revealed that practically all TDs in the image are pure edge type.



Figure 2.22: Dark field TEM images showing anti-phase boundaries (APBs) in $La_{0.7}Ca_{0.3}MnO_3$ bulk oxides under different diffraction conditions. Images by Ding et al.¹⁴⁹

Anti-phase boundaries (APBs) are planar boundaries that separates two domains whose unit cells are displaced by a translation vector **R**. They have been observed by TEM in both oxide thin films¹⁵³ and bulk materials.¹⁴⁹ **Figure 2.22** presents the dark field TEM images of anti-phase boundaries (APBs) in $La_{0.7}Ca_{0.3}MnO_3$ bulk sample.¹⁴⁹ APBs exhibit meandering line morphologies and enclose domains between tens to hundreds of nanometers. The translation vector \mathbf{R} can be identified through the invisibility criteria, which states that the APB contrast is extinct when the phase shift $\alpha = 2\pi \mathbf{g} \cdot \mathbf{R}$ is an even multiple of π . In doped lanthanum manganites, APB formation are related to changes in the MnO₆ rotation patterns.¹⁵⁴ Contrast from APBs can arise from either a change in the structure factor or strain. Quantitative analysis has shown differences in the strain fields around dislocations and APBs. In highly ordered Pb(Sc_{1/2}Ta_{1/2})O₃ ceramics, the maximum in-plane strain (%) and lattice rotation (°) induced by a dislocation are 9.5% and 5.4°, respectively.¹⁴⁸ These values are much smaller in an antiphase boundary, being 1.8% and 0.9°, respectively.¹⁴⁸



Figure 2.23: Geometric phase analysis (GPA) of a (100)- twin walls (TW) in a strained epitaxial $La_{0.7}Sr_{0.3}MnO_3$ thin film on $SrTiO_3$. Images (a) show the twin angle Ω map, and (b) shows the perpendicular strain component E_{xx} map, and their respective averaged profile. Images by Balcells et al.¹⁶

The atomic structure of twin walls (TWs) in coherently strained epitaxial $La_{0.7}Sr_{0.3}MnO_3$ thin films have been studied with high-resolution TEM and geometric phase analysis (GPA). **Figure 2.23** shows the map of twin angle Ω in (a), and the perpendicular strain component E_{xx} in (b) across a $(100)_{pc}$ twin wall.¹⁶ Their corresponding averaged profiles are also plotted. Intensity profiles clearly indicate that film materials in the twin wall show an increase in Ω angle of up to 1.5° and an perpendicular compressive strain of approximately -3.5%. The structural distortions are highly localized within an approximately 1 nm slab centered at the twin walls. Interestingly, while the twin walls are under large compressive strain, the majority of the LSM film remains under coherent tensile strain (+0.6%) induced by the substrate. Thus, the twinned film can be viewed as a self-organized nanostructure consisting of 1 nm thick sheets of strongly compressed LSM embedded in a matrix of tensilely strained LSM. The strong compressive strain in within the TW likely promotes stronger Mn 3d - O 2p orbital overlapping, leading to higher electronic conductivity and more robust magnetic interactions.¹⁶

2.6.2 X-ray rocking curve (RC)

An X-ray rocking curve (RC) is a scan in the X-ray diffractometer around the ω axis at fixed 2θ values. RCs are used to determine the mosaic spread, which is directly correlated with the type and density of defects in a thin film. It has been successfully applied to measure dislocation density in metals,¹⁵⁵ semiconductors^{145,156,157} and oxide thin films.¹⁵⁸ Such measurements are accurate in the dislocation density range of $10^5 - 10^9 \text{cm}^{-2}$.¹⁵⁶ The RC peak broadening depends on the dislocation density, the Burgers vector, and the relative orientation of the dislocations.^{145,156} According to models developed by Hordon et al.,¹⁵⁹ sources contributing to RC broadening are listed in **Equation 2.8**, where $\Delta\beta^2$ represents the measured rocking curve full width at half maximum (FWHM) for (hkl) reflection:

$$\Delta\beta^2 = \beta_0^2 + \beta_d^2 + \beta_\alpha^2 + \beta_\epsilon^2 + \beta_L^2 + \beta_r^2 \tag{2.8}$$

where β_0^2 is the intrinsic rocking curve width for the crystal being examined (this is a small term); β_d^2 is the intrinsic rocking curve width for the double-crystal diffractometer; β_{α}^2 is the rocking curve broadening caused by angular rotation at dislocations; β_{ϵ}^2 is the rocking curve broadening caused by the strain surrounding dislocations; β_L^2 is the rocking curve broadening due to crystal size effect; β_r^2 is the rocking curve broadening due to curvature of the specimen. Using triple-axis X-ray diffractometer on a flat thin film specimen, the β_0^2 , β_d^2 , β_L^2 , and β_r^2 terms can be eliminated, leaving behind only the angular rotation (β_{α}^2) and strain (β_{ϵ}^2) contributions to the RC broadening. Assuming a uniform dislocation distribution, a simple model can be derived to estimate dislocation density (ρ) based on the FWHM value ($\Delta\beta$). This is listed in **Equation 5.1**,¹⁵⁵ where $\Delta\beta$ is in radians, and *b* is the magnitude of the Burgers vector of the dislocation:

$$\rho = \frac{(\Delta\beta)^2}{9b^2} \tag{2.9}$$

2.6.3 Electron channelling contrast imaging (ECCI)

Electron channeling contrast imaging (ECCI) is a scanning electron microscopy (SEM) based technique that offers non-destructive characterization of extended defects on the mesoscale. ECCI makes use of the fact that, at high magnifications, BSE intensity is strongly dependent on the orientation of crystal lattice planes relative to the incident beam.¹⁴⁶ When the incident beam is set for the Bragg condition on a single crystal, beam-sample interactions produce a uniform BSE intensity everywhere in the background. However, when crystal defects near the surface region distorts the local crystal plane orientations, the Bloch wave extinctions are significantly modified.¹⁶⁰ This leads to a small but recordable change in the BSE intensity, and thus allows for direct imaging of surface penetrating or subsurface defects.^{124,161} An example is shown in **Figure 2.24**, which shows the schematics of the crystal plane distortions near a surface-penetrating edge dislocation (left), and the BSE intensity modulation result due to local modifications to the Bragg conditions (right). This allows edge dislocations near the surface to be detected as characteristic bright-to-dark spot contrasts.



 Figure 2.24: Schematics of the crystal plane distortions near a surface-penetrating edge dislocation (left), and the BSE intensity modulation result due to local modifications to the Bragg conditions (right). This allows edge dislocations near the surface to be detected as characteristic bright-to-dark spot contrasts. Figure by Wilkinson et al.¹⁴⁶

Still a relatively new technique, ECCI has been mostly used study dislocations and



Figure 2.25: ECCI micrograph of surface defects in a GaN film with dark/light spots indicative of threading dislocations. Low-angle grain boundaries are perceptible where the areas transition from one grayscale to another. Dark curved lines denote atomic steps. Image by Picard et al.¹⁶²

stacking faults structures in metals,^{146,147,163,164} and has recently been applied to semiconductors,^{161,165} oxide crystals,¹²⁴ and heteroepitaxial thin films.¹⁶⁶ **Figure** 2.25 shows an ECCI micrograph of surface defects in a GaN thin film.¹⁶² In this image, dark curved lines denote atomic steps; dark/bright contrast spots represent threading dislocations, which form low-angle grain boundaries. Note the similarity between TD and low-angle grain boundary images in ECCI (**Figure** 2.25) and TEM (**Figure** 2.21), both on GaN thin films. The areas within the low-angle grain boundaries transition from one grayscale to another, indicative of small amount of orientation change. The average density of threading dislocations measured by ECCI is close to that measured by bright field TEM.¹⁶⁷ In addition, the dislocation invisibility criteria in TEM diffraction contrast also applies to ECCI, due to similarities in their image formation. This phenomenon has been used to resolve dislocation types and identify burgers vectors of dislocations in metals¹⁶³ and semiconductors.¹⁶⁸ For example, edge dislocations disappear completely only when $\mathbf{g} \cdot \mathbf{b} = 0$ and $\mathbf{g} \cdot \mathbf{b} \times \mathbf{u} = 0$, where **b** is the burgers vector of edge dislocation, **g** is the diffraction condition in TEM or ECCI, and **u** is the dislocation line direction.

CHAPTER III

Experimental methods

3.1 Chapter overview

This chapter provides an overview of the experimental techniques for sample preparation and characterization. Section 3.2 reports the experiment methods in preparation of a dense, stoichiometric target for film deposition. Section 3.3 summarizes experiments of LSM thin film deposition by pulsed laser deposition (PLD). Section 3.4 details the crystal structure characterization by high resolution X-ray diffraction (XRD) and related techniques. Section 3.5 reports the details regarding defect analysis in LSM thin films using electron channeling contrast imaging (ECCI). Section 3.6 documents the conditions for atomic force microscopy (AFM) experiments. Section 3.7 summarizes the parameters in electrical conductivity and surface exchange property measurements using electrical conductivity relaxation (ECR).

3.2 Target preparation

A dense perovskite $La_{0.7}Sr_{0.3}MnO_3$ (LSM) pellet was prepared using solid state reaction methods for use as thin film deposition target. A flow chart showing the experimental steps is given in **Figure 3.1**. To start, La_2O_3 (Alfa Aesar, 99.999%) powder was annealed in air at 1000 °C to remove chemically absorbed H₂O, and SrCO₃ powder (Alfa Aesar, 99.99%) was annealed in a pure CO₂ atmosphere at 800 °C to remove anionic impurities (such as nitrate groups). Next, stoichiometric amounts of La_2O_3 , SrCO₃, and MnO₂ (Alfa Aesar, 99.9%) powders were weighed and added to a plastic bottle. The mixture was ball milled for 24 hours using zirconia balls and reagent alcohol. Afterwards, the powder was calcinated at 1000 °C in air for 12 hours. Approximately 20 drops of poly(vinyl alcohol) (PVA) were then added to the calcinated powder as binder and the mixture was ground. The powder was uniaxially pressed at 12,500 psi into a pellet of 1-inch diameter. During pressing, caution was exercised to ensure the pellet had no visible cracks. The pellet was then annealed at 1450 °C for 48 hours in air, allowing for perovskite phase formation by solid state reaction and target sintering/densification. Slow heating and cooling rates (1 °C/min) were used to avoid cracking. Following the annealing, the pellet density was measured to be $\geq 95\%$ the theoretical density of LSM (6.45 g cm⁻³).¹⁶⁹ Scanning electron microscopy (SEM) (Quanta 600, FEI) images revealed that the average grain size of the pellet was 65 µm in diameter; there were no observable micron-sized pores. Finally, the La:Sr:Mn cation ratio was confirmed by energy dispersive X-ray spectroscopy (EDS) in SEM, and the crystallographic phase was confined by X-ray diffraction (PANalytical X'pert Powder).



Figure 3.1: Flow chart of solid state reaction steps used in preparation of a dense, perovskite $La_{0.7}Sr_{0.3}MnO_3$ (LSM) target.

3.3 Pulsed laser deposition (PLD)

Pulsed laser deposition (PLD) is a physical vapor deposition technique commonly used to deposit high quality, complex oxide thin films, such as perovskite oxides, perovskite heterostructures, and high temperature superconductors.^{170–173} During the PLD process, a high energy laser pulse transfers a large thermal energy to the target surface region, causing ablation of target material, which is followed by the plasma generation and propagation in a background gas. At the substrate surface, highly nonequilibrium processes occur, such as adsorption, adatom diffusion, desorption, thermalization, cluster formation and ultimately nucleation and attachment to substrate steps.¹⁷⁴ High quality thin film samples with well controlled composition, crystallinity, microstructures and thickness can be achieved through careful tuning of the deposition parameters.^{175,176} Different growth modes, such as island growth, or layer by layer growth, can also be achieved by tuning the growth conditions.¹⁷⁵ In this work, high quality, epitaxial, LSM thin films were fabricated and their microstructures and defect populations controlled.



Figure 3.2: Schematic of the pulsed laser deposition process, showing the location of the substrate and target, and their relation to the pulsed laser beam. Figure by Shultz.¹⁷⁷

The PLD system used in this study (Neocera Inc.) consists of a KrF excimer laser ($\lambda = 248 \text{ nm}$), focusing optics, a vacuum deposition chamber, which is equipped with a rotating target carousel, a substrate heater, and a thermocouple to monitor the growth temperature. The substrate heater to target distance is fixed at 6 cm. The vacuum deposition chamber includes a dry pump, a turbomolecular pump, and pressure gauges. A schematic of the PLD growth chamber is presented in **Figure 3.2** (figure by Andy Shultz¹⁷⁷). During deposition, the excimer laser is focused to the surface of a rotating polycrystalline target, transferring a large amount of energy (the laser energy density was 2 J/cm^2) during a short pulse (20 nanoseconds). This ablates the top surface of the target material, and generates a forward directed plasma of vaporized and ionized species. The substrate is situated in the direction of the ablation plasma. Arriving at the substrate surface, ionized species go through a series

of events including adsorption, surface diffusion, desorption, and nucleation.

Effects of PLD deposition parameters on the quality of LSM thin films have been demonstrated in many previous studies.^{176,178} Several key deposition parameters need to be controlled to ensure successful film growth. First, a dense (density $\geq 95\%$ of theoretic density) ceramic target is a prerequisite because micro-pores inside a porous target cause thermal instabilities and result in deteriorated film quality. Next, an optimum growth kinetic is required for the successful surface diffusion and nucleation events on the substrate surface. The growth kinetics are controlled by a combination of substrate temperature, laser fluence and oxygen gas pressure. For example, low temperature growth often results in crystallization of other orientations or secondary phases; while high temperature growth can cause material decomposition or undesirable film-substrate reaction. The laser fluence has been shown to affect the cation stoichiometry. For example, excess SrO layers have been detected in $SrTiO_3$ film deposition when the laser fluence is too high.¹⁷⁹ Finally, a proper background gas pressure is necessary to ensure full oxidization of deposited cations, which also affects the growth kinetics. In this study, the optimum deposition condition for all LSM films was determined to be 750 $^{\circ}$ C, 50 mTorr of background oxygen, a laser fluence of $2 \,\mathrm{J/cm^2}$, and 1 Hz repetition rate. Directly following the deposition, the chamber oxygen pressure was increased to 200 Torr and the sample cooling proceed at cooling rates between 1-25 °C/min.

(110)-SrTiO₃ and (100)-NdGaO₃ single crystal substrates (10 mm x 10mm x 0.5 mm, one-side polished, MTI Corp. USA) were used in this study. Before each deposition, the substrate was treated with a 10 min ultrasonic bath in acetone, followed by a 10 min ultrasonic bath in methanol, to remove any contamination during packaging or handling. The unpolished side of the dried substrate was then attached to the heater surface via silver paste (Ted Pella, Inc.), to ensure good adhesion during high temperature deposition.

3.4 X-ray diffraction (XRD) and related techniques

The crystallographic nature of as deposited thin films, including their phase and orientation, in-plane and out-of-plane lattice parameters (strain status), mosaic spread, and epitaxial relationship, were determined by high resolution X-ray diffraction (XRD).^{9,28,173} Measurements were completed on a Philips X'pert MRD diffractometer, operated at 40 kV and 45 mA, using Cu- $K\alpha$ monochromatic radiation ($\lambda = 1.5418$ Å for Cu- $K\alpha_1$). A high-resolution mode was achieved by using a hybrid optical module, in which an X-ray mirror and a 4x Ge(220) crystal monochromator were inserted in the incident beam path, and a triple-axis Ge(220) 3-bounce channel-cut analyzer was inserted in the diffracted beam path to eliminate crystal size effect.¹⁷³ As illustrated in **Figure 3.3**, the four-circle X-ray diffractometer allows four degrees of freedom: 2θ , ω , ϕ and ψ . A variety of scans were performed, including: $2\theta - \omega$ scans, which were used to determine the film's phase, orientation, and out of plane lattice parameter; ω scans (rocking curves), which were used to measure the mosaic spread of the film and to estimate the dislocation content; ϕ scans, which were used to probe the in plane epitaxial relationship of the heterostructure; reciprocal space maps (RSMs), which were used to measure the crystal structure of the unit cell (such as the orthorhombic and monoclinic distortions) and the in-plane film-substrate coherency.



Figure 3.3: Schematic of the X-ray diffraction (XRD) set up. The three independent axes are ω , ϕ and ψ , about which sample rotations could be controlled. θ represents the angle between the incident beam and the sample out-of-plane normal.

The lattice parameters of the films were determined from $2\theta - \omega$ scans in high resolution mode.^{9,173} In all measurements, the substrate peaks were used as references to account for instrument drift. The lattice parameters were calculated according to Bragg's law, which is given in **Equation 3.1**, where *d* is the inter-atomic spacing of the measured plane, $\lambda =$ 1.5418 Å is the X-ray wavelength for Cu- $K\alpha_1$, and θ is the diffraction angle between the incident beam and the sample normal. The lattice parameter measurement uncertainty is ± 0.001 Å using high resolution mode.

$$2 \cdot d \cdot \sin\theta = \lambda \tag{3.1}$$

A 360° scan around the ϕ axis at fixed ω and 2θ values (ϕ scan) were used to determine the epitaxial relationship between the film and the substrate.^{28,89} In the case of LSM_{pc} (110) films deposited on STO_c (110) substrates, all films (f) were found to exhibit a single epitaxial relationship with the substrates (s): $(110)_f [001]_f \parallel (110)_s [001]_s$, relative to the pseudocubic cells. Details related to monoclinic and orthorhombic distortions will be discussed later.

X-ray rocking curve analysis is done using a scan around ω axis at fixed 2θ values. It is used to measure the mosaic spread of the hetrostructure, which provides nondestructive estimate of the defect density. For example, the misfit dislocation content in semiconductor thin films can be estimated from the full width at half maximum (FWHM) values of Xray rocking curve peaks.^{145,156,180} This is because the strain fields around dislocation cores introduce crystal plane tilting, which alters the local Bragg condition and increases the rocking curve width. The amount of peak broadening depends on the dislocation density, the Burgers vector and the relative orientation of the dislocations.^{145,156} In addition, twinning in LSM thin films have been observed to increase the rocking curve peak width.¹⁸¹ In this study, all rocking curve measurements were performed in high resolution triple axis mode. The results indicate that the coherently strained films have high crystalline quality and low defect content, with rocking curve FWHM values comparable to the substrates; while in strain relaxed films, the FWHM values is much higher due to a high density of misfit dislocations.

Reciprocal space maps (RSM) are a series of $2\theta - \omega$ scans at different ω angles that probe the reciprocal space nature of the heterostructure by X-rays. They provide valuable information on the epitaxy status and film-substrate coherency. In-plane lattice parameters can be deduced and crystal structures can be identified from RSMs.^{21,182} Recent studies have shown small amount of monoclinic distortions in pseudocubic LSM deposited on SrTiO₃ (110) substrate.¹⁸³ In this study, RSMs were collected using high resolution optics in tripleaxis mode, where a Ge(220) crystal analyzer was inserted in the diffracted beam path.



3.5 Electron channelling contrast imaging (ECCI)

Figure 3.4: Schematic showing electron beam interaction with the sample surface in a scanning electron microscope (SEM), producing secondary electrons, backscattered electrons and X-rays.

Electron channelling contrast imaging (ECCI) is a nondestructive defect imaging technique based on scanning electron microscopy (SEM).^{146,184} Figure 3.4 shows the beam electron interaction with a sample's near surface region, producing secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, X-rays, etc.. SEs are produced via inelastic collisions when incident beam electrons or backscattered electrons knockout valence electrons from the sample surface. SEs have shallow escape depth (usually only a few nanometers) and are suited for surface topography imaging. BSEs are produced through elastic collisions between the beam electrons and the sample atomic nuclei, while the beam electrons are subsequently reflected or back-scattered out of the specimen. BSEs possess higher kinetic energy compared with SEs. The BSE yield increases with atomic number (Z) of the sample material, allowing for Z-contrast (chemical composition) imaging. In addition, the BSE intensity also depends sensitively on the relative orientations between lattice planes and incident beam, which allows for orientation mapping through electron backscattered diffraction (EBSD) and defect characterization through ECCL.¹⁴⁶

At low magnifications, the electron beam rasters across a large area of a single crystal sample to produce an electron channeling pattern (ECP). Similar to Kikuchi bands in EBSD, ECPs can be used to identify crystallographic orientation and to determine the channeling condition (g).¹⁴⁶ In this study, experimental ECPs were collected at low magnifications (37x) by sweeping the beam over an angular range of 4 - 5°. Simulated ECPs were computed using dynamic scattering of Bloch waves and have a larger angular range of 15 - 20°.¹⁶⁵ The simulated and experimental ECPs showed good agreement with each other.

Electron channelling contrast imaging (ECCI) makes use of the fact that at high magnifications, BSE intensity is strongly dependent on the orientation of crystal lattice planes relative to the incident beam.¹⁴⁶ When the incident beam is set for Bragg condition on a single crystal, beam-sample interactions produce a uniform BSE intensity everywhere in the background. However, when crystal defects near the surface region distorts local crystal plane orientations, the Bloch wave extinctions are significantly modified.¹⁶⁰ This leads to a small but recordable change in the BSE intensity, and thus allows for direct imaging of surface penetrating or subsurface defects.

In this work, a field emission scanning electron microscope (Quanta 600 FEG, FEI) coupled with a pole-piece mounted GAD Quanta BSE detector was used for backscattered (BS) ECCI. Different Bragg conditions were achieved through a combination of sample tilting and rotation. Images were recorded at an electron acceleration voltage of 20 kV, spot size 6.0 and working distance of 8 mm. Forescatter (FS) ECCI was completed by mounting the sample surface at 45° with respect to the electron beam and placing the detector parallel to the electron beam to maximize scattered electrons detection.¹⁸⁵ SrTiO₃ single crystal substrates and epitaxial LSM thin films were studied.

3.6 Atomic force microscopy (AFM)

Given that the surface exchange properties of thin film electrodes are very sensitive to surface morphology,⁷⁷ samples with low surface roughness are preferred for accurate surface exchange measurement. Atomic force microscopy (AFM) was used to measure the surface morphology of all PLD deposited thin films. During a typical AFM scan, a cantilever was placed near the sample surface, while a small piezoelectrical element mounted in the tip holder drives the tip to oscillate up and down near its resonance frequency.¹⁸⁶ The magnitude of the interaction between the AFM tip and the sample surface, mainly the van der Waals force, is related to the distance between the sample surface and the tip. As the

cantilever scans across the sample surface, its height is adjusted according to height of the surface features to maintain a constant oscillation amplitude. A laser beam reflected from the back of the cantilever records its up-and-done movement and converts it to a surface profile.¹⁸⁷ All scans were completed in semicontact mode using one of two AFM instruments: a Veeco (Dimension 3100) or a Solver Next (NT-MDT, Moscow, Russia). For tapping mode, aluminum coated silicon tips (NSG10, NT-MDT) with a rated resonant frequency of 240 Hz were used. The scan areas were typically $2 \ge 2 \mu m^2$ or $5 \ge 5 \mu m^2$, with a scan frequency of 1 Hz. Root-mean-square (rms) roughness values measured over different areas were averaged for the determination of the film roughness.

3.7 Electrical conductivity relaxation (ECR)

Electrical conductivity relaxation (ECR) measures the kinetics of the oxygen reduction reaction at the electrode surface by monitoring the conductivity change upon an abrupt change of oxygen partial pressure. This causes the lattice oxygen to exchange with the surrounding oxygen molecules, in order to achieve a new electrochemical equilibrium. The reaction is accompanied by a change in the oxygen stoichiometry through the generation and annihilation of vacancies, as well as a charge transfer process involving a change in the electronic conductivity of the sample. Thus, by fitting the electronic conductivity profile with established models, kinetics of the electrode reaction can be determined.⁷⁷ ECR has been used to measure the surface exchange ^{77,188} and bulk diffusion properties^{86,189} of many oxide electrode materials.

A schematic of the experimental setup for ECR is given in **Figure 3.5** (a). The electrical conductivity of the square thin film sample (10 mm x 10 mm x 0.5 mm) was measured by a four-point van der Pauw method. The van der Pauw geometry eliminates contact resistance by applying contacts on four corners, as shown in **Figure 3.5** (b). Gold (Ted Pella, Inc.) is chosen as contact material because it is chemically inert and, unlike silver or platinum, gold does not catalyze oxygen reduction reactions. The sample was connected to a Keithley 6620 (Keithley Instruments Inc.) precision current source, which delivers a fixed current of 1 mA, and a Keithley 2182A nanovoltmeter, which measures the voltage response every 0.2 seconds. The sample was then placed inside a three zone tube furnace in vacuum for high

temperature measurement. A mass flow controller (MKS Instruments) was used to adjust the oxygen gas flow rate and to create a step change in the oxygen pressure. A convection vacuum gauge (InstruTech Inc.) was used to monitor the chamber pressure. At pressure equilibrium, the gas input rate equals the pumping throughput and the sample is under laminar flow in the furnace. A thermocouple was placed next to the sample to monitor the temperature.



Figure 3.5: a) Schematic diagram of the ECR reactor. b) Schematic of the thin film sample used in ECR measurements (c) Example of ECR data and curve fitting using surface control model.⁸⁹

A Labview program was used to record the sample's conductivity change in the transient experiments. The ECR data was analyzed using models published elsewhere, ^{77,89,190} which relates the flux of mass into or out of the sample to the time dependent composition that influences the transient conductivity.²⁸ A typical conductivity relaxation curve is presented in **Figure 3.5**(c). In this figure, g(t), the relative conductivity of the sample was plotted against time, after the oxygen pressure step change from 50 to 500 mTorr at 700 °C. This corresponds to sample changing from equilibrium state 1 to equilibrium state 2. The equation for fitting the relaxation data and for extracting the surface exchange coefficient (k_{chem}) is given in **Equation 7.1**,⁷⁷ where g(t) is the normalized conductivity; σ_t , $\sigma_{initial}$, and σ_{final} represent the sample conductivity at time t, at the beginning (initial), and finish (final) of the exchange process; L is the sample thickness; τ is the sample reaction time; and $k_{chem} = \frac{L}{\tau}$.

$$g(t) = \frac{\sigma_t - \sigma_{initial}}{\sigma_{final} - \sigma_{initial}} = 1 - \exp(-\frac{t}{\tau}) = 1 - \exp(-\frac{k_{chem}t}{L})$$
(3.2)

A reactor flush time correction introduced by Otter et al.⁷⁶ was applied to all ECR data in this study. It has been demonstrated that the flushing behavior of the reactor volume has critical influence over the early stage of the relaxation process and can introduce errors in transport property measurement.⁷⁶ Equation $3.3^{89,191}$ gives the formula for flush time correction, where τ_{flush} is the reactor flush time, τ_{sample} is the real sample reaction time. The chamber flush time was estimated to be 2.5 s and 1 s for oxidation and reduction steps, respectively.⁸⁹

$$\tau_{total} = \tau_{flush} + \tau_{sample} \tag{3.3}$$

CHAPTER IV

Electron channeling contrast imaging of anti-phase boundaries in coherently strained $La_{0.7}Sr_{0.3}MnO_3$ thin films on $(110)_c$ -oriented $SrTiO_3$

4.1 Chapter overview

This chapter describes the discovery and analysis of anti-phase boundaries (APBs) in coherently strained $La_{0.7}Sr_{0.3}MnO_3$ films on $SrTiO_3$ by electron channeling contrast imaging (ECCI). The morphology, areal density, intensity profile and **g**-dependent contrast behaviors of APBs were analyzed. Their formation with respect to the MnO_6 octahedral rotations are discussed, and a schematic APB model was proposed. It demonstrates the nondestructive capabilities of ECCI to study defects on the mesoscale in thin films. Most results in this chapter have bee published elsewhere.¹⁶⁶

4.2 Background

Epitaxial strain and extended defects impact the functionalities of thin film devices.¹ As such, it is important to characterize and map defects over large length scales. Transmission electron microscopy (TEM) provides information on the nanometer scale, but sample preparation is destructive.⁴⁸ X-ray diffraction (XRD) provides information over much longer length scales, but is not suited to isolate or map individual defects.¹⁴⁵ Electron channeling contrast imaging (ECCI) offers a non-destructive way to characterize extended defects on the mesoscale.^{146,147}

ECCI is a scanning electron microscopy (SEM) technique in which backscattered elec-

trons (BSE) are recorded while the incoming electron beam satisfies a Bragg condition. The electron yield is sensitive to extended structural perturbations, including dislocations, ^{124,163} stacking faults, ¹⁹² and twin boundaries. ¹⁸¹ The density of threading dislocations measured by ECCI is nearly identical to that measured by TEM. ¹⁶⁷ The Burgers vector of dislocations has been found using ECCI, similar to the way it is done in TEM. ^{163,168} ECCI has been used to study metals, ^{146,147,163,164} semiconductors, ^{161,165} oxide crystals, ¹²⁴ and nitride films. ^{162,193} ECCI has not been used to characterize heteroepitaxial oxide films or anti-phase boundaries (APBs), which are the focus of this work.

 $La_{1-x}Sr_xMnO_3$ exhibits colossal magnetoresistance, is of interest for spintronics, and is an important electrocatalyst. These functional properties can be modified using heteroepitaxial strains.^{9,182,183} Bulk $La_{0.7}Sr_{0.3}MnO_3$ (LSM) is rhombohedral (r) with lattice parameters a_r = 5.506 Å and $c_r = 13.3564$ Å (using a hexagonal setting for $R\bar{3}c$),⁴⁷ and has $a^-a^-a^-$ Mn-O octahedral rotations (ORs).⁴⁶ r-LSM can be approximated as pseudocubic (pc) with a_{pc} = 3.893 Å.¹⁸² Structural modifications occur on (La,Sr)-site doping,⁴⁷ on variation in the oxygen content,¹⁹ or under epitaxial coherency strains,^{29,182} which can drive LSM to be orthorhombic (o) or monoclinic (m); the ORs of each depends on the driving force for the distortion. Lattice parameters of strained LSM are approximately $a_{o,m} \approx 5.49$ Å, $b_{o,m} \approx$ 5.52 Å, $c_{o,m} \approx 2a_{pc} \approx 7.78$ Å.¹⁸²

Substrate effects arise primarily from cell length variations owing to lattice parameter misfit and secondarily from OR perturbations arising from coherency requirements at interfaces with OR misalignments.^{29,182,183,194–196} SrTiO₃ (STO) is cubic (c) with $a_c = 3.905$ Å, resulting in tensile strain to LSM, and lacks ORs ($a^0a^0a^0$). NdGaO₃ (NGO) is orthorhombic with $a_o = 5.428$ Å, $b_o = 5.498$ Å, and $c_o = 7.709$ Å,¹⁹⁷ resulting in compressive strain to LSM, with a tilt system of $a^-a^-c^+$. Herein, coherently strained *m*-LSM (*o*-LSM) thin films were grown on (110)_{pc} surfaces: (110)_c STO ((100)_o NGO). ECCI was used to identify extended defects, including threading dislocations and antiphase boundaries (APBs) for LSM on STO. We focus on describing their contrast and determine the direction of the displacement vector **R** for the APB.

4.3 Experimental

Films were prepared by pulsed laser deposition (PLD), as described elsewhere.⁹ 50 nm and 600 nm thick LSM were deposited on $(110)_c$ -STO and/or $(100)_o$ -NGO (MTI Corporation, USA) at 750 °C in 50 mTorr O₂, and cooled at 25 °C/min in 200 Torr O₂. The growth rate was calibrated at 0.3 Å/pulse using x-ray reflectivity (XRR). Orientation, epitaxy, strain, and out-of-plane mosaic spread were characterized by high resolution (HR-)XRD in triple axis mode (Philips XPert MRD).⁹ A Quanta 600 field emission SEM (FEI Corp.), coupled with a pole-piece mounted GAD Quanta diode BSE detector, was used for conventional back-scattered (BS) ECCI.¹²⁴ Images were recorded at 20 kV, 6.0 spot size, and 8 mm working distance. Forescatter (FS) ECCI was completed by mounting the sample surface at 45° with respect to the electron beam and placing the detector parallel to the electron beam to maximize scattered electrons detection.¹⁹⁸

4.4 Results

4.4.1 Structural characterization by reciprocal space mappnig

HR-XRD confirmed that both LSM films were epitaxial and coherently strained with the substrates. The epitaxial nature of m-LSM on STO is described as: $(100)_{m,LSM}[001]_{m,LSM} \parallel (110)_{c,STO}[001]_{c,STO}$. The m-LSM film has lattice parameters of $a_m = 5.455$ Å, $b_m = 5.523$ Å ($= 2d_{1\bar{1}0,STO}$), $c_m = 7.81$ Å ($= 2d_{001,STO}$), and $\beta_m = 90.5^{\circ}$. Figure 5.1 presents the reciprocal space maps around the $(40 \pm 4)_m$ (or $(22 \pm 2)_{pc}$) reflections of the m-LSM film on STO. The two scans are separated by 180° in ψ space. Different d spacings of the LSM peaks are clearly observed, indicating a monoclinic distortion where the LSM $(00l)_m$ planes tilt toward the in-plane [001] axis, consistent with that reported by Boschker et al.¹⁸³ The single film peak in either scan indicates that only one m-LSM domain exists in the film. As such, we do not expect monoclinic variants (or variant boundaries). Meanwhile, the LSM film on NGO is orthorhombic with $a_o = 5.530$ Å, $b_o = 5.498$ Å ($= b_{NGO}$), $c_o = 7.708$ Å ($= c_{NGO}$). The full width at half maximum (FWHM) of LSM (200)_{m,o} rocking curves were identical to those of the substrates, being ≈ 108 arcseconds for LSM/STO and ≈ 54 arcseconds for LSM/NGO.



Figure 4.1: Reciprocal space maps around the (a) $(404)_m$ and (b) $(40\bar{4})_m$ reflections of the film on STO. The different d spacings indicate a specific monoclinic distortion.

4.4.2 Simulated and experimental electron channeling patterns

A simulated (using techniques published elsewhere¹⁶⁵) electron channeling pattern (ECP) for a $[110]_{pc}$ -LSM crystal at 20 kV is shown in **Figure 4.2**. The wide horizontal band corresponds to the $(1\bar{1}0)_{pc}$ or $(020)_{m,o}$ planes and the and narrower vertical band to the $(001)_{pc}$ or $(002)_{m,o}$ planes. An experimental ECP centered around $\mathbf{g} = (002)_m$ is overlayed, with a scale bar of 1 millimeter. Experimental ECPs are produced by sweeping the beam at low magnification across an angular range of $4 - 5^{\circ}$; the angular range in the simulated ECP is $15 - 20^{\circ}$. There is good agreement between the two patterns.

4.4.3 Electron channeling contrast images of 50 nm films

An ECCI micrograph from $(110)_c$ -STO is presented in **Figure 4.3**(a) ($\mathbf{g} = (001)_c$). The uniform grey background arises from the average BSE yield. Point-like features exhibiting "dark-to-bright" contrast variations are characteristic of dislocations intersecting the surface at near normal incidence.^{146,163} Short line-segment features, or "comet tails" (one labeled "t"), are characteristic of dislocations inclined to the surface.¹²⁴ A band of bright contrast bounded by rows of dislocations is observed running diagonally through the image (between



Figure 4.2: A simulated ECP for $[110]_{pc}$ LSM crystal is overlayed with an experimental ECP centered on the $\mathbf{g}_1 = (002)_m$ band edge. Channeling conditions used elsewhere herein are marked with \mathbf{g} vectors for the relevant band edges.

offset dashed lines). Such regions of clustered dislocations, having densities on the order of $10^8 - 10^9$ cm⁻² and likely resulting from surface polishing,¹⁹⁹ occurred in bands a few millimeters long and a few microns wide. Large regions in between such dislocation bands exhibited low dislocation densities, on the order of $10^5 - 10^6$ cm⁻². Almost no contrast was observed for the $(100)_o$ -NGO surface (not shown), consistent with the narrower XRD rocking curves.

An ECCI micrograph from the m-LSM on STO is presented in Figure 4.3(b) (g = $(002)_m$). Point like features correspond to surface particles (p), exhibiting bright contrast, or threading dislocations (d), exhibiting bright-to-dark contrast. The distribution of dislocations in the film is similar to the substrate, consistent with coherent nature of the film. Surprisingly, line features that form meandering loops (MLs) and exhibit strong dark contrast under $\mathbf{g} = (002)_m$ are also observed. The MLs close themselves in domains of varying complexity and size, typically on the order of microns. The mean linear spacing between ML line segments is 0.7 ± 0.3 µm and the average areal density is 1 - 3 µm/µm². Interestingly, ECCI micrographs for o-LSM deposited on $(100)_o$ -NGO, shown in Figure 4.3(c), did not reveal any MLs. Using $\mathbf{g} = (002)_o$, only surface particles ("p") are visible.



Figure 4.3: ECCI micrographs of (a) STO, (b) m-LSM on STO, and (c) o-LSM on NGO. Channeling conditions are given.

The MLs are invisible in secondary electron and atomic force microscopy images, suggesting that they are not surface topographic features. They are also invisible in BSE imaging with the beam parallel to the $[100]_m$ zone axis, indicating they are sensitive to an acting channeling condition and are not local chemical segregation. The MLs are not monoclinic variant boundaries, as there is only one variant. The morphology and contrast profiles of the MLs differ from that observed in ECCI from various extended defects, including inclined dislocations or buried dislocation loops¹²⁴, twin boundaries¹⁸¹, and stacking faults.¹⁹² Their morphology and contrast resemble that of APBs observed in TEM.^{149,200}

Measured BSE intensity profiles are plotted in **Figure 4.4** when traversing (a) a surfacepenetrating dislocation in STO and (b) a ML in m-LSM, each registered using two opposite channeling conditions (\pm **g**). The dislocation exhibits "bright-to-dark" intensity undulations whose contrast inverts when using the opposite **g**.¹⁴⁶ The ML exhibits only bright or dark contrast for a given **g**, but exhibits contrast inversion with **g** inversion. Contrast inversion suggests the ECCI intensity arises from a structural perturbation associated with an extended crystallographic defect.¹⁶⁵ The overall width of the contrast variation from a dislocation is much larger (≈ 800 nm) than that from a ML (≈ 80 nm). This can arise from either a different spatial extent of the structural perturbation or a different mechanism causing contrast in ECCI (e.g., strain fields around dislocations versus phase shifts of the structure factor around stacking faults).^{147,148}

BS- & FS- ECCI micrographs recorded from the same location of a m-LSM film using 6 different **g** vectors are presented in **Figure 4.5**. In all micrographs, a contrast band



Figure 4.4: BSE intensities across (a) a dislocation in STO and (b) a ML in m-LSM on STO. Solid grey and dashed black curves were registered at opposite $\pm \mathbf{g}$.

associated with dislocations runs from the bottom left to the center of the image (between offset dashed lines), and a number of isolated threading dislocations (marked with arrows near "d") and surface particles (two near "p") are visible. These were used as fiducial markers. In (a,b), contrast from MLs is clearly visible, being uniformly dark (bright) under $\mathbf{g}_1 = (002)_m$ ($\mathbf{g}_2 = (00\bar{2})_m$). MLs were also observable (but not shown) using $\mathbf{g} = \pm (02\bar{2})_m$. In comparison, MLs are invisible in (c,d) ($\mathbf{g}_{3,4} = \pm (020)_m$) and (e,f) ($\mathbf{g}_{5,6} = \pm (2\bar{2}0)_m$, collected in a FS-geometry). The FS-ECCI micrographs generally have lower lateral resolution and worse contrast than the BS-ECCI geometry.¹⁴⁷ But, the MLs were observable under $\mathbf{g} = \pm (002)_m$ using the FS-geometry (not shown). The invisibility of MLs further supports that their origin is related to a structural perturbation related to crystallography. The contrast of MLs is strongly dependent on the channeling conditions: they show strong contrast under $\mathbf{g}_{1,2} = \pm (002)_m$ (in BS- & FS-geometries), weak contrast under $\mathbf{g} = \pm (02\bar{2})_m$, and they were invisible under \mathbf{g}_{3-6} .



Figure 4.5: ECCI micrographs (with inset ECPs and 2 μ m scale bars) from the same location of m-LSM on STO under different channeling conditions (as marked). Images a-d (e,f) were collected using a backscattered (forescattered) geometry. The contrast between dotted lines provide a fiducial marker. The MLs exhibit strong contrast in (a,b), but are invisible in other conditions.

4.4.4 Electron channeling contrast images of 600 nm film

A 600 nm LSM film was deposited on $(110)_c$ STO substrate in the same deposition condition. Its crystal structure was characterized by X-ray diffraction and related methods. Results suggest that despite the large thickness, the film remains coherently strained to the substrate and exhibits two monoclinic domains. The film has a very low dislocation content, similar to the 50 nm LSM film on STO. Detailed descriptions of the structural characterization of the 600nm LSM film can be found in **Chapter V**.

Figure 4.6 shows the ECCI micrographs of the 600 nm m-LSM on STO under $\mathbf{g} = (002)_m$, including: (a) a low magnification image showing the ML contrast and distribution, and high magnification images of (b) the periodic background intensity undulation, and (c-d) the interactions between ML and background undulation. The scale bar is 2 µm in (a), and 500 nm in (b-d). The MLs in 600 nm film present dark contrast under $\mathbf{g} = (002)_m$, consistent with previous results on 50 nm film. In addition, the morphology, areal density,



Figure 4.6: ECCI micrographs ($\mathbf{g} = (002)_m$) of a 600 nm m-LSM on STO, including: (a) a low magnification image showing the ML contrast and distribution, and high magnification images of (b) the periodic background intensity undulation, and (c-d) the interactions between ML and background periodicity. The scale bar is 2 µm in (a), and 500 nm in (b-d).

and contrast width (ca. 80 nm) are also similar to previous findings on the 50 nm film.

An interesting observation is the periodic undulation in the background intensity in the 600 nm film, as shown in **Figure 4.6**(b). They present bright to dark wave-like contrast. Analysis with ImageJ shows that such undulation has an average periodicity of 60 nm, and its amplitude is on the order of 10 - 15% of total intensity. This is comparable to the contrast of MLs, which have an average width of ca. 80 nm, and an intensity gain/loss of 15 - 20 % of the average background. The intensity undulation is highly anisotropic, having a propagation direction along LSM [001] (parallel to the channeling condition). More interestingly, the contrast from the periodic undulations clearly interacts with the dark line contrast from the MLs. The interaction results in local constructive and destructive interference. As shown in **Figure 4.6**(c-d), when the ML line direction is along the undulation propagation direction (LSM [001]), their contrast summation between the background undulations and the ML line contrast. In comparison, when the ML line direction is along



Figure 4.7: A 1 x 1 μ m² AFM image of 600 nm strained LSM surface on STO. The bottom image shows the surface height profile in the dotted region of the film. Height undulations increase the root-mean-square (RMS) roughness to 1.5 nm in this film.

 $[1\bar{1}0]_{pc}$, its contrast is often "washed off" by the periodic background beating, resulting in the ML contrast appearing to be broken along these directions. Note that the "broken" contrast in the ECCI micrographs does not indicate that MLs are actually disconnected. Instead, the broken contrast is a result of destructive interference between ML contrast and background undulation.

We suggest that such periodic undulations in ECCI are caused by surface ripples near the LSM surface, likely due to the large residual tensile strain induced by the substrate. Surface ripples have been previously reported in strained semiconductor thin films as a sinusoidal undulations at the surface consisting of ridges and troughs,^{201,202} consistent with the morphology observed here. AFM scans from the film surface is shown in **Figure 4.7**. The bottom image shows a surface height profile in the dotted region of the film. Periodic undulations in surface height was observed, with an average periodicity of 60 nm, similar to the features observed in ECCI. The root-mean-square (RMS) roughness is 1.5 nm, much rougher than the 50 nm film (RMS roughness 0.5 nm). The driving force for ripple formation on the strained layers is the lowering of the system free energy by partial elastic strain relief.²⁰³ In strained $Si_{1-x}Ge_x$ epitaxial layer on Si, lattice distortion measurements have suggested that the ripple peak regions have near-complete strain relaxation in a direction normal to the ripple rows (or parallel to the propagation direction), and the additional compressive lattice plane distortion at ripple troughs is likely to promote misfit dislocation nucleation by reducing the energy barrier.²⁰¹ Thus, surface rippling is an elastic strain relaxation mechanism, one that is precedent to the plastic strain relaxation via dislocation nucleation. The ripples have an effective Burger's vector along the propagation direction of the sinusoidal undulations, allowing them to be imaged by transmission electron microscopy.^{201,204} Contrast from surface ripples are visible in ECCI in this study due to modifications to the local strain. For more discussions on the relations between surface ripples and dislocations in the 600 nm film, please refer to **Chapter V**.

4.5 Discussions

The contrast behavior of the MLs is consistent with a structural perturbation from an extended crystallographic defect. We propose the MLs are APBs, 2-D crystalline defects separating domains related by a translation vector **R**. APBs are commonly observed by TEM in ordered alloys,²⁰⁰ thin films,¹⁵³ and oxide materials.¹⁴⁹ Their morphology and contrast in TEM are similar to that observed for MLs with ECCI.^{149,153,200} TEM contrast from APBs depends on **g**, exhibiting contrast inversion and extinction.¹⁴⁹ The APBs should be invisible when the phase shift $\alpha = 2\pi \mathbf{g} \cdot \mathbf{R}$ is an even multiple of π . Using the contrast observed from the 3 independent **g** vectors in **Figure 4.5**, the direction of the displacement (the fractional displacement could not be determined) is $[001]_m$.

We propose that the MLs correspond to APBs with $\mathbf{R} = \frac{1}{2}[001]_m$. The *r*-, *m*-, and *o*-polymorphs of LSM (regardless of their precise *ORs* or space groups), and *o*-NGO have a cell doubling along the c-axis (with respect to the *pc*-cell: $c_{o,m} \approx 2a_{pc}$). As such, the *c*-axis of *m*-LSM has a clear "double positioning" degeneracy on the *c*-axis of STO, leading to natural APBs with $\mathbf{R} = \frac{1}{2}[001]_m$. Schematics of the two types of domains are shown in **Figure 4.8**, where the bulk *r*-LSM structure ($a^-a^-a^-$ tilt system) is depicted, and the axes are given in cubic notation. In **Figure 4.8**(a), a bilayer of octahedra are shown for the



Figure 4.8: Schematics of an APB in LSM $(R\bar{3}c)$ viewed along different axes: (a) $[110]_{pc}$, (b) $[1\bar{1}0]_{pc}$, and (c) $[001]_{pc}$.

 $(110)_{pc}$ growth plane. Domain 1 (2, lower right) has yellow (orange) octahedra in the lower layer and blue (purple) octahedra in the upper layer. The APB is schematically placed at the connecting oxygen positions (though other possibilities exist¹⁹⁴). The APB is associated with the ORs,¹⁹⁴ which can be seen at the domain boundary where adjacent octahedra have identical tilts. Such an undistorted APB in the perovskite oxide would result in disconnected octahedra. These disconnections are marked with different symbols in **Figure 4.8**. They are more clearly observed in **Figure 4.8** (b) and (c), which provide views of the APBs along the $[1\bar{1}0_{pc}]$ and $[001]_{pc}$, respectively. The real APB must maintain connectivity of the octahedra across the interface, either by straining locally to new symmetries (rotating octahedra resulting in strain) or by shuffling atoms within the cell (distorting the octahedra while maintaining the overall cell size), or by a combination of both.

In both TEM and ECCI experiments, the contrast level of a crystalline defect is a function of the local perturbation, the contrast mechanism, and the diffraction conditions used.^{146,149} APB contrast in TEM arises from a phase shift that is sensitive to the local ordering of atom positions at the APB boundary, such as in ordered metal alloys,²⁰⁰, or cation ordered ceramics.¹⁴⁸ In such cases, there is virtually no strain present. In ECCI, contrast of APBs formed by octahedra rotations can either arise from atom shuffling effects (which affect the local structure factor) or local strain effects (which affect cell size). Both

can be spatially extended normal to the interface, but would result in APB contrast being narrower than the dislocation contrast. Recent investigations of tilt system variations at substrate film interfaces^{195,205} indicate the spatial extent of an OR perturbation is on the order of 1 to 10 unit cells (i.e., on the order of a few nanometers). In contrast, the spatial extent of local structural variations around a dislocation core is on the order of tens of nanometers.^{13,150} This agrees qualitatively with our measurement of ECCI contrast extent between APBs and dislocations (**Figure 4.4**). However, we cannot presently determine the precise contrast mechanism nor quantify the spatial extent of the structural perturbation around the APBs: simulations using an improved structural understanding are required.

In comparison, such double positioning boundaries are not necessarily expected in o-LSM on NGO, because both have doubled axes along the pseudocubic c-axis. However, because the tilt system of NGO is $a^-a^-c^+$, the absence of APBs indicates that the LSM tilt system is either $a^-a^-c^+$ (Pnma) or $a^-a^-c^0$ (Imma), neither of which would require phase shifts in the ORs along the c-axis.¹⁹⁴ These tilt systems are consistent with prior observations of LSM bulk and film systems.^{19,29} It should be noted that $\mathbf{R} = \frac{1}{2}[001]_m$ is not typical for APBs in manganese-based perovskite oxides, which are generally $\mathbf{R} = \frac{1}{2}[111]_o, \frac{1}{2}[101]_o, \text{ and } \frac{1}{2}[010]_o.^{149,153}$ The atypical \mathbf{R} seems to be directed by the specific tensile strain state of m-LSM on $[110]_c$ STO, which results in a single type of double positioning degeneracy that likely affects the $ORs.^{206}$

4.6 Conclusions

In summary, ECCI was used to non-destructively and quantitatively analyze extended defects in coherently strained $La_{0.7}Sr_{0.3}MnO_3$ thin films. Low densities of surface penetrating dislocations were heterogeneously distributed on the surfaces of LSM films in similar fashion to those of the substrates. Importantly, meandering loop features were observed. They exhibit a uniform contrast variation from the background that is dependent on channeling condition (**g**), including contrast extinction and inversion. The MLs are consistent with APBs having a displacement vector of $\mathbf{R} = \frac{1}{2}[001]_m$ and associated with the double positioning of the MnO₆ octahedral rotations on the rotation-free STO substrate. They represent a class of mesoscale extended defects in oxide thin films that can be studied by ECCI. In addition, periodic intensity undulations induced by the surface ripples were observed in a strained 600 nm LSM film on STO. Their sinusoidal undulation contrast were found to interact with the APB line contrast. These results highlight the use of ECCI in thin film research, which provides unique opportunities to selectively identify and to study defect distributions on the mesoscale.
CHAPTER V

Dislocations and strain relaxation in $La_{0.7}Sr_{0.3}MnO_3$ thin films on $(110)_c$ -oriented $SrTiO_3$

5.1 Chapter overview

This chapter summarizes experimental findings on the characterization of dislocations and strain relaxation in $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$ (LSM) thin films on $(110)_c$ -oriented SrTiO₃. LSM thin films of different strain status were prepared by pulsed laser deposition (PLD). Strain relaxation was found to be influenced by thickness and thermal processing, including by varying the cooling rate at 200 Torr pO₂ post deposition and by high temperature annealing. The crystal structures of strained and relaxed LSM were characterized by high resolution X-ray diffraction (XRD) and reciprocal space mapping (RSM). The defect contents were characterized by X-ray rocking curve (RC) and electron channeling contrast imaging (ECCI). The dislocation density was found to increase with increasing strain relaxation, varying up to three orders of magnitude. In addition, dislocation density values measured by RC and ECCI are complementary to each other.

5.2 Introduction

Understanding the effects of epitaxial strain and extended defects on the functionalities of thin film devices has been a growing research area.^{1,2} Perovskite $La_{1-x}Sr_xMnO_{3\pm\delta}$ (LSM) is an interesting candidate for applications in magnetic tunnel junction (MTJ) and solid oxide fuel cell (SOFC) cathodes.^{20,71,183} It has been shown that the magnetic domain structure,⁷ the Curie temperature,⁸ and the magnetization anisotropy²¹ of LSM are strongly dependent on the extent and sign of epitaxial strain. In addition, strain also changes the catalytic properties of LSM towards oxygen reduction by modifying the oxygen vacancy formation energy, the cation stoichiometry, and the surface electronic states.^{6,207}

Strain in LSM material can be accommodated through several independent mechanisms. For example, LSM thin films under epitaxial strain exhibit changes in the crystal symmetry,^{29,182} modifications to the MnO₆ octahedral rotation patterns,^{205,208}, introduction of rhombohedral twins,¹⁸¹, and changing the Mn^{3+/4+} oxidation state.²⁰⁹ In addition, strain relaxation in LSM thin films can be accompanied by severe microstructure changes. For example, the critical relaxation thickness of $(100)_{pc}$ oriented LSM deposited on STO was found to be about 70 nm.⁴⁸ A columnar structure was observed above this thickness, which consists of periodic cracks that relax in-plane strain. These atomic and microstructural changes can have strong effects on the functional properties of LSM.^{16,29} Thus, characterization of structure distortions under strain and defects generatation during strain relaxation are topics of great research interests.

Bulk $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3\pm\delta}$ (LSM) has rhombohedral $R\bar{3}c$ (No. 167) structure with lattice parameters $a_r = 5.506$ Å and $c_r = 13.3564$ Å.^{18,47} It can be approximated using a pseudocubic (*pc*) structure with $a_{pc} = 3.893$ Å.¹⁸² LSM exhibits a rich phase diagram including monoclinic (*m*) or orthorhombic (*o*) phases, with structural modifications that occur on A-site doping,⁴⁷ or variations in the oxygen content,¹⁹ and/or under epitaxial coherency strain.^{29,182} SrTiO₃ (STO) has cubic (*c*) *Pm3m* structure with $a_c = 3.905$ Å.²¹⁰ The lattice mismatch between STO and LSM results in $\approx 0.3\%$ in-plane tensile strain.¹⁸²

The $(110)_{pc}$ orientation of LSM is an ideal electrode for MTJs, due to its strong magnetic anisotropy and the ability to prevent interfacial charge transfer.^{21,183} In addition, the $(110)_{pc}$ orientation exhibits superior oxygen exchange kinetics than other low index surfaces for SOFCs applications.²⁸ In this study, we focus on characterization of the structural distortions under strain and the quantitative analysis of defect densities in $(110)_{pc}$ LSM thin films deposited on SrTiO₃. The crystal structures of strained and relaxed LSM were characterized by high resolution X-ray diffraction (XRD) and reciprocal space mapping (RSM). The defect contents were characterized by X-ray rocking curve (RC) and electron channeling contrast imaging (ECCI). The dislocation density was found to increase with increasing strain relaxation, varying up to three orders of magnitude. In addition, dislocation density

values measured by RC and ECCI are complementary to each other.

5.3 Experiment

A dense, stoichiometric perovskite $La_{0.7}Sr_{0.3}MnO_{3\pm\delta}$ target was prepared by solid state reaction. Single crystal SrTiO₃ substrates (MTI Corporation, USA) with (110)_c- orientation were cleaned with methanol and acetone before each deposition. Three LSM films were deposited at 750 °C, 50 mTorr O₂, and 1 Hz by pulsed laser deposition (PLD).¹⁶⁶ After deposition, the chamber pressure was increased to 200 Torr O₂, and the sample was cooled immediately after, at cooling rate between 1-25 °C/min. In the case of Sample C* (naming will be discussed later), additional post annealing was performed at 900 °C in 50 mTorr O₂ for 48 hours. The PLD growth rate was calibrated at 0.3 Å per pulse using X-ray reflectivity (XRR). High resolution X-ray diffraction (XRD) related experiments were performed in a triple-axis diffractometer (Philips X'Pert MRD).¹⁷³ A Quanta 600 field emission SEM (FEI Corp.), coupled with a pole-piece mounted GAD Quanta diode BSE detector, was used for back-scattered electron channeling contrast imaging (ECCI).^{124,166} Images were recorded at 20 kV, 6.0 spot size, and 8 mm working distance.¹⁶⁶

5.4 Results

5.4.1 Structural characterization by X-ray diffraction

Three samples, one of thickness 50 nm and two of thickness 600 nm were prepared, and their strain status varied from fully strained (FS), almost relaxed (AR), to fully relaxed (FR), depending on sample thickness and thermal processing conditions. All samples exhibit a single epitaxial relationship between the film (f) and the substrate (s): $(110)_f[001]_f \parallel (110)_s[001]_s$, relative to the pseudocubic cells. Their in-plane (IP) and out-of-plane (OP) lattice parameters were measured by high resolution XRD (±0.001 Å) and are presented in **Table 5.1**, along with the sample naming convention. The processing conditions include post deposition cooling rate (°C/min) in 200 Torr O₂ and 900 °C annealing in 50 mTorr O₂. Lattice parameters of relaxed, bulk LSM¹⁸² are also listed for comparison.

Despite their difference in thickness, Sample A (50 nm) and Sample B (600 nm) have identical lattice parameters and both are fully strained to the substrates. Their in-plane

Table 5.1: Lattice parameters of three $(110)_{pc}$ -oriented LSM thin films on $SrTiO_3$ determined by high resolution X-ray diffraction (Unit: Å), using pseudocubic notation. The strain status includes fully strained (FS), almost relaxed (AR) and fully relaxed (FR). Relaxed, bulk LSM lattice parameters¹⁸² are listed for comparison.

Sample	Thickness	Strain	IP $d_{(001)}$	IP $2d_{(1\bar{1}0)}$	OP $2d_{(110)}$	Processing
$SrTiO_3$	Single Crystal	-	3.905	5.523	5.523	-
Sample A	50 nm	FS	3.905	5.523	5.455	25 °C/min
Sample B	600 nm	\mathbf{FS}	3.905	5.523	5.455	$25^{\circ}\mathrm{C/min}$
Sample C	600 nm	AR	3.893	5.512	5.470	1°C/min
Sample C [*]	600 nm	\mathbf{FR}	3.893	5.506	5.476	$900^{\circ}\mathrm{C}$ annea
$La_{0.7}Sr_{0.3}MnO_3^{-182}$	Bulk	Relaxed	3.893	5.506	5.506	

Note: Sample C^{*} is Sample C after an additional 48 hour annealing at 900 °C to induce full relaxation. 1 or $25 \,^{\circ}$ C/min refers to the post deposition cooling rate in 200 Torr O₂.

lattice parameters are $d_{001} = 3.905$ Å and $2d_{(1\bar{1}0)} = 5.523$ Å, which exactly match the STO values, suggesting a coherent film-substrate interface. The out-of-plane lattice parameters are $2d_{(110)} = 5.455$ Å, which is smaller than the relaxed, bulk value, and are consistent with out-of-plane contraction due to Poisson effects on the coherent strain status. As such, both films are under coherent tensile strain induced by the substrates, without any strain relaxation. This is the first time that a fully strained film of 600 nm thickness was reported. Previous studies of LSM films on STO showed an onset of strain relaxation after 70 nm.⁴⁸ Thus at 600 nm, Sample B is at a non equilibrium state by remaining fully strained and coherent with the substrate, despite the high strain energy. Further discussions on the factors governing strain relaxation and accommodation will be provided.

Sample C (600 nm) was deposited in the same condition as Sample A and B, yet it was cooled at 1 °C/min in 200 Torr O₂. This cooling is much slower than the 25 °C/min post deposition cooling for Sample A and B. The slower cooling rate results in Sample C being almost relaxed (AR) compared with the bulk value. Its in-plane lattice parameters are $d_{001} = 3.893$ Å, identical to the relaxed, bulk LSM value; and $2d_{(1\bar{1}0)} = 5.512$ Å, in between the LSM bulk and STO substrate values. This suggests an anisotropic strain relaxation has taken place, where the strain is fully relaxed along $[001]_{pc}$, and only partially relaxed along $[1\bar{1}0]_{pc}$. After initial characterization, Sample C was subject to an additional anneal at 900 °C for 48 hr in the electrical conductivity relaxation chamber (discussed in later chapters). This additional anneal results in fully relaxed in-plane lattice parameters identical to bulk values. The out-of-plane $2d_{(110)}$ also increases to 5.476 Å, which is the



Figure 5.1: Reciprocal space maps (RSMs) around the (a) $(222)_{pc}$ and (b) $(22\bar{2})_{pc}$ reflections of Sample A (FS 50 nm), and (c) $(222)_{pc}$ reflection of Sample B (FS 600 nm), and (d) $(222)_{pc}$ reflection of Sample C (AR 600 nm), showing the crystal structural evolution during strain relaxation. The single monoclinic domain of Sample A is coherent with the substrate, so are the two monoclinic domains of Sample B; while the two domains of Sample C are incoherent with the substrate. The dashed lines are for visual guidance. RSM of Sample C* were not collected.

largest value among all samples. The new film was named Sample C^{*}, where * denotes the additional 900 °C anneal. As such, two processing parameters, cooling rate in 200 Torr oxygen, and high temperature anneal, were found to control the strain relaxation in LSM films on STO. To achieve a fully relaxed 600 nm film, slower cooling rate and high temperature annealing processing steps are desirable. This suggests that strain relaxation is initiated by the increased oxidation state in higher pO_2 (200 Torr) conditions, which chemically shrinks the LSM lattice parameter and increase the strain energy. In addition, high temperature annealing favors the completion of strain relaxation, likely by providing thermal energy for the climb of misfit dislocations from the film surface down to the filmsubstrate interface, which require point defect diffusion. On the other hand, the opposite processing (increasing cooling rate or no post annealing) allows one to quench strained LSM films on STO beyond its equilibrium critical thickness, allowing possible investigations to the early stages of strain relaxation, and/or alternative strain accommodation mechanisms (such as cracks).

The lattice parameter measurements in **Table 5.1** are supported by reciprocal space maps (RSMs) shown in **Figure 5.1**. For Sample A (FS-50nm), RSMs around the $(222)_{pc}$

and $(222)_{pc}$ reflections are shown in (a) and (b). In both scans, the LSM reflections have identical in-plane values (Q_x) as the substrate, suggesting that it is coherent with substrate along [001] direction. In contrast, the out-of-plane values (Q_y) are larger than STO, suggesting a smaller $d_{(220)}$ spacing. In addition, scans (a) and (b), which are separated by 180 ° in ϕ space, clearly exhibit different Q_y values for the LSM reflections. This is evidence of a monoclinic distortion where the LSM [110]_{pc} orientation tilts toward the in-plane [001]_{pc} axis, consistent with that reported by Boschker et al.? The monoclinic distortion is characterized by $\beta = 89.5$ °, where β is the angle between [110]_{pc} and [001]_{pc}. The single film peak in either scan indicates that only one monoclinic domain exists in Sample A.

The RSM around the $(222)_{pc}$ reflection of Sample B (FS-600nm) is shown in **Figure 5.1** (c). The STO substrate has a misoriented region, which introduces a secondary reflection to the bottom right of the scan. This substrate crystallite propagates to the film, introducing a secondary reflection to one of the monoclinic domains. Apart from the twin reflections, Sample B exhibits two monoclinic reflections which have identical Q_x but different Q_y . These two LSM peaks represent two monoclinic domains. Further analysis using RSM contour plot revealed that the film $(110)_{pc}$ surface is parallel to the STO $(110)_{pc}$ surface. The distribution of two monoclinic domains are discussed later.

The reciprocal space map around the $(222)_{pc}$ reflection of Sample C (FR-600nm) is shown in **Figure 5.1** (d). Similar to (c), the film also exhibits two LSM reflections due to the presence of two monoclinic variants. More importantly, both LSM reflections are severely smeared, causing their in-plane and out-of-plane lattice parameters to differ from the fully strained samples. This confirms that relaxed Sample C is no longer coherent with the substrate, which likely requires formation of misfit dislocations for strain relief.

5.4.2 Evolution of LSM structure during strain relaxation

Schematics of the LSM crystal structure viewed along $[1\bar{1}0]_{pc}$ are shown in **Figure 5.2**. Their construction was based on the reciprocal space maps and their respective contour plots $(2\theta - \omega \text{ plot})$ around $(222)_{pc}$ reflections of LSM. The dotted black lines and solid red lines represent the pseudocubic unit cells of STO and LSM, respectively. **Figure 5.2** (a) shows the single monoclinic domain of 50 nm Sample A. The film is coherent with the



Figure 5.2: Schematics of the LSM film structures viewed along $[1\bar{1}0]_{pc}$: (a) fully strained 50 nm Sample A, having a single monoclinic domain which is coherent with the substrate; (b-d) 3 possible configurations of fully strained 600 nm Sample B, having two monoclinic domains that are coherent with the substrate, and (e) almost relaxed 600 nm Sample C, having two monoclinic domains, and slanted $(110)_{pc}$ planes that are incoherent with substrate. The strain relaxation is accompanied by an increase in the β angles from 89.5° to 89.8°.

substrate and has a β angle of 89.5 ° between $[001]_{pc}$ and $[1\overline{1}0]_{pc}$. Schematics for three likely domain arrangements in the 600 nm Sample B are shown in **Figure 5.2** (b-d). The film has two monoclinic domains, which could be vertically distributed (b), horizontally distributed (c), or a combination of both (d). The film still maintains in-plane coherency with the substrate, and the LSM (110)pc planes are flat and parallel to the substrate $(110)_c$. The vertical $(001)_{pc}$ boundaries in (c) and (d) can be compensated by either an array of edge dislocations or cracking. Due to the lack of strain relaxation in this sample, the dislocation density is very small. However, cracks were observed in this sample with an average spacing of 1-100 µm. On the other hand, all the $(110)_{pc}$ domain boundaries are coherent, requiring no additional defect generation. **Figure 5.2** (e) shows the two monoclinic domains and their boundaries in 600 nm Sample C. This sample is incoherent with substrate due to strain relaxation, and a large density of dislocations are present (will be discussed later). Misfit dislocations that insert extra half planes produce tensile strain fields along both $\pm [001]_{pc}$ directions. This introduces angular distortion to the $(110)_{pc}$ planes and likely facilitates the formation of two monoclinic domains. It also lifts off the LSM $(110)_{pc}$ planes, forming a roof-top structure with an increased β angle of 89.8°. Calculations based on β angle predicts that the average domain width should be ca. 150nm (or its multiples). This is because for every monoclinic domain with width of 75 nm along $[001]_{pc}$, the β angle shifts the LSM lattice by half a unit cell along $[110]_{pc}$ direction. This effectively produces interfacial misfit dislocations with Burgers vector of $\mathbf{b} = \frac{1}{2}[110]_{pc}$.

In summary, the crystal structure evolution during strain relaxation of $(110)_{pc}$ LSM on STO is characterized. Fully strained 50nm LSM exhibits a single monoclinic domain, and its $(110)_{pc}$ planes are flat and parallel to the substrate. During strain relaxation, edge dislocation arrays insert extra half planes and lift off the $(110)_{pc}$ planes to form a roof top structure. The β angle increases from 89.5° in fully coherent film to 89.8° in a relaxed film.

5.4.3 Defect analysis by X-ray rocking curve

The $(110)_{pc} 2\theta - \omega$ scans of Samples A, B, C, and C* were plotted in Figure 5.3 (top). 2θ positions and scan intensities were normalized with respect to the STO $(110)_c$ peak. The 2θ positions of the LSM $(110)_{pc}$ peaks decrease from Sample A to Sample C*, suggesting an increase in the out-of-plane *d*-spacing during strain relaxation. The $(110)_c$ rocking curves of STO (blue dashed curves) and LSM (red solid curves) reflections of the same set of samples were shown in Figure 5.3 (bottom). Numbers denote the corresponding FWHM values, which are proportional to the defect density in the film. The FWHM of fully strained LSM (Samples A and B) are identical to their underlying substrates, all being ca. 0.01° . Such narrow RCs indicate that the films have a high structural quality, consistent with their coherent strain status. In relaxed samples C and C* however, the rocking curves broaden significantly, with the LSM FWHM values reaching 0.20° in Sample C and 0.25° in



Figure 5.3: Top: $2\theta - \omega$ scans of $(110)_{pc}$ reflections of Samples A, B, C, and C^{*}, as listed in **Table** 5.1. Bottom: $(110)_c$ RCs of STO (blue dashed curves) and $(110)_{pc}$ LSM (red solid curves) of the same set of samples.

Sample C*. In addition, the $(110)_{pc}$ reflection shifts to a smaller ω value during relaxation, suggesting the out-of-plane d-spacing shifts to a larger value (consistent with XRD data).

Dislocation densities in the range of $10^5 - 10^9 \text{cm}^{-2}$ can be estimated from the X-ray rocking curve FWHM.^{155,156} This is shown in **Equation** 5.1,¹⁵⁶ where ρ represents the dislocation density, $\Delta\beta$ the rocking curve FWHM value in radians, and b the magnitude of the dislocation Burgers vector (c.f. **Section 2.6.2** for more information)

$$\rho = \frac{(\Delta\beta)^2}{9b^2} \tag{5.1}$$

The overall dislocation density (ρ) estimated from RC are listed in **Table 5.2**, assuming the Burgers vectors are $\mathbf{b} = \frac{1}{2} \langle 110 \rangle_{pc}$. Comparing the lowest dislocation density (5 × 10⁶ cm⁻²) in fully strained Sample A and B with the highest dislocation density (3 × 10⁹ cm⁻²) in fully relaxed Sample C*, an increase in the dislocation density of nearly three orders of magnitude was observed during strain relaxation. Assuming dislocations are uniformly distributed, the average dislocation spacing in Sample C* is ca. 180 nm. The theoretical equilibrium dislocation spacing in a fully relaxed film equals to b/f, where b is the magnitude of the Burgers vector **b**, and $f = (a_{sub} - a_{film})/a_{film}$ is the lattice mismatch between the film and substrate. Taking b = 0.27 nm and f = 0.3%, the theoretical equilibrium average spacing is then ca. 90 nm, which corresponds to $\rho = 1 \times 10^{10}$ cm⁻², or about 3 times greater than the highest dislocation density experimentally observed in our system (Sample C*). This discrepancy is likely due to the interactions of existing dislocations at high density, which can hinder the multiplication of new misfit dislocations in relaxed oxide thin films, resulting in the saturation of dislocation densities at a nearly constant value below the equilibrium prediction.²¹¹

5.4.4 Defect analysis by electron channeling contrast imaging

Electron channeling contrast imaging (ECCI) was applied to nondestructively characterize extended defects in strained and relaxed LSM thin films on the mesoscale. ECCI has been used to study defect structures in metals, ^{146,163,164} semiconductors, ^{161,165} oxide crystals, ¹²⁴ and oxide thin films. ¹⁶⁶ For more details regarding the advantages and applications of ECCI for defect analysis, c.f. **Chapter IV** and **Chapter II**.

Figure 5.4 (a) shows the ECCI micrograph of an area of the $SrTiO_3$ (110)_c surface $(\mathbf{g} = (001)_c)$. The "bright-to-dark" spot contrasts are characteristic of threading dislocations normal to the sample surface, while the "tail" like features represent inclined dislocations near the surface.¹²⁴ The dislocation distribution on the STO surface is heterogeneous: most regions show a low dislocation density on the order of 10^6 cm⁻². However, regions



Figure 5.4: (a) An ECCI micrograph of $SrTiO_3$ (110)_c surface, showing surface penetrating dislocations heterogeneously distributed inside parallel bands. The "d" and "t" represent dislocations and tail features. (b) An electron channeling pattern at 20kV corresponding to $\mathbf{g} = (001)_c$. (c) BSE intensity profile measured across a dislocation normal to the surface, showing the characteristic "bright-to-dark" undulation.

with highly clustered dislocations (ca. $10^8 - 10^9 \text{ cm}^{-2}$) are identified inside band-like regions. Such bands are a few millimeters long and a few microns wide, as indicated by the offset dashed lines in **Figure 5.4** (a). They resemble the surface polishing induced dislocation bands on NiAl single crystal.¹⁹⁹ Dislocations created by mechanical polishing on STO (100) surfaces have been studied by Lin et al.²¹² The authors observed a high density of $\langle 110 \rangle$ - type dislocations having line direction of $\mathbf{u} = \langle 111 \rangle$. It is worth noting that the substrate threading dislocations will propagate into the film and can under certain conditions relax the local strain by depositing a misfit segment.²¹³ The electron channeling pattern at 20kV corresponding to $\mathbf{g} = (001)_c$ is shown in **Figure 5.4** (b). The BSE intensity profile measured across a dislocation normal to the surface is shown in **Figure 5.4** (c), exhibiting the characteristic "bright-to-dark" undulation. The contrast width of a dislocation is about 800 nm.

In LSM films, polishing induced dislocation bands similar to those in the STO substrates are visible, with similar dislocation densities on the order of $10^8 - 10^9$ cm⁻². However, away from these dislocation bands, ECCI revealed large differences in dislocation density in the three LSM samples (Sample D was not studied after annealing). **Figure 5.5** are the ECCI micrographs showing different dislocation densities in Sample A (a, c) and Sample C (b, d)



Figure 5.5: ECCI micrographs showing different dislocation densities in Sample A (a, c) and Sample C (b, d) under different magnifications ($\mathbf{g} = (1\overline{1}0)_{pc}$). The dislocation density in the images are 6×10^6 for Sample A, and $\geq 10^9$ cm⁻² for Sample C.

under different magnifications ($\mathbf{g} = (1\overline{1}0)_{pc}$). The dislocation density is estimated to be $6 \times 10^6 \text{ cm}^{-2}$ for Sample A, similar to its underlying substrate. For Sample C, a high density of spot features are present, corresponding to individual dislocations. The dislocation density in this sample is sufficiently high that contrasts from neighboring dislocations begin to overlap. This means the ρ is approaching the detection limit, which is approximately $1 \times 10^9 \text{ cm}^{-2}$. Other than spot contrasts, Sample C surface also exhibits domains with varying grey scale intensities. Such domains resemble the subgrain features in semiconductor thin films, including small angle grain boundaries formed by a high density of threading dislocations. ¹⁴⁵

The dislocation density (ρ in cm⁻²) estimated from $(110)_{pc}$ rocking curves and ECCI

	_			_	
Sample	Rocking	g Curve	ECCI		
	FWHM	$ ho_{ave.}$	$ ho_{min.}$	$ \rho_{max} $.	
STO	0.01°	$5 imes 10^6$	$1 imes 10^6$	1×10^9	
Sample A (FS- 50nm)	0.01°	5×10^6	1×10^{6}	1×10^9	
Sample B (FS- 600nm)) 0.01 °	$5 imes 10^6$	1×10^{6}	1×10^9	
Sample C (PR- 600nm) 0.20 °	2×10^9	≥ 1 :	$\times 10^{9}$	
Sample C^* (FR- 600nm	n) 0.25°	$3 imes 10^9$	≥ 1 :	$\times 10^9$	

Table 5.2: Dislocation densities (ρ) in cm⁻² estimated from $(110)_{pc}$ rocking curves and ECCI. The dislocation Burgers vectors are assumed to be $\mathbf{b} = \frac{1}{2} \langle 110 \rangle_{pc}$ for RC analysis. High dislocation densities $(\rho_{max.})$ in ECCI refer to the threading dislocation bands as illustrated in **Figure** 5.4.

micrographs are listed in **Table 5.2**. X-ray rocking curve was used to provide an average dislocation density assuming a homogeneous distribution. And ECCI was used to map the extend of heterogeneity in dislocation distributions. For Sample A and B, ECCI revealed that the dislocation distribution is rather heterogeneous: while most of the film surfaces are dislocation-free, bands of highly clustered dislocation (likely induced by substrate polishing) were observed with high densities up to 1×10^9 . The average dislocation density ($\rho_{ave.}$) measured by RC is in between the minimum ($\rho_{min.}$) and maximum ($\rho_{max.}$) values obtained by ECCI. For Sample C and C*, the dislocation distribution in the near surface region is much more homogeneous, with a high density above the ECCI detection limit. In this case, the average estimates by RC become useful. To summarize, this study demonstrates the complementary characterization in both quantifying the defect densities and mapping their distributions on the mesoscale using nondestructive techniques such as RC and ECCI.

5.5 Discussions

Results in this chapter suggest that strain relaxation in epitaxial oxide thin films is governed by both the relative amount of strain energy (which is proportional to the film thickness) and the kinetics of dislocation nucleation and motion. In particular, the cooling rate was found to be critical to the introduction of misfit dislocations, and additional high temperature anneal increased dislocation climb to achieve full strain relaxation. Comparing the fully strained LSM (Sample A and B) and the fully relaxed 600 nm LSM (Sample C^{*}), an increase in the dislocation density of nearly 3 orders of magnitude was discovered.

We postulate that increasing the chamber pO_2 from 50 mTorr during deposition to 200

Torr before cooling induces dislocation generation in $(110)_{pc}$ LSM on STO. Recent high temperature X-ray diffraction studies have revealed that the LSM unit cell parameters are strongly dependent on the partial pressure of oxygen, which was attributed to chemical expansion/contraction due to reduction/oxidation of Mn.²⁰⁹ In particular, an increase in pO_2 (by almost 4 orders of magnitude in this case) results in an increased Mn oxidation state and a contraction of the LSM unit cells. Such contraction of the film unit cell adds to the substrate induced tensile strain, and reduces the energy barrier for dislocation nucleation and movement. In addition, the thermal expansion of the long axis c was found to be close to twice as high as the thermal expansion of the short axis a (using a rhombohedral notation).²⁰⁹ This could explain why the $[001]_{pc}$ direction of the unit cell achieved full relaxation first in Sample C.

The crystal structure evolution during strain relaxation of $(110)_{pc}$ LSM on STO is characterized and the results presented in **Figure 5.2**. Fully strained 50nm LSM Sample A exhibits a single monoclinic domain, and its $(110)_{pc}$ planes are flat and parallel to the substrate. During strain relaxation in Sample C and C^{*}, edge dislocation arrays insert extra half planes and lift off the $(110)_{pc}$ planes to form a roof top structure. The β angle increases from 89.5° in fully coherent film to 89.8° in a relaxed film. The case for coherently strained Sample B is rather interesting. This sample was quenched to a nonequibrium state due to fast cooling, and likely captures the early stage of dislocation generation. Results from **Chapter IV** suggests that a sinusoidal surface rippling morphology was developed to relax the strain at the surface. Such surface ripples had been observed to lower the energy barrier for dislocation nucleation, and proceed to strain relaxation process in semiconductor films.

5.6 Conclusion

In summary, the crystal structures and the dislocation density during strain relaxation of $(110)_{pc}$ -oriented LSM thin films grown on STO were studied. A monoclinic distortion was found on all films, where the LSM $[110]_{pc}$ tilts toward the in-plane [001] axis, consistent with that reported by Boschker et al.¹⁸³ The coherently strained 50 nm film exhibits a single monoclinic domain, whereas the 600 nm LSM films have two domain variants. Strain relaxation is accompanied by the following structural changes in LSM films: (1) a increase

of β angle from 89.5° in the fully strained film to 89.8° in the relaxed film; (2) an increase of domain boundaries from zero in the single domain fully strained 50 nm film, to the two domain variants in the fully relaxed film; and (3) an increase in the dislocation density of nearly three orders of magnitude from the fully strained Sample A and B ($\rho = 5 \times 10^6 \text{ cm}^{-2}$) to the fully relaxed Sample C* ($\rho = 3 \times 10^9 \text{ cm}^{-2}$), according to average density estimated by X-ray rocking curve. Strain relaxation in LSM films on STO was found to be governed by the film thickness (which determines the overall strain energy), the cooling rate in 200 Torr pO_2 (which controls the kinetics of misfit dislocation generation) and additional high temperature annealing (which favors climb of existing dislocations by point defect diffusion and full strain relaxation). To achieve full relaxation, slower cooling rate at high (200 Torr) pO_2 and post deposition annealing are favorable. Other the other hand, fast cooling helps capture coherently strained LSM films beyond its critical relaxation thickness in a non equilibrium state. Such observations highlight the importance of dislocation formation and motion kinetics in strain relaxation in epitaxial oxide thin films. Lastly, dislocation densities measured by X-ray rocking curve and ECCI show the complementary nature of the two techniques: while rocking curve provides a global estimate of the total density, ECCI reveals the heterogenous distribution of dislocations in the near surface region.

CHAPTER VI

Coherent domain boundaries in coherently strained $(110)_{pc}$ -La_{0.7}Sr_{0.3}MnO₃ thin films on $(100)_{o}$ - NdGaO₃

6.1 Chapter overview

This chapter documents the observation and analysis of extended coherent planar domain boundaries in coherently strained $(110)_{pc}$ -oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ thin films on $(100)_o$ NdGaO₃ substrates. Section 6.2 and Section 6.3 introduce the relevant background and the experimental methods used in this study. Section 6.4 summarizes the results of structural characterization using reciprocal space mapping (RSM), and the observation of extended defect that is consistent with planar domain boundaries by electron channeling contrast imaging (ECCI) and transmission electron microscopy (TEM). Finally, the conclusions are summarized in Section 6.6.

6.2 Introduction

 $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM) is a perovskite oxide material which possesses many interesting electromagnetic and electrochemical properties. Bulk LSM is commonly used as cathode material for solid oxide fuel cells due to its high reactivity towards oxygen reduction.²² In addition, LSM exhibits room temperature ferromagnetism, colossal magnetoresistance, and near 100% spin polarization.^{19,20} LSM thin films are used as magnetic tunnel junctions (MTJs), where the (110)_{pc} orientation is preferred, due to strong uniaxial anisotropy and its ability to eliminate interfacial charge transfer.²¹

Applications of LSM thin films are strongly influenced by the presence of epitaxial strain and extended defects. For example, the magnetic domain structure,⁷ the magnetic

Table 6.1: Orthorhombic lattice parameters (in Å) and lattice mismatch (in %) of $(100)_o$ - and $(010)_o$ - LSM grown on $(100)_o$ NdGaO₃. OP and IP represent out-of-plane and in-plane, respectively. A minus sign refers to smaller substrate value than film value, and consequently a compressive strain.

Material & Mismatch	$OP(a_o)$	IP (b_o)	IP (c_o)	Total IP
$\overline{\mathrm{NdGaO}_3~(100)_o}$	5.428 Å	$5.498 \ { m \AA}$	$7.709 \ { m \AA}$	-
LSM $(100)_o$	5.488 \AA	5.524 Å	$7.787 { m ~\AA}$	-
Lattice mismatch	-	-0.47%	-1.01%	-1.48%
LSM $(010)_o$	5.524 Å	5.488 Å	7.787 Å	-
Lattice mismatch	-	0.18%	-1.01%	-0.83%

anisotropy,²¹ the formation of insulating antiferromagnetic phases,^{29,214} and the electronic band gap and surface electronic density of states⁶ are all dependent on strain and the substrate-film interface. The electrochemical properties of LSM towards oxygen reduction are also dependent on strain⁹ and the population of extended defects. For example, the surface exchange and diffusion kinetics along LSM grain boundaries are several orders of magnitude higher than within native grains.^{15,30} Thus, structural and defect characterization in epitaxial LSM thin films under strain is of great research interests.

Bulk $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) is rhombohedral (r) (space group $R\bar{3}c$) with lattice parameters of $a_r = 5.506$ Å and $c_r = 13.3564$ Å (using a hexagonal setting).⁴⁷ It can be approximated by an orthorhombic structure, with $a_o = 5.488$ Å, $b_o = 5.524$ Å and $c_o = 7.787$ Å ($c_o/2 = 3.893$ Å).¹⁸² NdGaO₃ (NGO) has an orthorhombic structure (space group *Pbnm*) with lattice parameters of $a_o = 5.428$ Å, $b_o = 5.498$ Å, and $c_o = 7.709$ Å ($c_o/2 = 3.854$ Å).¹⁹⁷ The octahedral rotation system is $a^-a^-a^-$ for bulk LSM and $a^-a^-c^+$ for NGO.⁴⁶ The lattice parameters and the in-plane lattice mismatch of $(100)_{o^-}$ and $(010)_{o^-}$ LSM grown on $(100)_{o^-}$ NGO are listed in **Table 6.1**. While both orientations produce a compressive overall strain, it can be seen that the lattice mismatch between $(010)_o$ LSM orientation on $(100)_{o^-}$ NGO results in lower in-plane compressive strain.

In this work, we report the structural and defect characterization of 50 and 600 nm coherently strained $(110)_{pc}$ oriented $La_{0.7}Sr_{0.3}MnO_3$ films deposited on $(100)_o$ - NdGaO₃ by pulsed laser deposition. LSM films adopt an orthorhombic structure under strain. Despite additional annealing at growth temperature and slow cooling $(1 \,^{\circ}C/\text{min} \text{ in } 200 \text{ Torr } O_2)$, the 600 nm film remains coherent with the substrate. X-ray rocking curve revealed the FWHM of LSM reflection as narrow as 8 arcseconds in 600 nm film, suggesting a very high

structural quality in the coherent film. Very few dislocations were observed by electron channeling contrast imaging (ECCI) or transmission electron microscopy (TEM). Yet both ECCI and TEM revealed the presence of planar domain boundaries, slanted at near 45 degrees with respect to the substrate surface. Two domain variants were observed, their spatial density, contrast width, and **g**-dependent contrast were studied. These domains are possibly associated with (1) octahedral tilt polymorphs (such as *Pbnm* and *Imma*), and/or (2) symmetry inversion domains (such as an inversion of the *b*-glide and *n*-glide in *Pbnm*), and/or (3) antiphase boundaries of the orthorhombic LSM. Further characterizations are underway to investigate their nature.

6.3 Experimental

Both 50 and 600 nm LSM films were deposited on $(100)_o$ -NGO substrates (MTI Corporation, USA) by pulsed laser deposition (PLD), as described elsewhere.¹⁶⁶ The films were deposited at 750 °C in 50 mTorr O₂, and cooled at 5 °C/min in 200 Torr O₂. The 600 nm LSM went through additional 10 hours annealing at deposition condition and was subsequently slowly cooled at 1 °C/min in 200 Torr O₂. The growth rate was calibrated using x-ray reflectivity (XRR) and was used to determine the film thickness. Orientation, epitaxy, mosaic spread and reciprocal space maps (RSMs) were collected by high resolution X-ray diffraction in triple axis mode (Philips X'Pert MRD).^{9,166} Surface morphology was measured by atomic force microscopy (AFM) in semicontact mode, using aluminum coated silicon tips (NSG10, NT-MDT) on Solver Next (NT-MDT, Moscow, Russia) instrument. Electron channeling contrast imaging (ECCI) was conducted in in back-scattered geometry on either a Quanta 600 field emission SEM (FEI Corp.) and a Tescan Mira 3 microscope.^{124,166} Images were recorded at 20 kV, a 6.0 spot size, and an 8 mm working distance.

6.4 Results

6.4.1 Structural characterization by X-ray diffraction

The crystal structures of $(010)_o$ - LSM films on $(100)_o$ - NGO were determined by high resolution X-ray diffraction in triple axis mode. Both 50 and 600 nm LSM films are epi-



Figure 6.1: Reciprocal space maps around the (a) $(420)_o$ (b) $(4\overline{2}0)_o$ (c) $(404)_o$ and $(d)(40\overline{4})_o$ reflections of NGO substrate (top reflections) 600 nm LSM (bottom reflections). LSM has an orthorhombic structure and remains coherent with the substrate.

taxial and coherently strained to the NGO substrates. The epitaxial relationship follows $(010)_{o,LSM}[001]_{o,LSM} \parallel (100)_{o,NGO}[001]_{o,NGO}$, in an orthorhombic (*o*) notation. Their outof-plane lattice parameters are both $b_{o,LSM} = 5.530$ Å. The film-substrate coherency and the orthorhombic structure of LSM were determined from X-ray reciprocal space maps (RSMs) around asymmetric reflections. **Figure 6.1** shows the reciprocal space maps collected in triple axis mode around the (a) $(420)_o$ (b) $(4\overline{2}0)_o$ (c) $(404)_o$ and $(d)(40\overline{4})_o$ reflections of NGO. Since LSM film has a larger out-of-plane lattice parameter (5.530 Å) than NGO (5.428 Å), the LSM reflections exhibit smaller $Q_{out-of-plane}$ values than NGO reflections and are at the bottom in **Figure 6.1**. In all scans, LSM reflections exhibit the same in plane momentum transfer $(Q_{in-plane})$ to the substrate reflections, suggesting that the films are coherently strained to the substrate in both in plane directions. The orthorhombic structure of LSM is determined from the fact that film reflections in (a) and (b), separated by 180 in ϕ space, exhibit the same $Q_{out-of-plane}$ values. And the same is true for scans (c)

and (d). The orthorhombic structure of LSM/NGO films is consistent with previous reports by Boschker et al. on the same system²¹ In **Chapter IV**, we found that LSM thin films deposited on $(110)_c$ SrTiO₃ substrates exhibit a monoclinic structure, with a β angle of 90.5°.¹⁶⁶ Thus, epitaxial strain distorts the rhombohedral bulk structure of LSM, resulting in orthorhombic LSM under compressive strain on NGO and monoclinic LSM under tensile strain on STO.



Figure 6.2: Reciprocal space map contour plot $(2\theta - \omega \text{ plot})$ around the $(200)_o$ reflection of NGO and the $(020)_o$ reflection LSM, with b_o direction of NGO aligned parallel to the X-ray bea. Two LSM satellite reflections (Variant- 1&2) are separated by ca. $\pm 0.35^{\circ}$ in ω space and ca. 0.2° in 2θ space from the main LSM $(020)_o$ reflection.

Figure 6.2 shows the reciprocal space map contour plot $(2\theta - \omega \text{ plot})$ around the $(200)_o$ reflection of NGO and the $(020)_o$ reflection LSM, with b_o direction of NGO aligned parallel to the X-ray beam. Other than the film (bottom) and substrate (top) reflections, two satellite peaks separated by ca. $\pm 0.35^{\circ}$ in ω space and ca. 0.2° in 2θ space from the

main LSM $(020)_o$ reflection are clearly visible. These satellite reflections are symmetrically distributed around the major LSM intensity, suggesting a twin relationship between the two variants. The ca. $\pm 0.35^{\circ}$ rotation in ω space suggest that the out of plane crystal planes of the variants are no longer parallel to the substrate. The out-of-plane lattice parameter corresponding to the twin variants is $d_{OP,variant} = 5.496$ Å, smaller than $d_{OP,film} = 5.530$ Å for the majority of the film. The absence of satellite peaks near the NGO indicates that the twin variants are not inherited from the substrate.





Figure 6.3: X-ray rocking curves (ω scans) around the (200)_o reflection of NGO (blue) and the (020)_o reflection of LSM (red) of the 600 nm LSM film. In (a), the b_o direction of NGO is aligned parallel to the X-ray, and in (b), the c_o direction is aligned parallel to the X-ray.

The X-ray rocking curves (ω scans) around the (200)_o reflection of NGO (blue) and the (020)_o reflection LSM (red) of the 600 nm LSM film are shown in **Figure 6.3**. In (a), the

 b_o direction of NGO is aligned parallel to the X-ray, and in (b), the c_o direction is aligned parallel to the X-ray. All intensities are normalized and plotted on a linear scale. The 600 nm film exhibits extremely narrow rocking curves that are comparable with those of the substrate. The smallest full width at half maximum (FWHM) value is 8 arcseconds for 600 nm LSM, which is among the smallest reported value for epitaxial oxides and approaches those of semiconductors. Such narrow rocking curves indicate a very high structural quality of the LSM thin film. In addition, rocking curves around the asymmetric (204)_o and (224)_o reflections of NGO and LSM were also scanned, and the FWHM of LSM are also identical to the NGO substrate. This is consistent with the in-plane film-substrate coherency revealed by reciprocal space maps.

An interesting observation is the symmetric shoulder peaks around main LSM rocking curve in figure (b). The shoulder peaks are distributed $\pm 0.017^{\circ}$ in *omega* space, and their intensities are only 1/200 of the main LSM reflection. These shoulder peaks are not observed along b_o direction in (a). Similar should peaks were seen in coherent LSM thin films on NGO and were attributed to periodic lattice modulations as a stress relief mechanism.^{182,215} Such lattice modulations are highly anisotropic, suggesting that strain is accommodated differently along perpendicular in-plane directions.¹⁸²

6.4.3 Surface morphology by atomic force microscopy

The surface morphology of the (a) 50 nm and (b) 600 nm LSM film on NGO were measured by atomic force microscopy (AFM) and shown in **Figure 6.4**. The scan areas are 5 x 5 μ m² and the scale bars are 5 nm. The root-mean-square (RSM) roughness values are labeled in the image. The height profile of a line scan is provided below each AFM image (note that the line scan direction was from right to left). In (a), the 50 nm LSM film exhibits an island surface morphology, with island height being 2 - 4 unit cells with respect to the background. Such islands suggest that the film growth proceed by 2D island nucleation and growth. The island density is approximately 6 per μ m². In addition, periodic dark line features show weak contrasts in image (a), and are aligned along the vertical ([001]_o) direction of the sample. Despite the presence of atomic islands, the 50 nm film has a root-mean-square (RMS) roughness of 0.5 nm. In (b), the 600 nm LSM NGO film exhibits a smooth surface



Figure 6.4: AFM images of the (a) 50 nm and (b) 600 nm LSM on NGO. The scan areas are 5 x 5 μ m² and the scale bars are 5 nm. The root-mean-square (RMS) roughness is approximately 0.5 nm in both images. Height profiles from the line scans are shown below the AFM images.

with a similar RMS roughness of 0.4 nm. No atomic islands are observed, while the most prominent surface features are surface stripes aligning along the vertical direction in the image (or $[001]_o$ of the sample). The surface stripes have a maximum height of ca. 2 unit cells, and a shadowed regions of about 300 nm.

6.4.4 Defect characterization by electron contrast channeling imaging

Figure 6.5 shows the ECCI micrographs for (a) 50 nm and (b) 600 nm LSM films under $\mathbf{g} = (020)_o$, and their corresponding intensity line profiles measured across locations labeled in (a) & (b). For 50 nm film imaged in (a), a high density of stripe features aligned along $[001]_o$ direction are observed, with an average spacing of ca. 0.3 µm between them. The stripe contrast shows a bright-to-dark intensity undulation in (c). The bright region is ca. 70 nm wide, and the dark region ca. 50 nm, on par with film thickness. For 600 nm film imaged in (b), the stripe features also align along $[001]_o$ direction but exhibit a reduced density, with an average spacing of about 1.5 µm in between. In addition, two stripe contrast



Figure 6.5: ECCI micrographs for (a) 50 nm and (b) 600 nm LSM films under $\mathbf{g} = (020)_o$, showing stripe contrast features with different spatial densities. (c) & (d) are the corresponding intensity line profiles measured across locations labeled in (a) & (b).

variants exist in the 600 nm film, exhibiting either predominantly bright or dark contrast. Their intensity profiles are shown in (d) by the blue or red lines. The width of the strong bright or dark contrast is about 200 nm. In addition, the stripes also exhibit a shadowing region showing diffusive contrast of the opposite type, i.e. dark diffusive regions next to bright stripes. Such a diffusive contrast region has a width of ca. 600 nm, or on par with film thickness. It is likely due to the stripes being slanted, introducing small distortions to the near surface regions immediately next to the stripes.

Figure 6.6 shows the (a) backscattered electron (BSE) image on $[010]_o$ zone axis, and ECCI micrographs under (b) $\mathbf{g} = (002)_o$, (c) $\mathbf{g} = (200)_o$ and (d) $\mathbf{g} = (\bar{2}00)_o$ on the same location of the 600 nm LSM film on NGO. Scale bars are 5 µm in all images. The two surface particles which exhibit bright contrast act as Fiducial markers. Stripe features exhibit weak contrast in the BSE image on $[010]_o$ zone axis in (b). This imaging mode is sensitive to both composition (Z-contrast) and crystal orientation. The contrast level increases under $\mathbf{g} = (002)_o$ in (b). Stripe features show strongest contrast under $\mathbf{g} = (\pm 200)_o$ in (c-d). In addition, their contrast profiles invert upon the inversion of channeling condition (\mathbf{g}). This



Figure 6.6: (a) BSE image on $[010]_o$ zone axis, and ECCI micrographs under (b) $\mathbf{g} = (002)_o$, (c) $\mathbf{g} = (200)_o$, and (d) $\mathbf{g} = (\bar{2}00)_o$ on the same location of the 600 nm LSM film on NGO. Scale bars are 5 µm in all images. The contrast of the stripes increase from (a-d). (Please refer to the electronic version for best image quality.)

suggests that their contrast in ECCI are due to distortions to the crystal planes. The fact that the strongest contrasts are collected under $\mathbf{g} = (\pm 200)_o$ suggest that the $(200)_o$ planes of LSM are under the most distortions.

6.4.5 Defect characterization by transmission electron microscopy

Transmission electron microscopy was conducted on a cross section area of the 600 nm LSM film on NGO. The sample was viewed near the $[001]_o$ zone axis under (a) $\mathbf{g} = (110)_o$ and (b) $\mathbf{g} = (\bar{1}10)_o$ as shown in **Figure 6.7**. The sample is approximately 7 µm wide. The scale bars in the images are 200 nm. The most prominent contrast arise from domains slanted at \pm 45 degrees from the substrate-film interface. Two domain variants were observed, and their contrast depends strongly on the \mathbf{g} condition. In (a), 3 domains tilted to the left were observed under $\mathbf{g} = (110)_o$; in (b) 13 domains tilted to the right were observed under $\mathbf{g} = (\bar{1}10)_o$; in (b) 13 domains are between 50 to 150 nm wide.



Figure 6.7: Cross section TEM images showing domains slanted at \pm 45 degrees in 600 nm LSM on NGO. Sample is viewed near the $[001]_o$ zone axis under (a) $\mathbf{g} = (110)_o$ and (b) $\mathbf{g} = (\bar{1}10)_o$. White arrows indicate locations of the slanted domains.

A higher magnification TEM image of slanted domains in 600 nm LSM on NGO is shown in **Figure 6.8**. The slanted domains exhibit darker contrast than the matrix. Regions near the substrate-film interface, matrix-domain boundaries, and the film surface all exhibit strong contrast. Contrast from dislocations were not observed near domain boundaries, suggesting they are coherent boundaries.

Further work using selective area electron diffraction (SAED) and Convergent Beam Electron Diffraction (CBED) are underway to identify the nature of these tilted domain boundaries. They are likely coherent domain boundaries associated with (1) octahedral tilt polymorphs (such as *Pbnm* and *Imma*), and/or (2) symmetry inversion domains (such as an inversion of the *b*-glide and *n*-glide in *Pbnm*), and/or (3) antiphase boundaries of the orthorhombic LSM.



Figure 6.8: A higher magnification TEM image of slanted domains in 600 nm LSM on NGO viewed near $[001]_o$ zone axis under $\mathbf{g} = (\bar{1}10)_o$. The slanted domains exhibit darker contrast than the matrix. Regions near the substrate-film interface, matrix-domain boundaries, and the film surface all exhibit strong contrast.

6.5 Discussions

The crystal structure of $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3-\delta}$ depends on Sr doping level, temperature and epitaxial strain status.^{18,19,182} At room temperature, LSM bulk is orthorhombic (space group *Pbnm*) when $x \leq 0.175$, and rhombohedral (space group $R\bar{3}c$) when x is greater. In bulk $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3-\delta}$ (x = 0.175), Arao et al. reported that the $R\bar{3}c$ to *Pbnm* structural phase transition is characterized by changes in the rotational displacement of the MnO₆ octahedra, which results in the appearance of antiphase boundaries, and changes in the crystal system, which produces $\{110\}_{o}$ and $\{112\}_{o}$ twins.¹⁵⁴ Similarly, Lebedev et al. observed the formation of $(100)_{pc}$ (equivalent to $(110)_{o}$) microtwins in $(110)_{pc}$ - oriented $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_{3-\delta}$ (LSM) thin film deposited on SrTiO_{3} . The microtwins have a periodic arrangement and relax strain at the film-substrate interface, which eliminates the need for the formation of interfacial dislocations.²¹⁶ However, both studies used LSM compositions of which the stable bulk structure is orthorhombic, which is different from the rhombohedral bulk structure in LSM (x = 0.3) used in this study.

Transformation twins have been reported in LSM (x=0.3) thin films under epitaxial strain.^{48,181} In (001)_{pc}-oriented LSM films on STO, $(100)_{pc}$ and $(010)_{pc}$ twins have been

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reported with a twinning angle of $2\phi = 0.52^{\circ}$. Such twinned films remain fully strained in-plane up to the explored thickness range (475 nm), as confirmed by reciprocal space mapping. The twin size follows a $t^{1/2}$ (t = film thickness) dependence as predicted for homogeneous films by equilibrium models.¹⁸¹ Insitu X-ray diffraction reported that the twin angle decreases with increasing temperature.¹⁸¹ In addition, LSM powder is cubic (space group $Pm\bar{3}m$) above ca. 900 °C.²⁰⁹ Thus, the formation of $(001)_{pc}$ twins in LSM (x=0.3) occurs as a result of cubic to rhombohedral phase transition during cooling.

The effect of twin walls on the electronic, magnetic and electrochemical properties of oxide materials are only beginning to be understood. It has been predicted that the ferroe-lastic $(100)_o$ twin walls of the orthorhombic CaTiO₃ (*Pbnm*) possess a more stable binding with oxygen vacancies, thus effectively trapping oxygen vacancies within twin walls.¹⁴⁴ This is attributed to changes in the electrostatics and strain within the twin wall. Experimental evidence have recently revealed that a severe compressive strain exist within an ca. 1 nm slab of material centered at the $(100)_{pc}$ twin walls of LSM thin films on STO.¹⁶ Such twin walls exhibit higher electronic conductivity and more robust magnetic interactions, due to a broader bandwidth and enhanced magnetic interactions caused by a stronger Mn 3d - O 2p orbital overlapping near the twin wall. Previous studies have demonstrated that grain boundaries in LSM exhibit several orders of magnitude higher surface exchange and diffusion kinetics than within native grains.^{15,30} The effects of twin walls on the electrochemical properties are unknown. One can hypothesize that due to a higher concentration of oxygen vacancy and the presence of local strain, twin boundaries could potentially act as higher oxygen diffusion pathways.

6.6 Conclusions and future work

In summary, the crystal structure and defects in coherently strained $(010)_{o}$ - La_{0.7}Sr_{0.3}MnO₃ thin films on $(100)_{o}$ - NdGaO₃ were investigated. As deposited films remain coherently strained to the substrate and adopt an orthorhombic structure, according to X-ray reciprocal space maps. Films exhibit a high degree of structural coherency and rocking curve FWHM as low as 8 arcseconds. Almost no dislocations were observed by ECCI. The predominant defects in the film are stripe contrasts in ECCI and domains slanted at \pm 45 degrees with respect the the substrate surface in TEM, which are likely correlated with each other. Stripe contrasts in ECCI have two variants, are aligned along the [001] direction, and show strongest contrast under $\mathbf{g} = (200)_o$. Slanted domains in TEM have two variants, show strong contrast near the domain-matrix boundaries, film-substrate interface and film surface. They are likely coherent domain boundaries associated with (1) octahedral tilt polymorphs (such as *Pbnm* and *Imma*), and/or (2) symmetry inversion domains (such as an inversion of the *b*-glide and *n*-glide in *Pbnm*), and/or (3) antiphase boundaries of the orthorhombic LSM. Future work using electron diffraction in transmission electron microscopy (TEM) is underway to identify their atomic structure and associated strain fields.

CHAPTER VII

Effects of strain and extended defects on the oxygen surface exchange properties of $(110)_{pc}$ -oriented $La_{0.7}Sr_{0.3}MnO_3$ thin films

7.1 Chapter overview

This chapter provides a summary on the effects of strain and extended defects on the oxygen surface exchange properties of $(110)_{pc}$ -oriented $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) thin film electrodes. LSM films with controlled structure and microstructures were selected to study the effects of: (1) coherent tensile and compressive strain, (2) surface penetrating dislocations, and (3) coherent domain boundaries on the oxygen surface exchange properties of $(110)_{pc}$ - LSM. The surface exchange coefficient (k_{chem}) and their activation energy (E_a) were measured using electrical conductivity relaxation (ECR) between 580 – 890 °C in 50 - 500 mTorr O₂ similar to prior work.^{9,28}

7.2 Introduction

The performance of $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM) as a solid oxide fuel cell (SOFC) cathode material is highly temperature dependent. At 800 – 1000 °C, LSM exhibits excellent catalytic properties towards the oxygen reduction reaction, is highly conductive to electron holes, and has a matching thermal expansion coefficient with YSZ.^{22,26} However, reducing the temperature from 1000 °C to 500 °C results in a cathode polarization resistance increase of over 3 orders of magnitude.²⁶ This is mostly due to the sluggish oxygen reduction reaction (ORR) kinetics at LSM electrode surface.²³ Therefore, one of the key challenges to develop-

ing efficient intermediate temperature SOFCs lies in the optimization of oxygen reduction reaction kinetics at cathode surface. 26,38

Microstructural control has shown great promises in improving the intrinsic materials properties in this aspect. As introduced in **Chapter II**, both the surface oxygen exchange coefficient (k), which quantifies the net transfer of oxygen across the solid-gas interface, and the diffusion coefficient (D), which quantifies the oxygen transport rate through the solid, are very sensitive to material microstructure, such as grain boundaries, grain orientations, and strain.^{9,15,28,30} For example, previous studies have identified that grain boundaries in LSM exhibit faster oxygen surface exchange and diffusion kinetics by several orders of magnitude.^{15,30} Epitaxial strain has been reported to reduce the vacancy formation energy ¹²² and to increase the oxygen exchange kinetics on $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) (100)_{pc} surface.¹⁰. One implication from the combined results of previous studies is that the surface exchange on the (110)_{pc} orientation of LSM is faster than other low index surfaces and can be further improved by microstructure engineering.²⁸

In this chapter, the effects of strain and extended defects on the surface exchange kinetics on $(110)_{pc}$ orientation of LSM epitaxial thin films are investigated. Specifically, the presence of: (1) coherent tensile and compressive strain, (2) surface penetrating dislocations, and (3) coherent domain boundaries are controlled in LSM thin films. Their effects on the surface exchange coefficients (k_{chem}) and activation energy (E_a) of (110)_{pc} LSM were studied using electrical conductivity relaxation (ECR) between 580 – 890 °C in 50 - 500 mTorr pO₂.^{9,28}

7.3 Experimental

 $(110)_{pc}$ oriented $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ thin films were deposited on single crystal SrTiO₃ and NdGaO₃ substrates by pulsed laser deposition (PLD). Four samples were prepared, two of 50 nm and two of 600 nm thickness. Their deposition conditions were recorded in **Chapter IV**, **V**, and **VI**. The surface morphology was measured by atomic force microscopy (AFM) (Veeco Dimension 3100 and Solver Next) in tapping mode. The growth rate was calibrated at 0.3 Å/pulse by x-ray reflectivity (XRR) and used to determine sample thickness. The crystal structures were characterized by high resolution X-ray diffraction (XRD) and reciprocal space mapping (RSM). The defect contents were studied by X-ray rocking

curve (RC) and electron channeling contrast imaging (ECCI). The surface exchange properties were measured by electrical conductivity relaxation (ECR) between $580 - 890 \,^{\circ}\text{C}^{.9,28}$ The oxygen partial pressure was switched between 50 and 500 mTorr. For homogeneous oxygen exchange on a flat surface, its surface exchange coefficient (k_{chem}) can be extracted from **Equation 7.1**^{77,89}, where g(t) is the normalized conductivity; σ_t , $\sigma_{initial}$, σ_{final} represent the sample conductivity at time t, at the beginning (initial) and finish (final) of the exchange process; L is the sample thickness; τ is the sample reaction time, and $k_{chem} = \frac{L}{\tau}$.

$$g(t) = \frac{\sigma_t - \sigma_{initial}}{\sigma_{final} - \sigma_{initial}} = 1 - \exp(-\frac{t}{\tau}) = 1 - \exp(-\frac{k_{chem}t}{L})$$
(7.1)

For heterogeneous surface exchange, i.e., when the surface exhibits two distinct responses bearing k_{chem} values that are significantly different, the conductivity relaxation behavior can be fitted with the following equation 92,102 :

$$g(t) = \frac{\sigma_t - \sigma_{initial}}{\sigma_{final} - \sigma_{initial}} = 1 - A_1 \exp(-\frac{k_{chem,1}t}{L}) - A_2 \exp(-\frac{k_{chem,2}t}{L})$$
(7.2)

where $k_{chem,1}$ and $k_{chem,2}$ represent kinetics of the two different responses. A_1 and A_2 represent their relative contributions to the overall surface exchange $(A_1 + A_2 = 1)$. All sample responses have been corrected by the chamber flush time (τ_{flush}) according to: $\tau_{total} = \tau_{flush} + \tau_{sample}$, where τ_{sample} is the real sample reaction time. The chamber flush time is 2.5 s during oxidation and 1 s during reduction.

7.4 Results

7.4.1 Microstructural characterization of LSM thin film electrodes

The four LSM thin films investigated by ECR are listed in **Table 7.1**. The film thickness, strain status, substrate selection, and the primary defect type and their densities are included. It is worth noting that all LSM films on STO exhibit low densities of anti-phase boundaries (APBs). They likely possess different affinity towards oxygen vacancies and/or surface exchange activities towards oxygen reduction reaction, due to modifications in the MnO_6 rotation. Because of a lack of appropriate control samples, the effects of APBs on the oxygen surface exchange are not elucidated in this study.

Table 7.1:	List of	$(110)_{pc}$ -ori	iented La	$_{0.7}\mathrm{Sr}_{0.3}\mathrm{Mn}$	O_3 thin	films	measured	by E	ECR.	Film	thickness,	strain
	status, s	substrate, a	and the p	rimary ext	ended de	efect t	ype and de	ensity	are in	nclude	ed.	

Sample	Thickness	Strain	Substrate	Primary defect and density
Sample A	50 nm	Tensile	$SrTiO_3$	Dislocations (10^6 cm^{-2})
Sample B	600 nm	Tensile	$SrTiO_3$	Surface ripples
Sample C^*	600 nm	Relaxed	$SrTiO_3$	Dislocations (10^9 cm^{-2})
Sample D	50 nm	Compressive	NdGaO_3	coherent domain boundaries $(3 \ \mu m^{-1})$

Sample A is under coherent tensile strain induced by the STO substrate. It has high structural quality, including a pristine surface with only low densities of threading dislocations ($\rho_{ave.} = 5 \times 10^6 \text{ cm}^{-2}$). For Sample B, the majority of the film is under coherent tensile strain induced by STO, but the film surface develops periodic ripples, which modifies local strain fields and facilitate dislocation dislocations (c.f. **Chapter IV**). For Sample C*, the tensile strain induced by the STO substrate is fully relaxed via dislocation generation. Its dislocation density (ca. $\rho_{ave.} = 3 \times 10^9 \text{ cm}^{-2}$) is 3 orders of magnitude higher than Sample A. Lastly, Sample D is under coherent compressive strain induced by the NGO substrate. The film has an extremely low dislocation density, but exhibits a periodic array of extended surface penetrating planar defects. It is also worth noting that strained LSM on STO has a monoclinic crystal structure, and an orthorhombic structure on NGO, while the relaxed LSM on STO shifts towards the Rhombohedral structure

7.4.2 Topography characterization by atomic force microscopy

Surface morphology were obtained by atomic force microscopy (AFM) in tapping mode.¹⁷³ Results from Sample (a) A, (b) B, (c) C, and (d) D are shown in **Figure 7.1**. Scan areas are 1 x 1 μm^2 in all images. As deposited film surfaces are smooth and uniform, with root-mean-square (rms) roughness values between 0.5 - 1.4 nm. The surface of Sample B is the most rough, consistent with its rippled surface structure proposed in earlier chapters. Interestingly, the surface of Sample D shows an island morphology, with island height being 1 or 2 unit cells and an island density of ca. 6 islands per μm^2 . Despite such islands, the rms roughness is still only 0.5 nm. The surface roughness is related to the total surface area available to participate in the oxygen surface exchange, and higher roughness can increase the measured k_{chem} value for thin films.⁷⁷ As suggested by the smooth, uniform surfaces, contributions from surface roughness variations to the measurement of k_{chem} should be



Figure 7.1: AFM images of Sample (a) A, (b) B, (c) C, and (d) D. Scan areas are $1 \ge 1 \ \mu m^2$. The scale bars are 5 nm for top images, and 10 nm for bottom images. The root-mean-square (rms) roughness values are labeled.

small in this study.

7.4.3 Electronic conductivity characterization by van der Pauw method

According to Mizusaki et al.⁴⁹, bulk $\text{La}_{1-x}\text{Sr}_{x}\text{MnO}_{3\pm\delta}$ with $x \leq 0.5$ exhibits p-type conductivity. The predominant electronic conduction mechanism is small polaron hopping via electron holes localized on the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions. The temperature dependent electronic conductivity of LSM follows **Equation 7.3**, where E_a represents the activation energy and σ_0 is a preexponential factor determined by experiments.

$$\sigma \cdot T = \sigma_0 \cdot exp(-E_a/kT) \tag{7.3}$$

The temperature dependent (a) electronic conductivity (σ) and (b) $\sigma \cdot T$ values of the four samples were measured at pO₂= 500 mTorr and are plotted in **Figure ??**. The conductivity values were measured using van der Pauw method in ECR. A geometric factor, i.e. the film thickness, was used to convert the measured thin film conductance to LSM con-



Figure 7.2: Plot of temperature dependent (a) electrical conductivity (σ) and (b) $\sigma \cdot T$ values of Sample A (50 nm fully strained LSM on STO), Sample B (600 nm fully strained LSM on STO), Sample C* (600 nm fully relaxed LSM on STO), and Sample D (50 nm fully strained LSM on NGO) measured at pO₂ = 500 mTorr.

ductivity values. It is worth noting that small amount of inaccuracies in the film thickness might be present especially in the thicker films. Nevertheless, LSM conductivity shows a weak dependency on temperature, but vary significantly with film strain status and thickness. Sample C^{*} exhibits the highest conductivity at ca. 200 S/cm during the experimental condition. It is followed by the 50 nm Sample A and Sample D. In comparison, the bulk conductivity value of LSM is ca. 240 S/cm at similar temperature in 1 bar O₂.⁴⁹ In addition, the slopes in **Figure ??b** for Samples A, C and D correspond to an activation energy of 0.1 eV, close to the value measured in bulk LSM.⁴⁹ Interestingly, Sample B exhibits the lowest conductivity and the highest transport activation energy (0.27 eV) of all films. We hypothesize that the abnormal conductivity of Sample B is caused by the large residual strain state, which modifies the chemical composition and/or the MnO_6 octahedral rotation to accommodate for the strain. As mentioned earlier, Sample B was quenched at a nonequilibrium state via fast cooling. Due to a lack of misfit dislocations, the large strain energy in this film had to be accommodated chemically by reducing Mn^{4+} to Mn^{3+} , which reduces the concentration of localized holes ($[Mn_{Mn}]$), increases $[V_o^{..}]$, and modifies their migration barrier for hole conduction. The fact that the electronic conductivity of bulk LSM decreases with increasing oxygen nonstoichiometry has been observed previously.⁴⁹

7.4.4 Oxygen surface exchange on Sample A: 50 nm strained LSM on ${\rm SrTiO}_3$



Figure 7.3: Electrical conductivity relaxation profiles of Sample A during (a) oxidation and (b) relaxation at 780 °C. The blue and red curves represent experimental data and non-linear fit, respectively.



Figure 7.4: Arrhenius plot of surface exchange coefficient (k_{chem}) versus inverse temperature for Sample A. The red and blue symbols represent oxidation and reduction data, respectively. Activation energies (E_a) are labeled.

The electrical conductivity relaxation profiles of Sample A (coherently strained 50 nm LSM on STO) are plotted in **Figure 7.3** during (a) oxidation and (b) relaxation at 780 °C. The blue and red curves represent experimental data and non-linear fit, respectively. The oxidation process corresponds to a step change of pO_2 from 50 to 500 mTorr. The reduction process is the inverse change (from 500 to 50 mTorr). All relaxation curves can be fit with **Equation 7.1** using one surface exchange coefficient (k_{chem}) variable. The surface exchange coefficient (k_{chem}) values of Sample A were extracted from relaxation profiles
and plotted versus inverse temperature in **Figure 7.4**. The orange and cyan diamonds represent oxidation and reduction data, respectively. 10 data points were collected between 580 - 890 °C. The error for activation energy measurement is ± 0.1 eV in both cases. The oxygen surface exchange property of Sample A closely follows the Arrhenius behavior, with an activation energy (E_a) of 1.1 (± 0.1) eV for both oxidation and reduction. The oxidation k_{chem} is consistently faster than reduction k_{chem} , which is consistent with the finding that the surface exchange coefficient increases with the final pO₂.²⁸

7.4.5 Oxygen surface exchange on Sample C*: 600 nm relaxed LSM on ${\rm SrTiO}_3$



Figure 7.5: Electrical conductivity relaxation profiles of Sample C* during (a) oxidation and (b) relaxation at 780 °C. The blue and red curves represent experimental data and non-linear fit, respectively.



Figure 7.6: Arrhenius plot of the surface exchange coefficients (k_{chem}) versus inverse temperature for Sample C^{*}. The red and blue symbols represent oxidation and reduction data, respectively.

The electrical conductivity relaxation profiles of Sample C* (fully relaxed 600 nm LSM on STO) are plotted in **Figure 7.5** during (a) oxidation and (b) relaxation at 780 °C. The blue and red curves represent experimental data and non-linear fit, respectively. Similar to Sample A, the surface exhibits a homogeneous response. All conductivity relaxation curves can be fit with **Equation 7.1** using a single surface exchange coefficient (k_{chem}). Values of k_{chem} were extracted from relaxation profiles and plotted versus inverse temperature in **Figure 7.6**. The red and blue triangles represent oxidation and reduction data, respectively. The oxygen surface exchange closely follows the Arrhenius behavior, with a single activation energy (E_a) of 1.6 eV for both oxidation and reduction. Again, the oxidation k_{chem} is consistently faster than reduction k_{chem} .

7.4.6 Oxygen surface exchange on Sample B: 600 nm strained LSM on ${\rm SrTiO}_3$



Figure 7.7: Electrical conductivity relaxation profiles of Sample B during (a) oxidation and (b) relaxation at 820 °C. The blue and red curves represent experimental data and non-linear fit, respectively. Data is fitted with **Equation** 7.2 using two k_{chem} variables.

The electrical conductivity relaxation profiles of Sample B (strained 600 nm LSM on STO) are plotted in **Figure 7.7** during (a) oxidation and (b) relaxation steps at 820 °C. The blue and red curves represent experimental data and non-linear fit, respectively. Different from previous samples, non linear fit using a single k variable produced a poor fit on Sample B. Instead, all relaxation curves exhibit two different response regimes, a faster response with $k_{chem,1}$ dominating the beginning of the relaxation curve; followed by a slower response with $k_{chem,2}$, dominating the latter part of the relaxation. The relaxation curves were successfully



Figure 7.8: (a) Arrhenius plot of surface exchange coefficient (k_{chem}) versus inverse temperature for Sample B. The closed and open symbols represent the faster $(k_{chem,1})$ and slower $(k_{chem,2})$ surface response, respectively. (b) Plot of temperature dependency of A_i , which represents the relative contribution from response *i* for Sample B. All data were collected at final pO₂ = 500 mTorr.

fitted with **Equation 7.2** using two k variables. As such, oxygen surface exchange on LSM is heterogeneous, i.e. two different reaction kinetics exist and are both contributing to the overall reaction.

The surface exchange coefficients (k_{chem}) of Sample B were plotted versus inverse temperature in **Figure 7.8(a)**. All data were collected at final $pO_2 = 500$ mTorr between 740 – 890 °C. Interestingly, Sample B displayed two surface exchange kinetics, consisting of a faster $k_{chem,1}$ response with a small E_a of 1.4 eV (closed circles), and a slower $k_{chem,2}$ response with a large E_a of 3.2 eV (open circles). $k_{chem,1}$ was one to two orders of magnitude faster than $k_{chem,2}$. Interestingly, their different activation energies (E_a) are unexpected. For $k_{chem,1}$ response, $E_{a,1} = 1.4$ eV is similar to values of other samples, and typical of surface exchange reaction measured in thin films and bulk electrodes (1- 2 eV).^{28,72,78}. For the $k_{chem,2}$ response, however, $E_{a,2} = 3.2$ eV is much higher, and comparable to the vacancy formation energy (3.0 - 3.5 eV)²⁷ and/or the bulk diffusion barrier (2.5 - 3.0 eV)^{22,217} in LSM. Given that Sample B likely already has a large oxygen vacancy concentration due to its processing history, the generation of new vacancies is not likely the limiting step. Therefore, $E_{a,2} = 3.2$ eV is assigned to the activation energy for oxygen diffusion in this sample. As mentioned in **Chapter II**, large discrepancies exist in the characteristic length (L_c), which determines the relative contribution from the surface exchange and bulk diffusion to the overall reaction response. L_c derived for LSM span from a few nanometers^{22,72} to 30 µm,⁵⁵ depending on the experimental method, temperature, pressure, and possibly microstructure. The residual substrate effect modifies the oxygen transport behavior in this sample, possibility decreasing the $V_o^{..}$ mobilities. Thus, Sample B (strained 600 nm) could be in the mixed response regime, where oxygen transport is co-limited by surface exchange and bulk diffusion. In addition, when temperature decreases, the contribution from the slower response (A_2) increases (**Figure 7.6 b**), effectively "shutting off" the overall response very quickly. Such temperature controlled behavior where the slower response becomes dominant is indicative of two serial processes, which is consistent with surface exchange and bulk diffusion. Simulation of the response data with a mixed controlled model should be performed to confirm this.

The faster response 1 is assigned to the oxygen surface exchange process, due to its similarities in E_a and k_{chem} to other samples. The majority of Sample B is coherently strained to the substrate. Low density of surface cracks are present in this film. The average spacing between cracks is between 1-100 µm, likely too far apart to contribute significantly to the overall exchange. On the other hand, surface ripples are present and can relax surface strain. They produce a periodically undulated BSE intensity contrast, presenting bright to dark wave-like features in electron channeling (**Chapter IV**). Their associated surface strain field consists of periodic tensile and compressive strain. The strain relaxation at the surface coupled with changes in the surface area can modify the surface exchange properties ($k_{chem,1}$ and E_a) of this film.

7.4.7 Oxygen surface exchange on Sample D: 50 nm strained LSM on $NdGaO_3$

The electrical conductivity relaxation profiles of Sample D (coherently strained 50 nm LSM on NGO) are plotted in **Figure 7.9** during (a) oxidation and (b) relaxation at 710 °C. The blue and red curves represent experimental data and non-linear fit, respectively. Similar to Sample B, data is fitted with **Equation 7.2** using two k_{chem} variables. As such, Sample D exhibits two different response regimes, suggesting that two different reaction kinetics exist and contribute to the overall response. The surface exchange coefficients $(k_{chem,i})$



Figure 7.9: Electrical conductivity relaxation profiles of Sample D during (a) oxidation and (b) relaxation at ca. 710 °C. The blue and red curves represent experimental data and non-linear fit, respectively. Data is fitted with **Equation** 7.2 using two k_{chem} variables.



Figure 7.10: (a) Arrhenius plot of surface exchange coefficient (k_{chem}) versus inverse temperature for Sample D. The closed and open symbols represent the faster $(k_{chem,1})$ and slower $(k_{chem,2})$ surface response, respectively. (b) Plot of temperature dependency of A_i , which represents the relative contribution from response *i* for Sample D. All data were collected at final pO₂ = 500 mTorr.

of Sample D were plotted versus inverse temperature in Figure 7.10 (a). All data were collected at final $pO_2 = 500$ mTorr between 600 - 820 °C. Closed squares represent the low activation energy response $(k_{chem,1})$, and open squares represent the high activation energy response $(k_{chem,2})$. $k_{chem,1}$ is approximately an order of magnitude higher than $k_{chem,2}$, and its activation energy $(E_{a,1} = 1.3 (\pm 0.1) \text{ eV})$ is smaller than the slower response $(E_{a,2} = 1.9 \text{ eV})$. Figure 7.10 (b) plots the temperature dependency of A_i , which represents the relative contribution from response 1 and 2 for Sample D. The contribution from the slower (high activation energy) response $(k_{chem,2})$ becomes more dominant as temperature increases. At 820 °C, $k_{chem,2}$ accounts for approximately 90% of total response. This is consistent with the transitioning of rate determining steps between two parallel processes, where the faster process becomes more dominant.

We hypothesize that the higher E_a response $(k_{chem,2})$ corresponds to oxygen exchange across the native LSM surface, while the lower E_a response $(k_{chem,1})$ corresponds to oxygen surface exchange along the coherent domain boundaries observed in Chapter VI. The majority of the film is orthorhombic and under coherent compressive strain induced by the substrate. Yet periodic arrays of coherent domain boundaries were observed, with an average spacing of ca. 330 nm in-between boundaries. They are likely through-thickness microtwins (TEM work is underway to confirm their nature) that exhibit different surface exchange properties than the intrinsic film surface. Extended boundaries such as grain boundaries in textured LSM thin films were observed to exhibit higher oxygen surface exchange and diffusion kinetics by several orders of magnitude than the native grains.^{15,30} Simulations have predicted that coherent twin walls in CaTiO₃ exhibit higher affinity to oxygen vacancies, leading to an increase in local $[V_o^{..}]$.¹⁴⁴ In addition, recent studies on $(100)_{pc}$ LSM film on STO revealed that coherent $(100)_{pc}$ twin walls are under large local strain and exhibit higher electronic conductivity.¹⁶ Both increased $[V_o^{..}]$ and increased electronic conductivity can result in a higher local oxygen reduction reaction kinetics, following Equation 2.1.

7.5 Discussions

7.5.1 Effects of surface penetrating dislocations

The surface exchange coefficients (k_{chem}) versus inverse temperature for Sample A (orange diamonds) and Sample C^{*} (red triangles) are shown in **Figure** 7.11. All k_{chem} values were collected at final pO₂ = 500 mTorr. Both samples exhibit homogeneous, single surface response. Comparing responses from the two samples, two conclusions can be reached: (1) heavily dislocated surface of Sample C^{*} exhibits k_{chem} value up to 25 times faster than the low dislocation density surface of Sample A, between 580 – 890 °C; and (2) the activation energy for oxygen surface exchange on LSM is lower (by 0.6 eV) on tensilely strained compared with relaxed surface. These findings are discussed below.

The first observation is that surface penetrating dislocations increase the surface ex-



Figure 7.11: Arrhenius plot of surface exchange coefficients (k_{chem}) versus inverse temperature for Sample A (50 nm strained LSM on STO, orange diamonds) and Sample C* (600 nm relaxed LSM on STO, red triangles).

change coefficient, k_{chem} . The dislocation density in Sample C^{*} is approximately 3 orders of magnitude higher than Sample A due to a dislocation mediated strain relaxation process. This corresponds to an increase of k_{chem} value up to 25 times. It is worth noting that an increase in domain boundary population is also present in Sample C^* , even though the exact boundary population could not be determined. Dislocations are known to introduce lattice rotations and local strain,^{13,123} which can have associated segregation of anion or cations species.¹²⁷ Recent studies have suggested that the formation energy of oxygen vacancies is reduced at dislocation cores in $SrTiO_3$ and CeO_2 single crystals, leading to a higher oxygen vacancy concentration $([V_o^{..}])$.^{127,136,137} Since the surface exchange kinetics is proportional to the amount of oxygen vacancy that are available to participate in surface reactions, 23,27 an increase in $[V_o^{\cdot}]$ will result in higher surface exchange coefficient (k), consistent with the experimental observation in this study. Interestingly, the same studies predicted that dislocations increase the migration barrier for oxygen ions diffusion, and can lead to slower diffusion along dislocation cores.^{127,136,137} This is attributed to a space charge zone formed by the redistribution of charged species.^{136,137} Such hinderance on ionic diffusion was not observed in our study, likely because oxygen diffusion is not rate-limiting in the samples under investigation, and the overall oxygen exchange is dominated by the surface exchange reaction.

For dislocations to act as faster reaction pathways, the oxygen flux along dislocations (J_D) must be greater than oxygen flux through the native surface (J_S) , as illustrated in the schematic in **Figure 7.11**. In addition, lateral diffusion flux (J_L) from dislocations to the regions unaffected by the dislocations must be efficient. It is worth noting that J_D and J_L act as serial steps. Recall that in serial reactions, the slower process is rate-limiting and gets measured experimentally. The relative importance between J_D and J_L depends on the area of the active region near a dislocation core, which is likely dependent on temperature, pO₂, and the Burgers vector of the dislocation, and the lateral spacing of neighboring dislocations. The fact that a homogeneous response was measured on the heavily dislocated surface of Sample C* (600 nm relaxed LSM on STO) suggests that the predominant oxygen transport pathway is through dislocations, not a mixture of dislocations and native surface.

The second observation is that tensile strain reduces the activation energy for oxygen surface exchange on LSM. As discussed in previous chapters, Sample A is under coherent tensile strain (ca. 0.3%) induced by lattice mismatch with the STO substrate. In contrast, the lattice parameters of Sample C* are fully relaxed to bulk LSM values. The activation energy on the surface of Sample A ($E_a = 1.0 \text{ eV}$) is approximately 40% smaller than that on the surface of Sample C* ($E_a=1.6 \text{ eV}$). And the latter is closer to previous reported E_a values on bulk La_{0.8}Sr_{0.2}MnO₃ (1.4 eV) and thin film La_{0.8}Sr_{0.2}MnO₃ (1.5 - 2.1 eV) surfaces. Recent *ab initio* studies have predicted that biaxial tensile strain can reduce the energy barriers for oxygen vacancy formation and migration on the surface of a variety of ABO_3 oxides.^{11,122} Experimental studies performed using scanning tunneling microscopy suggested that tensile strain enhances the Sr²⁺ enrichment on the surface of La_{0.7}Sr_{0.3}MnO₃ thin films, which facilitates the oxygen vacancy formation.⁶ Thus, our second observation is in agreement with both simulation and experimental data.

7.5.2 Effects of tensile and compressive strain

The surface exchange coefficients (k_{chem}) versus inverse temperature for Sample A (50 nm strained LSM on STO, orange diamonds) and Sample D (50 nm strained LSM on NGO, blue open squares) are shown in **Figure 7.12**. As mentioned earlier, Sample A is under coherent



Figure 7.12: Arrhenius plot of surface exchange coefficients (k_{chem}) versus inverse temperature for Sample A (50 nm strained LSM on STO, orange diamonds) and the native surface response $(k_{chem,2}$ of Sample D (50 nm strained LSM on NGO, blue open squares).

tensile strain (ca. 0.3%) induced by STO, and exhibits a homogeneous surface exchange. Sample D is under overall compressive strain (ca. -0.8%), and exhibits a heterogeneous surface exchange response, where $k_{chem,2}$ is associated with the native LSM surface response. The difference in strain also results in different crystal structures: LSM is monoclinic on STO (Sample A) and orthorhombic on NGO (Sample D). Comparing the surface response from the two samples, one can conclude that on the $(110)_{pc}$ LSM surface: tensile strain decreases the activation energy to 1.0 eV, while compressive strain increases the activation energy to 1.9 eV. Such conclusions are consistent with previous simulation results, which predict that the oxygen migration barrier in a variety of ABO₃ is reduced by biaxial tensile strain and increased by compressive strain.¹¹ In addition, surface exchange kinetics is faster on the tensilely strained compared with the compressively strained surface within the measured temperature range. This could be due to a higher concentration of oxygen vacancy on the tensile strained surface, which can participate in surface exchange reaction.



Figure 7.13: Arrhenius plot of surface exchange coefficient (k_{chem}) versus inverse temperature for Sample D (50 nm strained LSM on NGO). The closed and open symbols represent the domain boundary response and native surface response, respectively.

7.5.3 Effects of coherent domain boundaries

As shown in **Figure 7.13**, the surface exchange on Sample D (50 nm strained LSM on NGO) is heterogeneous: consisting of two responses with different k_{chem} and E_a . Previous analysis have suggested that the higher E_a response $(k_{chem,2})$ corresponds to oxygen exchange across the native LSM surface, while the lower E_a response $(k_{chem,1})$ corresponds to oxygen exchange along the coherent domain boundaries observed in **Chapter VI**. As such, the presence of coherent domain boundaries can both enhance the surface exchange coefficient by about an order of magnitude and reduce the activation energy on the surface. Simulations have predicted that coherent twin walls in CaTiO₃ exhibit higher affinity to oxygen vacancies, leading to an increase in local $[V_o^{\sim}]$.¹⁴⁴ In addition, recent studies on $(100)_{pc}$ LSM film on STO revealed that coherent $(100)_{pc}$ twin walls are under large local strain and exhibit higher electronic conductivity.¹⁶ Both increased $[V_o^{\sim}]$ and increased electronic conductivity can result in a higher local oxygen reduction reaction kinetics, following **Equation 2.1**. Previous studies^{15,30} reported that incoherent boundaries, such as grain boundaries in textured LSM films, can increase the surface exchange kinetics.^{15,30} However,

no findings of coherent domain boundaries in oxide materials exhibiting different catalytic properties have been reported. This study represents the first of its kind.



7.5.4 Overall effects of microstructure

Figure 7.14: Arrhenius plot of the surface exchange coefficients (k_{chem}) versus inverse temperature for Sample A (50 nm strained LSM on STO), Sample B (600 nm strained LSM on STO), Sample C* (600 nm relaxed LSM on STO), and Sample D (50 nm strained LSM on NGO). Schematics for the fastest and slowest response are included. Overall, k_{chem} varies by 2 orders of magnitude on the $(110)_{pc}$ orientation of LSM surface.

The surface exchange coefficients (k_{chem}) versus inverse temperature for all four samples are plotted in **Figure 7.14** Results on well controlled LSM thin film electrodes suggest that surface exchange properties on the $(110)_{pc}$ LSM orientation strongly depend on microstructure. Between $580 - 890 \,^{\circ}$ C, k_{chem} varies by more than 2 orders of magnitude, and E_a range between $1.0 - 1.9 \, \text{eV}$, depending on the strain status and the extended defect content. Specifically, the activation energy on $(110)_{pc}$ LSM is reduced by tensile strain and increased by compressive strain. In addition, extended defects can enhance the absolute value of the surface exchange coefficients (k_{chem}) . The highest k_{chem} was reported on the surface of fully relaxed LSM on STO, which exhibits a high density of dislocations of ca. 10^9 cm^{-2} . The lowest k_{chem} was reported on the native LSM surface under compressive strain, which also exhibits the highest activation energy (1.9 eV). Such results highlight the importance of microstructure (strain and defects) on the oxygen transport properties of LSM.

7.6 Conclusions

In summary, flat, epitaxial, $(110)_{pc}$ - oriented La_{0.7}Sr_{0.3}MnO₃ (LSM) thin films on STO and NGO substrates had been prepared by PLD. Effects of strain and extended defects on the oxygen surface exchange properties were investigated by electrical conductivity relaxation (ECR) between 580 – 890 °C. LSM films with controlled structure and microstructures were selected to study the effects of: (1) coherent tensile and compressive strain, (2) surface penetrating dislocations, and (3) extended coherent domain boundaries on the oxygen surface exchange properties. Specifically, this work represents the first report of coherent boundaries in oxide materials exhibiting different electrochemical properties than native materials. Our results suggest that between 580 - 890 °C, surface exchange coefficient (k_{chem}) on the $(110)_{pc}$ orientation of LSM varies by more than 2 orders of magnitude, and the activation energy range between 1.0 - 1.9 eV, depending on the strain status and the extended defect content. Specifically, the activation energy on $(110)_{pc}$ LSM is reduced by tensile strain and increased by compressive strain. In addition, extended defects can enhance the absolute value of the surface exchange coefficients (k_{chem}) . The highest k_{chem} was reported on the surface of heavily dislocated (fully relaxed) LSM on STO, which exhibits a high density of dislocations of ca. 10^9 cm^{-2} . The lowest k_{chem} was reported on the native LSM surface under compressive strain, which also exhibits the highest activation energy (1.9 eV).

CHAPTER VIII

Conclusions and future work

8.1 Conclusions

As mentioned in **Chapter I**, the three original goals of this research are to investigate: (1) the crystal structure distortions on the atomic scale of epitaxial $(110)_{pc} \operatorname{La}_{0.7} \operatorname{Sr}_{0.3} \operatorname{MnO}_{3-\delta}$ (LSM) thin films under tensile and compressive strain, (2) the nondestructive characterization of extended defects in $(110)_{pc}$ LSM films on the mesoscale, and (3) the effects of epitaxial strain and extended defects on the surface exchange properties of $(110)_{pc}$ LSM thin film electrodes.

To summarize, all three goals were achieved in this thesis. $(110)_{pc}$ LSM thin films with well controlled thickness, geometry, stoichiometry, surface morphology and microstructure were deposited by pulsed laser deposition (PLD). Epitaxial strain was induced by filmsubstrate lattice mismatch. The crystal structures of as deposited LSM were studied by X-ray diffraction (XRD) and related techniques. Extended defects within such films were controlled by substrate selection and controlled strain relaxation. Their densities and distribution were characterized on the mesoscale nondestructively by electron channeling contrast imaging (ECCI) and rocking curve (RC) analysis. The electronic conductivity and oxygen surface exchange properties were determined by electrical conductivity relaxation (ECR).

Specifically, the major conclusions in this thesis are as follows:

1. The crystal structures of $(110)_{pc}$ LSM depends critically on the epitaxial strain induced by the film-substrate lattice mismatch: LSM grown on SrTiO₃ under coherent tensile strain is monoclinic; while LSM grown on NdGaO₃ under overall compressive strain adopts an orthorhombic structure. Both are deviations from the rhombohedral structure $(R\bar{3}c)$ in bulk LSM.

- 2. The strain relaxation of epitaxial LSM films on $(110)_{pc}$ SrTiO₃ is controlled by both film thickness (strain energy) and thermal processing steps (the kinetics of dislocation generation and propagation). In addition, an increase in dislocation density of up to 3 orders of magnitude was observed during strain relaxation, comparing the fully strained $(1 \times 10^6 \text{ cm}^{-2})$ with fully relaxed $(1 \times 10^9 \text{ cm}^{-2})$ LSM films on STO.
- 3. Anti-phase boundaries (APBs) associated with modifications of the MnO_6 octahedral rotations were observed in $(110)_{pc}$ LSM thin films deposited on $SrTiO_3$. Their morphology, density, intensity profile, and contrast behaviors with respect to the channeling condition (**g**) were studied. A displacement vector of $\mathbf{R} = \frac{1}{2}[001]_m$ was identified using electron channeling contrast imaging (ECCI).
- 4. Coherent domain boundaries were observed in LSM thin films under compressive strain on $(100)_o$ NdGaO₃ substrates. The domains have two variants, are slanted at \pm 45 degrees, and exhibit strong contrast in ECCI and cross section TEM. The domain boundaries are likely associated with (1) octahedral tilt polymorphs (such as *Pbnm* and *Imma*), and/or (2) symmetry inversion domains (such as an inversion of the *b*-glide and *n*-glide in *Pbnm*), and/or (3) antiphase boundaries of the orthorhombic LSM.
- 5. Epitaxial strain modifies the oxygen exchange properties of LSM $(110)_{pc}$ surface by changing both the surface exchange coefficient (k_{chem}) and the activation energy (E_a) . Tensile strain reduces E_a to approximately 1.0 eV, while compressive strain increases E_a to approximately 1.9 eV on LSM $(110)_{pc}$ surface. In addition, k_{chem} on tensilely strained $(110)_{pc}$ LSM surface is up to 20 times higher than surface under compressive strain between 580 – 820 °C.
- 6. Surface penetrating dislocations generated during strain relaxation can enhance the surface exchange coefficient (k_{chem}) on the $(110)_{pc}$ surface of LSM on SrTiO₃. An increase of approximately 3 orders of magnitude in dislocation density results in up to 25 times increase in k_{chem} between 580 890 °C.

7. Extended coherent domain boundaries can facilitate the oxygen surface exchange kinetics in orthorhombic $(110)_{pc}$ LSM film on NdGaO₃. The transport kinetics (k_{chem}) along coherent domain boundaries is higher by more than an order of magnitude than native surface under compressive strain, and coherent domain boundaries exhibit a slightly reduced E_a for oxygen surface exchange reactions.

These findings offer direct experimental insights into the "microstructure - property" relationship of strontium doped lanthanum manganite (LSM) material. They also open up windows for improving the surface reaction kinetics of solid oxide fuel cell electrodes via defect engineering and microstructure control.

8.2 Future Work

Future work remains to elucidate the defect structures of epitaxial LSM thin films, and further correlate them with functional properties such as electronic conductivity, magnetic properties and oxygen surface exchange. Specifically, the following future work are suggested:

- 1. Conduct electron diffraction experiments in transmission electron microscopy (TEM) on $(110)_{pc}$ LSM thin films on NdGaO₃. Focus on understanding the atomic structure of coherent domain boundaries and origin of their contrast (strain vs. change in symmetry).
- 2. Measure the electronic conductivity, surface potential and magnetic properties of epitaxial $(110)_{pc}$ LSM thin films on STO and NGO. Focus on the possibility of mapping the electronic and magnetic signatures of extended antiphase boundaries and coherent domain boundaries.
- 3. Measure the oxygen exchange properties of the fully coherent 600 nm LSM on NGO thin film using electrical conductivity relaxation (ECR) under similar conditions. Compare the results with 50 nm LSM on NGO.

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