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THE GROWTH OF STRONTIUM TITANATE AND LUTETIUM FERRITE THIN FILMS BY MOLECULAR-BEAM EPITAXY

A Dissertation in

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by

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ABSTRACT

Included in this work is a range of studies on films of homoeptaxial and heteroepitaxial films of SrTiO₃ and the first reported phase-pure films of LuFe₂O₄. We report the structural properties of homoepitaxial (100) $SrTiO_3$ films grown by reactive molecular-beam epitaxy (MBE). The lattice spacing and x-ray diffraction (XRD) rocking curves of stoichiometric MBEgrown SrTiO₃ films are indistinguishable from the underlying SrTiO₃ substrates. The effect of off-stoichiometry for both strontium-rich and strontium-poor compositions results in lattice expansion with significant changes to the shuttered reflection high-energy electron diffraction oscillations, XRD, film microstructure, and thermal conductivity. Up to an 80% reduction in $Sr_{(1+x)}TiO_3$ film thermal conductivity is measured for x = -0.1 to 0.5. Significant reduction, from 11.5 to ~2 W·m⁻¹K⁻¹, occurs through the formation of Ruddlesden-Popper planar faults. The ability to deposit films with a reduction in thermal conductivity is applicable to thermal barrier coatings and thermoelectrics. Scanning transmission electron microscopy is used to examine the formation of Ruddlesden-Popper planar faults in films with strontium excess. We also show that the band gap of $SrTiO_3$ can be altered by >10% (0.3 eV) by using experimentally realizable biaxial strains providing a new means to accomplish band gap engineering of SrTiO₃ and related perovskites. Such band gap manipulation is relevant to applications in solar cells water splitting, transparent conducting oxides, superconductivity, two-dimensional electron liquids, and other emerging oxide electronics.

This work also presents the adsorption-controlled growth of single-phase (0001)-oriented epitaxial films of charge ordered multiferroic, LuFe₂O₄, on (111) MgAl₂O₄, (111) MgO, and (0001) 6H-SiC substrates in an iron-rich environment at pressures and temperatures where excess iron desorbs from the film surface during growth. Scanning transmission electron microscopy reveals reaction-free film-substrate interfaces. The magnetization increases rapidly below 240 K, consistent with the paramagnetic-to-ferrimagnetic phase transition of bulk LuFe₂O₄.

TABLE OF CONTENTS

| LIST OF FIGURES | iii |
|--|----------------------|
| LIST OF TABLES | vii |
| ACKNOWLEDGEMENTS | viii |
| Chapter 1 Introduction | 1 |
| 1.1 Motivation 1.2 Metal Oxides | 1 |
| 1.3 Properties and Applications 1.4 Arrangement of Material 1.5 Outcomes | 4 13 14 |
| 1.6 Contribution of the Author | 15 |
| Chapter 2 Background: Oxide thin films and epitaxial growth | 18 |
| 2.1 Oxide crystal systems | 18 22 27 35 |
| Chapter 3 Growth of homoepitaxial SrTiO ₃ thin films by molecular-beam epitaxy | 39 |
| Chapter 4 Reduced thermal conductivity in off-stoichiometric homoepitaxial SrTiO ₃ | 52 |
| Chapter 5 Manipulating the band gap of SrTiO ₃ with epitaxial strain | 64 |
| Chapter 6 The adsorption controlled growth of LuFe ₂ O ₄ by molecular-beam epitaxy | 75 |
| Chapter 7 Conclusions | 89 |
| 7.1 Summary7.2 Future Work | 89 90 |
| Appendix Additional Techniques | 92 |

LIST OF FIGURES

| Figure 1-1: Common binary oxide crystal structures. | 3 |
|--|----|
| Figure 1-2: Common ternary oxide crystal structures. ¹ | 3 |
| Figure 1-3: Elements known to exist in the perovskite structure of ABX ₃ . Adapted from Schlom <i>et al.</i> and based on Landolt-Börnstein | 4 |
| Figure 1-4: Thermal conductivity versus coefficient of thermal expansion for various dense thermal barrier coating oxides from Vaßen <i>et al.</i> | 7 |
| Figure 1-5: A thermoelectric module schematic operating in (a) cooling mode and (b) heating mode from Riffat <i>et al.</i> ²⁹ | 9 |
| Figure 1-6 : Photoelectrochemical cell diagram with a TiO_2 photoelectrode (1) and a platinum counter electrode (2). ³² | 11 |
| Figure 1-7: The band gap positions for a variety of semiconductors relative to the redox potential of water from Jing <i>et al</i> . | 12 |
| Figure 1-8: Relationship between ferroelectricity represented in yellow by polarization (P) and electric field (E), magnetism in blue by magnetization (M) and magnetic field (H), and ferroelasticity in red by strain (ε) and stress (σ). The coexistence or coupling between these phenomena is termed multiferroicity | 13 |
| Figure 2-1 : The perovskite crystal structure of SrTiO ₃ | 19 |
| Figure 2-2 : Phase equilibria in the system Sr-Ti-O at 1375°C from 30 to 70 at. % oxygen reproduced from McCarthy <i>et al.</i> ¹⁵ | 20 |
| Figure 2-3: A schematic of the Ruddlesden-Popper phases of the form $Sr_{n+1}Ti_nO_{3n+1}$ from $n = 1$ to 5 with $n = \infty$ being equivalent to the perovskite $SrTiO_3$. ¹⁶ | 21 |
| Figure 2-4 : The crystal structure of LuFe ₂ O ₄ | 22 |
| Figure 2-6 : A Veeco Gen 10 cluster schematic including 3 growth modules and the cluster module. The film deposition takes place in the growth module while sample transfer is automated and done through the cluster module. (Courtesy of Veeco) | 27 |
| Figure 2-7: A model of a EPI 930 with labeled components (a). A visualization of a molecular-beam incident on a substrate during a typical growth process is visualized in (b). The beams are controllable by shutters. ²² | 29 |
| Figure 2-8 : A kSA 400 Analytical RHEED by k-Space Associates. (http://www.k-space.com/) | 30 |

| Figure 2-9 : Typical RHEED patterns observed for the [100] and [110] directions for a SrTiO ₃ film. | . 31 |
|--|------|
| Figure 2-10: Electron diffraction from different crystal surfaces. Three common types of surfaces are (a) single crystal film with smooth surface, (d) single crystal film with islands, and (g) a polycrystalline film. The electron beam from these surfaces creates an Ewald sphere construction of electron scattering in these three cases in (b), (e) and (h). The corresponding diffraction patterns are shown in (c), (f) and (i), respectively. | . 32 |
| Figure 2-11: RHEED intensity oscillations resulting from layer completion | . 33 |
| Figure 2-12 : STM and corresponding RHEED intensity oscillations from Fe films on Fe (001) substrates deposited at 20°, 180°, and 250° C | . 34 |
| Figure 2-13: A plane wave incident on a crystal lattice results in Bragg diffraction | . 35 |
| Figure 3-1: Shuttered RHEED oscillation behavior at the beginning ((a), (c), and (e)) and middle ((b), (d), and (f)) of the growth process of $Sr_{1+x}TiO_{3+d}$ films with stoichiometric composition ($x = 0$), (a) and (b), ~10% strontium excess ($x = 0.1$), (c) and (d), and ~10% strontium deficiency ($x = -0.1$), (e) and (f) | . 46 |
| Figure 3-2: Out-of-plane x-ray diffraction data taken around the 200 peak of $Sr_{1+x}TiO_{3+d}$ films with $x = -0.2$ (a), -0.1 (b), 0 (c), 0.1 (d) and 0.2 (e). The vertical dashed line marks the 200 peak of the (100) SrTiO ₃ substrate. | . 47 |
| Figure 3-3 : Comparison of out-of-plane lattice constant as a function of strontium excess, x , in $Sr_{1+x}TiO_{3+d}$ for sets of homoepitaxial films grown by MBE, PLD,' and rf magnetron sputtering. The circles are from films grown by MBE in this study. The open circles were grown by codeposition, while the closed circles were grown by alternately shuttered monolayers. | . 48 |
| Figure 3-4 : STEM images of the interface between the (100) SrTiO ₃ substrate and film for Sr _{1+x} TiO _{3+d} films with $x = -0.2$ (a), -0.1 (b), 0 (c), 0.1 (d) and 0.2 (e). An arrow indicates the interface. | . 49 |
| Figure 3-S1 : STEM images of the film-substrate interface for films deposited with excess strontium by both shuttered growth (a) and codeposition (b). More RP planar defects are observed to form in the shuttered case while the codeposited film seems to display a higher density of point defects. | . 50 |
| Figure 4-1: X-ray diffraction data for stoichiomertic $SrTiO_3$ films deposited at different temperatures in 10% ozone and at 750°C in distilled ozone in (a). X-ray diffraction for strontium excess $Sr_{(1+x)}TiO_3$ films deposited at 900°C in (b). A wider range XRD scan reveals RP phase peaks that can be indexed for $Sr_5Ti_4O_{13}$ in (c) | . 59 |
| Figure 4-2: The apparent out-of-plane or <i>c</i> -axis lattice constant for $Sr_{(1+x)}TiO_3$ films versus Sr:Ti stoichiometry ratio as determined by x-ray diffraction. | . 60 |

| Figure 4-3: Bright field STEM images taken at different magnifications of the $Sr_{1.25}TiO_3$ at 900°C shown in (a) and (b) and the $Sr_{0.9}TiO_3$ sample deposited at 500°C shown in (c) and (d). The excess strontium is clearly seen to form layers perpendicular to the growth direction in (b). | 61 |
|--|----|
| Figure 4-4: Thermal conductivity for the same stoichiometric SrTiO ₃ samples as shown in Fig 1a is displayed in (a). The dependence of thermal conductivity in relation to film composition is shown in (b) with excess strontium films showing the largest decrease. (c) shows the thermal resistively versus the apparent out-of-plane lattice constant of the film. The excess strontium is clearly seen to form layers perpendicular to the growth direction in (b) | 67 |
| perpendicular to the growth direction in (b). | 02 |
| Figure 5-1: X-ray diffraction results for the strained SrTiO ₃ films | 70 |
| Figure 5-2 : The plot displayed in (a) is of out-of-plane strain versus in-plane strain for the (100) oriented SrTiO ₃ films. An example rocking curve measurement for the SrTiO ₃ film on GdScO ₃ is shown in (b). | 71 |
| Figure 5-3: The spectroscopic ellipsometry data is shown for epitaxially strained SrTiO ₃ films on NdScO ₃ and LaAlO ₃ compared with bulk in (a). An example of the band gap extraction from $(\alpha E)^2$ and $(\alpha E)^{1/2}$ for a SrTiO ₃ substrate is displayed in (b) | 72 |
| Figure 5-4: Band gap values for the various films versus the applied epitaxial strain for both (100) and (111) oriented films. | 73 |
| Figure 6-1: Arrhenius plot of oxygen partial pressure showing where LuFe ₂ O ₄ is thermodynamically stable. | 82 |
| Figure 6-2: (a) Substrate model for MgO with the (111) growth plane highlighted. (b) The epitaxial orientation relationship of a LuFe ₂ O ₄ lattice on (111) MgO, (111) MgAl ₂ O ₄ , and (0001) 6H-SiC lattices (see Ref. 21). (c) A model showing the alternating single layers of lutetium oxide (U layers) and double layers of iron oxide (W layers) in LuFe ₂ O ₄ . (d) θ -2 θ x-ray diffraction scans for three 50 nm thick LuFe ₂ O ₄ films grown on (111) MgAl ₂ O ₄ , (111) MgO, and (0001) 6H-SiC. Asterisks (*) indicate XRD peaks from the substrates. | 83 |
| Figure 6-3: HAADF-STEM images of the same LuFe ₂ O ₄ on MgAlO ₄ film studied in Fig. 2(d) showing (a) the presence of a clean interface and (b) the well-ordered structure of LuO _{1.5} U layers alternating with Fe ₂ O _{2.5} W layers | 84 |
| Figure 6-4: The magnetization as a function of temperature and magnetic field of the same $LuFe_2O_4$ films as in Fig. 2(d). | 85 |
| Figure 6-5: Optical response of a 75 nm thick (0001) $LuFe_2O_4$ film grown on (111) MgAl ₂ O ₄ along with the <i>ab</i> -plane response of a $LuFe_2O_4$ single crystal ²⁸ at 300 K. The film absorption was determined by a combination of direct calculation of absorption from transmittance (below ~ 3 eV) and a Glover-Tinkham analysis of both transmittance and reflectance to obtain absorption above 3 eV. The data were | |

| merged between 2.5 and 3 eV, where there was substantial overlap. The inset shows the indirect and direct band gap analysis. | . 86 |
|--|------|
| Figure A-1: RBS spectra for off-stoichiometric SrTiO ₃ films on SrTiO ₃ substrate | . 93 |
| Figure A-2: Time-domain thermoreflectance (TDTR) setup | . 94 |
| Figure A-3: Diagram of an ellipsometry setup. ³ | . 95 |
| Figure A-4: The components that make up a SQUID magnetometer | . 96 |

LIST OF TABLES

| Table 1.1: Examples of Properties found in Oxides updated from Schlom et. al ³ | 5 |
|---|----|
| Table 2.1: A comparison of various growth techniques | 23 |
| Table 2.2: A partial list of commercially available oxide substrates | 25 |
| Table 2.3: Chamber pressure and approximate particle mean free path length | 29 |
| Table 5.1: Partial list of substrates and biaxial strain states for SrTiO ₃ films. Lattice constant is a calculated average pseudocubic lattice parameter for the orthorhombic substrates. | 69 |
| Table 6.1: LuFe ₂ O ₄ film lattice parameters and rocking curve full width at half maximum values determined from XRD data | 81 |

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Chapter 1

Introduction

1.1 Motivation

Thin films are critical to numerous technologies that define the modern world and the current state of technology in society, particularly with regards to electronics. The ability to create a material in thin film form, referred to as deposition or growth, is vital to many applications. One material class that is becoming increasingly important in thin film form is metal oxides. This diverse family possesses an equally diverse range of properties that are useful in thin film form for a wide variety of applications. Implementations of oxide thin films encompass everything from sensors, solid-oxide fuel cells, and high-temperature superconductors to transparent conductors, high-temperature thermoelectrics, and ferroelectric memory. In order to take advantage of desired material properties, it is beneficial to understand the influence of the thin film deposition process and to compare the resulting films to the same material in bulk form. The research comprising this thesis aims to better understand how the deposition process influences film properties and how this understanding enables the tuning of material properties.

The initial focus of this work is strontium titanate, $SrTiO_3$, a well-studied perovskite oxide material with many useful properties, and includes both how the thin film deposition process affects the film and how properties can be modified with compositional defects and strain engineering. Since there is already a large body of literature regarding $SrTiO_3$, it is an excellent system to explore the effects of film growth on resulting structure and properties. This thesis finishes with research concerning the achievement of phase-pure thin-films of hexagonal lutetium ferrite, $LuFe_2O_4$, possessing a combination of interesting ferroelectric and magnetic properties, and the structure and properties of these films. The ability to create $LuFe_2O_4$ in thin film form enables the material to be modified and studied in ways not possible when limited to bulk crystals.

1.2 Metal Oxides

Metal oxide materials, particularly the transition metal oxides in the perovskite structure, are systems where phase transitions are prevalent. Even slight disturbances to the crystal structure of these materials often result in significant changes to material properties. Therefore, metal oxides often prove challenging to understand. At the same time, it also implies that the properties of these systems may be easily modified, which is appealing from an engineering perspective.

There are many different crystal structures that are formed by compounds that contain oxygen anions and metal cations. Binary metal oxides consist of a combination of a one type of metal cation with an oxygen anion in the form MO_x , where M is a metal cation. These form compounds with formulas that include MO, MO_2 , and M_2O_3 that range from insulators to superconductors.¹ Some common binary metal oxides structures are displayed in Figure 1-1.



Figure 1-1: Common binary oxide crystal structures.



Figure 1-2: Common ternary oxide crystal structures.¹

Ternary oxides, shown in Figure 1-2, provide an even wider range of possibilities from an engineering perspective as well as additional challenges due to the increased complexity of controlling additional components. In particular, the perovskites, of the form ABX₃, are able to

accommodate a majority of all of the elements in the periodic table, shown in Figure 1-3. Perovskite oxides have phase diagrams rich with transitions where small deviations in composition and structure can have a large effect on properties. For example, biaxial strain can induce ferroelectricity in normally non-ferroelectric $SrTiO_3$.² This thesis primarily focuses on two ternary oxide systems: $SrTiO_3$ and $LuFe_2O_4$.



Figure 1-3: Elements known to exist in the perovskite structure of ABX₃. Adapted from Schlom *et al.*³ and based on Landolt-Börnstein⁴

1.3 Properties and Applications

Oxides exhibit an extraordinarily wide range of useful properties. These are listed in

Table 1.1 along with a list of values achieved. The work in this dissertation applies to the creation

of oxide thin films; the results of which are potentially relevant to many of the applications listed. Some of the properties applicable to the research comprising this work that will be covered in more detail include: thermal conductivity, band structure, and multiferroicity.

| Property | Value | Oxide Material | Reference |
|----------------------------|---|--|---|
| High mobility | $30,000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ | La-doped SrTiO ₃ | J. Son <i>et al.</i> ⁵ |
| Metal-insulator | $\Delta R/R_T > 10^{13}$ | EuO | Petrich <i>et al.</i> ⁶ |
| transition | | | - |
| Superconductivity | $T_{c} = 135 \text{ K}$ | HgBa ₂ Ca ₂ Cu ₃ O ₈ | Schilling <i>et al.</i> |
| Ferroelectricity | $P_s = 105 \mu C/cm^2$ | PbZr _{0.2} Ti _{0.8} O ₃ | Vrejoiu <i>et al.</i> ⁸ |
| | $P_{\rm S} = 100 \mu \rm C/cm^2$ | BiFeO ₃ | Wang et al. ⁹ , Li et |
| | | | $al.^{10}$ Das <i>et al.</i> ¹¹ Dho |
| | | | et al. ¹² |
| Piezoelectricity | $d_{33} = 2500 \text{ pC/N}$ | $PbZn_{1/3}Nb_{2/3}O_3$ - | Park <i>et al.</i> ¹⁵ |
| | | PbTiO ₃ | 14 |
| Ferromagnetism | $M_{\rm S} = 6.9 \ \mu_{\rm B} / Eu$ | EuO | Matthias <i>et al.</i> ¹⁴ |
| Colossal magnetoresistance | $\Delta R/R_{\rm H} > 10^{11} (5 \text{ T})$ | $Pr_{0.7}Sr_{0.04}Ca_{0.26}MnO_3$ | Maignan <i>et al.</i> ¹⁵ |
| Magnetostriction | $\lambda_{100} = -590 \times 10^{-6}$ | $Co_{0.8}Fe_{2.2}O_4$ | Bozorth <i>et al</i> . ¹⁶ |
| Faraday effect | $v = 4 \times 10^5 (\text{T} \cdot \text{cm})^{-1}$ | EuO | Ahn and Shafer ¹⁷ |
| Spin Polarization | P > 98% | CrO ₂ | Soulen <i>et al.</i> , ¹⁸ |
| | | | Anguelouch et al. ¹⁹ |
| Multiferroic - | $T_{\rm C} = 105 \ {\rm K}$ | BiMnO ₃ | Hill and Rabe, ²⁰ |
| Simultaneously | | | Moreira dos Santos |
| ferromagnetic and | | | et al., ²¹ Sharan et |
| ferroelectric | | | al. ²² Baettig <i>et al.</i> ²³ |
| | $T_{\rm C} = 250 \ {\rm K}$ | LuFe ₂ O ₄ , FeTiO ₃ | Ikeda <i>et al.</i> , ²⁴ |
| | | | Fennie ²⁵ |
| Low thermal | $\kappa = 0.82 \text{ W/m} \cdot \text{K}$ | $La_2Mo_2O_9$ | Winter <i>et al.</i> ²⁶ |
| conductivity | (100° C) | | |

Table 1.1: Examples of Properties found in Oxides updated from Schlom *et.* al^3

1.3.1 Thermal Conductivity

Thermal behavior is an important aspect of a material to consider in many situations. Usually either a high or low thermal conductivity is desired for any given application. High thermal conductivity is often desired in order to distribute heat evenly or carry heat to or away from something. One example is the more even cooking provided by copper cookware over steel since copper has a much higher thermal conductivity, one of the highest of any metal. Metals typically have high thermal conductivity since electrons can transmit thermal energy and the electrons flow easily in a metal. Elastic vibrations in the lattice, or phonons, are also able thermal carriers that dominate the thermal conductivity in dielectric materials. Diamond, while electrically insulating, has thermal conductivities five times that of copper due to the strong covalent bonding that enables thermal transport by phonons. Low thermal conductivity is preferred in settings where insulation is desired such as beverage containers that keep drinks hot or cold and the heat shield of a space shuttle that protects the craft from the extreme heating that occurs during reentry. Two applications involving thermal properties that are relevant to this thesis are thermal barrier coatings and thermoelectrics.

Thermal Barrier Coatings

There are many situations where materials must be designed to withstand elevated operating temperatures. Examples include combustion engines, gas turbines, jet engines, and exhaust systems. The alloys that are optimized for the structural aspects of these applications experience degradation through oxidation and fatigue during operation at high temperature. Thermal barrier coatings that insulate these structural elements allow for higher operating temperatures and extended lifetimes. These thermal barrier coatings can enable components to operate at temperatures higher than the melting point of the base alloy the component is comprised of.

The two critical selection criteria for a thermal barrier coating are a low thermal conductivity and a thermal expansion similar to the underlying metal substrate. Yttria-stabilized zirconia (YSZ) is the standard material used for this application. One primary limitation for YSZ

is the phase transformation that occurs around 1200°C that causes cracks to form in the coatings.²⁷ There is a current push for alternative materials to avoid this problem and allow for higher operating temperatures. Figure 1-4 compares the thermal conductivity and thermal expansion for a number of alternative materials for thermal barrier coatings organized by structure type.



Figure 1-4: Thermal conductivity versus coefficient of thermal expansion for various dense thermal barrier coating oxides from Vaßen *et al.*²⁸

Thermoelectrics

Thermoelectric devices are solid-state devices that are able to generate electricity directly from heat or perform cooling when powered. Applications exist in generating power from a variety of heat sources including waste heat, geothermal, and solar thermal. Cooling applications exist for electronic devices, refrigeration, air-conditioning, and situations where precise temperature control is required. There are many advantages to using thermoelectric devices including low maintenance, long device lifetime, reversibility, environmental compatibility, and potential to be miniaturized.²⁹ Although the discovery of the phenomenon where electricity can

be generated from a temperature gradient, the Seebeck effect, occurred in 1821, thermoelectric devices have not come close to fully realizing their potential in energy generation or refrigeration; this is primarily due to material limitations. Thermoelectric materials are typically rated for thermoelectric potential by a figure of merit (ZT) described by:

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Where the *z* depends on the square of the Seebeck coefficient (S), is porportional to electrical conductivity (σ), and inversely proportional to thermal conductivity (κ). For thermoelectric applications it is ideal to reduce κ and increase σ .

A model of a thermoelectric device is shown in Figure 1-5 for solid-state cooling and heating applications. It is also possible to generate current directly from a thermal gradient from a similar setup. Both *n*-type and *p*-type thermoelectric materials are required for this particular setup.

Oxides show great promise for thermoelectrics, particularly in high-temperature applications. Developing an understanding of how the thermal conductivity can be affected by the growth process is an important contribution to the realization of efficient thermoelectric oxides. Specifically relevant to this work, *n*-type $SrTiO_3$ is a material that may be suitable for thermoelectric applications and has been observed to have a ZT of 0.28 at 873 K.³⁰



Figure 1-5: A thermoelectric module schematic operating in (a) cooling mode and (b) heating mode from Riffat *et al.*²⁹

1.3.2 Band structure

Electronic band structure describes the range in allowable electron energies within a solid. Regions of energy that are forbidden can give rise to an energy band gap. Band structure

can be used to explain many physical properties such as optical absorption and electrical resistivity. Electrons bound to an atom in isolation have specifically allowed discreet energy levels. When many atoms are combined to form a solid, atomic orbitals split into a large number of molecular orbitals with different energies. Since the electrons in close proximity must have different energies due to the Pauli exclusion principle, a band of allowable energies forms.

Band structure can describe the difference between metals, insulators, and semiconductors. The valence band is the highest range of energies typically occupied by electrons in a solid. Valence electrons are bound to individual atoms. The conduction band is a range of electron energies higher than the valence band where an electron is free to move between atoms and allow for the flow of electrical current. Metals have a partially filled band or overlapping conduction and valence band energies that can result in high conductivity since electrons do not need to be excited to higher energy levels in order to travel through the atomic lattice. Semiconductors and insulators have a small and large band gap respectively. Modifying the band gap by creating defect states makes it possible to create semiconductor devices including transistors, diodes, solid-state lasers, and solar cells. Any processes involving optical absorption in a crystal are also related to band structure.

Photocatalysis

Photocatalysis is the acceleration of a chemical reaction requiring light in the presence of a catalyst. Some applications include sterilization and water disinfection, organic waste destruction, self-cleaning coatings for surfaces and glass, and water splitting to produce hydrogen gas. The splitting of water in a photoelectrochemical cell, or photoelectrolysis, has the potential to be a promising renewable source for clean hydrogen fuel.³¹

$$H_2O + 2 hv \rightarrow \frac{1}{2}O_2 + H_2$$

Titanium dioxide has been the standard oxide material for photocatalysis since it was reported to have this property.³² A photoelectrochemical cell can be created to perform water splitting using a TiO₂ photo-anode and Pt cathode.

$$TiO_{2} + 2 hv \rightarrow 2 e^{-} + 2 p^{+}$$
(photoexcitation of TiO₂ by light)

$$2 p^{+} + H_{2}O \rightarrow \frac{1}{2}O_{2} + 2 H^{+}$$
(O₂ created at the TiO₂ electrode)

$$2 e^{-} 2 H^{+} \rightarrow H_{2}$$
(H₂ created at the platinum electrode)



Figure 1-6: Photoelectrochemical cell diagram with a TiO_2 photoelectrode (1) and a platinum counter electrode (2).³²

The wavelength of light required to excite an electron must be of an energy higher than the band gap. In TiO_2 the photon energy is 3 eV, which corresponds to a wavelength less than 415nm. Since the majority of the solar spectrum is in the visible range, it would be ideal to be able to use lower energy photons to do water splitting. The actual required energy to split water is 1.23 eV, so finding a material that has a smaller band gap than TiO_2 for hydrogen production would be highly desirable.

In addition to the overall band gap, the band offset of a material in relation to the energies required for water splitting is also important. Band energy levels for common semiconductor

materials are shown in Figure 1-7. Even though some materials may appear to have an ideal band location it must also be chemically stable during the water splitting process to be practical. SrTiO₃, of specific interest to this work, is shown with a band gap of 3.2 and band offsets appropriate for water splitting.³³



Figure 1-7: The band gap positions for a variety of semiconductors relative to the redox potential of water from Jing *et al.*³⁴

1.3.3 Multiferroicity

Materials where magnetic order, ferroelectricity, or ferroelasticity coexist are termed multiferroics. These properties and their relationships are shown in Figure 1-8. The benefits of having such a material include the ability to sense and control magnetic fields with electrical signals and vice versa. The search for these materials has been challenging due to the frequent incompatibility of the phenomena.^{35,36}

One form of multiferroicity is due to charge ordering, as in the case with $LuFe_2O_4$, where it has been reported to be simultaneously ferrimagnetic and ferroelectric below 250 K, the highest temperature of any known multiferroic.³⁷ The ferroelectric moment occurs through the ordering of the Fe²⁺ and Fe³⁺ cations giving rise to a net moment.



Figure 1-8: Relationship between ferroelectricity represented in yellow by polarization (P) and electric field (E), magnetism in blue by magnetization (M) and magnetic field (H), and ferroelasticity in red by strain (ϵ) and stress (σ). The coexistence or coupling between these phenomena is termed multiferroicity.³⁸

1.4 Arrangement of Material

Following the background on the relevant crystal systems and thin film growth, the

dissertation is organized into a series of journal articles on the growth of SrTiO₃ films for

chapters 3-5. Specifically, these chapters focused on SrTiO3 contain a basic growth study and

defects of stoichiometric and non-stoichiometric homoepitaxial films, reducing the film thermal

conductivity, and band gap engineering with strain. The first phase-pure growth of thin films of $LuFe_2O_4$ by molecular-beam epitaxy is covered in chapter 6.

1.5 Outcomes

There are numerous outcomes for this work. The most fundamental outcome being that the process of depositing an oxide thin film has a pronounced effect on the properties. This may seem obvious but the sensitivity observed in oxide systems cannot be overemphasized. Even a slight divergence in stoichiometry is enough to produce an easily noticeable change in film structure and properties when compared with bulk. These results for SrTiO₃ have general implications for all thin-film deposition techniques depositing any oxide material. This work encourages asking the question of whether any measured property or observed behavior in a thin film is truly intrinsic to the material or an effect of unintentional defects created during the deposition process.

Other more specific outcomes regarding $SrTiO_3$ include understanding how compositional defects affect structure and film thermal conductivity. Understanding thermal conductivity of oxide thin films has benefits for thermal barrier coatings and thermoelectics. The final contribution involving $SrTiO_3$ is experimental evidence of epitaixal strain-induced band gap modification of $SrTiO_3$. Band gap manipulation is useful for water-splitting applications and results that show a change in band gap of ~10% in $SrTiO_3$ with strain has implications for other oxide systems as well.

1.6 Contribution of the Author

This dissertation contains articles written by the author that either have been published or will soon be submitted to refereed journals. The primary experimental contribution of the author to these studies has been in the development and optimization of growth methods and the creation of all thin film samples by molecular-beam epitaxy (MBE) primarily using feedback from reflection high-energy electron diffraction (RHEED) and structural analysis by X-ray diffraction (XRD).

References

- ¹ L. W. Martin, Y.-H. Chu, and R. Ramesh, Mat. Sci. Eng. R 68, 89-133 (2010).
- ² J.H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y.L. Li, S. Choudhury, W. Tian, M.E. Hawley, B. Craigo, a K. Tagantsev, X.Q. Pan, S.K. Streiffer, L.Q. Chen, S.W. Kirchoefer, J. Levy, and D.G. Schlom, Nature 430, 758–61 (2004).
- ³ D. G. Schlom, L-Q. Chen, X-Q. Pan, A. Schmehl, and M. A. Zurbuchen, J. Am. Ceram. Soc. **91** 2429-2454 (2008).
- ⁴ K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 12a, pp. 126–206. Springer-Verlag, Berlin, 1978.
- ⁵J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N.J. Wright, R. Engel-Herbert, and S. Stemmer, Nature Materials **9**, 482-4 (2010).
- ⁶G. Petrich, S. von Molnár, and T. Penney, Phys. Rev. Lett. 26, 885-8 (1971).
- ⁷ A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott, Nature **363**, 56–8 (1993).
- ⁸ I. Vrejoiu, G. Le Rhun, L. Pintilie, D. Hesse, M. Alexe, and U. Gösele, Adv. Mater. **18**, 1657–61 (2006).
- ⁹ J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **299**, 1719–22 (2003).
- ¹⁰ J. F. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, Appl. Phys. Lett. **84**, 5261–3 (2004).
- ¹¹ R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, F. Zavaliche, S. Y. Yang, R. Ramesh, Y. B. Chen, X. Q. Pan, X. Ke, M. S. Rzchowski, and S. K. Streiffer, Appl. Phys. Lett., 88, 242904 (2006).
- ¹² J. Dho, X. Qi, H. Kim, J. L.MacManus-Driscoll, and M.G. Blamire, Adv. Mater. **18**, 1445–8 (2006).
- ¹³ S. E. Park and T. R. Shrout, J. Appl. Phys. **82**,1804–11 (1997).
- ¹⁴ B. T. Matthias, R. M. Bozorth, and J. H. Van Fleck, Phys. Rev. Lett. 7, 160–1 (1961).
- ¹⁵ A. Maignan, C. Simon, V. Caignaert, and B. Raveau, Solid State Commun. 96, 623–5 (1995).
- ¹⁶ R. M. Bozorth, E. F. Tilden, and A. J. Williams, Phys. Rev. **99**, 1788–98 (1955).
- ¹⁷ K. Y. Ahn and M. W. Shafer, J. Appl. Phys. **41**, 1260–2 (1970).
- ¹⁸ R. J. Soulen Jr., J.M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Science 282, 85–8 (1998).
- ¹⁹ A. Anguelouch, A. Gupta, G. Xiao, G. X. Miao, D. W. Abraham, S. Ingvarsson, Y. Ji, and C. L. Chien, J. Appl. Phys. **91**, 7140–2 (2002).
- ²⁰ N. A. Hill and K.M.Rabe, Phys. Rev. B **59**, 8759–69 (1999).
- ²¹ A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham, and C.N.R.Rao, Solid State Commun. **122**, 49–52 (2002).

- ²² A. Sharan, J. Lettieri, Y. Jia, W. Tian, X. Q. Pan, D. G. Schlom, and V. Gopalan, Phys. Rev. B, 69, 214109 (2004).
- ²³ P. Baettig, R. Seshadri, and N. A. Spaldin, J. Am. Chem. Soc., **129**, 9854–5 (2007).
- ²⁴ N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Mu- rakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, Nature **436**, 1136–8 (2005).
- ²⁵ C. J. Fennie, Phys. Rev. Lett., **100**, 167203 (2008).
- ²⁶ M. R. Winter and D. R. Clarke, J. Am. Ceram. Soc., **90** [2] 533–540 (2007).
- ²⁷ R. A. Miller, J. L. Smialek, and R. G. Garlick, Advances in Ceramics, Science and Technology of Zirconia, A. H. Heuer and L. W. Hobbs, Eds., Columbus, OH: American Ceramic Society, 1981.
- ²⁸ R. Vaßen, M.O. Jarligo, T. Steinke, D.E. Mack, and D. Stöver, Surface and Coatings Technology **205**, 938–942 (2010).
- ²⁹ S. B. Riffat, X. Ma, Appl. Therm. Eng. **23** 913-935 (2003).
- ³⁰ J. Ravichandran, W. Siemons, D.-W. Oh, J. T. Kardel, A. Chari, H. Heijmerikx, M. L. Scullin, A. Majumdar, R. Ramesh, and D. G. Cahill, Phys. Rev. B 82, 165126 (2010).
- ³¹ G.W. Crabtree, M.S. Dresselhaus, and M.V. Buchanan, Physics Today 57, 39 (2004).
- ³² A. Fujishima, Nature **238**, 37–38 (1972).
- ³³ Carr, R. G. & Somorjai, G. A. Nature **290**, 576-577 (1981).
- ³⁴ D. Jing, L. Guo, L. Zhao, X. Zhang, H. Liu, M. Li, S. Shen, G. Liu, X. Hu, and X. Zhang, Int. J. of Hydrogen Energ **35**, 7087–7097 (2010).
- ³⁵ N. A. Hill, J. Phys. Chem. B **104**, 6694-6709 (2000).
- ³⁶ S. W. Cheong and M. Mostovoy, Nature Mater. 6, 13-20 (2007).
- ³⁷ N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, Nature **436**, 1136-1138 (2005).
- ³⁸ N.A. Spaldin and M. Fiebig, Science **309**, 391 (2005).

Chapter 2

Background: Oxide thin films and epitaxial growth

In this section, epitaxial thin film deposition of oxides is discussed, including various growth methods, epitaxial growth, and substrate selection. The thin film growth process is central to this dissertation since the focus is on achieving a better understanding of the influence of the growth process on oxide thin films, the details of which can then be applied in a general way to many different applications.

2.1 Oxide crystal systems

The two oxides that are the main focus of this work are SrTiO₃ and LuFe₂O₄. This section will cover some background on the structure and properties for these two systems.

2.1.1 Strontium Titanate: SrTiO₃

SrTiO₃ is the archetypal perovskite and displays many of the interesting properties found in provskite materials. In addition to having a high dielectric constant up to 20,000,¹ it can also be made ferroelectric with strain. If doped it can also have a mobility in excess of 30,000 cm²/V·s,² or made superconducting. ³⁻⁵ With an indirect band gap of 3.2 eV, SrTiO₃ is a stable photocatalyst for water splitting.⁶⁻⁸ The perovskite structure of SrTiO₃ is shown in Figure 2-1. Since it is also used commonly used as a substrate material, a well developed understanding of SrTiO₃ is important for many oxide thin films, such as high temperature superconductor material YBa₂Cu₃O_{7-x}.⁹



Figure 2-1: The perovskite crystal structure of SrTiO₃

While $SrTiO_3$ is widely studied and has many interesting properties, it is also a system in which achieving precise control over properties is challenging. This is because defects, particularly oxygen vacancies, are readily formed in the $SrTiO_3$ structure and can have a significant effect on resulting properties. For example, although strain has been seen to induce ferroelectricity in $SrTiO_3$, evidence of ferroelectricity is also seen in strain-free films when slight non-stoichiometry exists.¹⁰ Oxygen vacancies in $SrTiO_3$ can cause the titanium to change valence state from Ti^{4+} to Ti^{3+} by the following defect reaction:

$$O_0^x + 2Ti_{Ti}^x = v_0^{\bullet \bullet} + 2Ti_{Ti}' + \frac{1}{2}O_2(g)$$

Non-stoichiometry can also result in valence changes for the titanium or the formation of other defects. There have been a number of studies exploring the role of defects in SrTiO₃ in both bulk¹¹ and thin film form¹² and how these defects affect properties.

 $SrTiO_3$ is also interesting from an engineering perspective in that it is compatible with the rocksalt structure of SrO giving rise to a set of layered phases, such as Sr_2TiO_4 , initially mentioned by Balz and Plieth in 1955¹³ and reported in more detail for structures including $Sr_3Ti_2O_7$ by Ruddlesden and Popper in1957.¹⁴ This provides a mechanism for tuning material

properties by the inclusion of excess SrO as Ruddlesden-Popper (RP) defects into the structure of SrTiO₃. The SrO-TiO₂ phase diagram, in Figure 2-2, shows where these phases occur.¹⁵ The only RP phases of the form $Sr_{n+1}Ti_nO_{3n+1}$, shown in Figure 2-3, that appear to be thermodynamically stable in bulk are the ones up to the n=3 (Sr₄Ti₃O₁₀). Nevertheless, it is possible to create the higher *n* phases in thin-film form.¹⁶ The formation of these RP defects is explored further in Chapters 3 and 4.



Figure 2-2: Phase equilibria in the system Sr-Ti-O at 1375°C from 30 to 70 at. % oxygen reproduced from McCarthy *et al.*¹⁵



Figure 2-3: A schematic of the Ruddlesden-Popper phases of the form $Sr_{n+1}Ti_nO_{3n+1}$ from n = 1 to 5 with $n = \infty$ being equivalent to the perovskite $SrTiO_3$.¹⁶

2.1.2 Lutetium Ferrite: LuFe₂O₄

The structure of lutetium ferrite, shown in Figure 2-4, is made up of single layers of lutetium separated by double layers of iron. The mix of Fe^{2+} and Fe^{3+} valence states present in the double iron layers give rise to a charge frustration on a triangular lattice. This material is a potentially interesting multiferroic due to the combination of dielectric and ferrimagnetic properties.¹⁷ The charge frustration creates a method of electric polarization different from the typical displacement ferroelectrics, such as BaTiO₃.

So far, attempts to fabricate this material in thin film form have only seen limited success.¹⁸⁻²⁰ A reliable method for depositing $LuFe_2O_4$ in thin film in order to better understand and manipulate the dielectric and magnetic properties of this material is presented in Chapter 6.



Figure 2-4: The crystal structure of LuFe₂O₄

2.2 Epitaxial growth of oxide thin films

Many applications for oxide materials require specific material dimensions not practically achievable or usable from mechanical methods of cutting and polishing oxide crystals. Thin film deposition techniques allow for the creation of modern electronic devices, a classic example for oxide materials is the dielectric gate oxide in silicon transistors. There are a range of growth techniques each with their advantages and disadvantages, shown in Table 2.1. Physical growth

mechanisms typically deposit material over an area that is in the line-of-sight of the deposition source while chemical deposition processes is conformal.

| Deposition Method | Mechanism | Advantages | Limitations |
|---------------------------------------|-----------|--|--|
| Pulsed Laser Deposition (PLD) | Physical | Simple to implement, adaptable to wide range of materials, inexpensive | Macroparticle ejection, far from equilibrium |
| Sputtering | Physical | Large-scale production, | Stoichiometry control, elements sputter at different rates |
| Molecular-beam epitaxy (MBE) | Physical | In-situ monitoring, high control, low energy atomic beams | High cost, typically low growth rate |
| Chemical vapor deposition (CVD) | Chemical | Large-scale production, film uniformity, conformal | Limited elemental selection based on metal-organic |
| Chemical solution deposition (CSD) | Chemical | Inexpensive, quick | Low precision, no atomic layer control |

Table 2.1: A comparison of various growth techniques²¹

Oxide thin films can be created with various degrees of crystal order anywhere from amorphous to single-crystalline. Although the presence of grain boundaries in polycrystalline or textured films, or disorder in amorphous films may be useful for particular applications, the focus of the experiments in this thesis is on single-crystal oxide films. In many applications, such as high mobility, single-crystals are far superior to polycrystalline materials. Single-crystals are also conceptually simpler to study in some respects since there is no need to take into account the effects of factors such as grain boundaries and crystallite size. In addition, single-crystal oxide thin films provide a large experimental playground for strain engineering. There are a wide range of factors that influence the deposition or growth of an oxide thin film. These can be narrowed down to three main factors: temperature, pressure, and starting surface. The starting surface or substrate is often another oxide single-crystal with a similar crystal structure to the desired film in order to achieve epitaxial growth. Epitaxy is where a film will form a crystalline layer according the underlying structure of the substrate; the substrate essentially acting as a seed crystal.

2.2.1 Lattice mismatch and epitaxial strain

The difference between the lattice constant of the film and substrate is referred to as lattice mismatch. Using lattice mismatch, it is possible to epitaxially strain film to the substrate.

In-plane lattice mismatch:
$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_{sub} - a_{film}}{a_{film}}$$

This epitaxial strain can often have a significant enough of an effect to noticeably alter material properties. In the case of SrTiO₃, this strain can induce ferroelectricity. By controlling the strain state of the film by appropriate substrate selection, it is possible to tune properties like the ferroelectric transition temperature as in the case with SrTiO₃.

Since the substrate has a significant influence on the structure of the thin film it is useful to have a wide range of substrates to provide a variety of strain states. Some commercially available substrates are listed in table 2.2. A number line of available perovskite substrates along with example film materials are shown according to pseudo-cubic lattice constant in Figure 2-5. Strained films of $SrTiO_3$ will be covered further in Chapter 5 where epitaxial strain is used to tune the band gap.

| Substrate | System | Space Group | pseudo-cubic |
|---|--------------|-------------|------------------|
| | | | Lattice Constant |
| MgO | Cubic | Fm3m (225) | 4.212 |
| KTaO ₃ | Cubic | Pm3m (221) | 3.988 |
| SrTiO ₃ | Cubic | Pm3m (221) | 3.905 |
| DyScO ₃ - NdScO ₃ | Orthorhombic | Pbnm (62) | 3.944 - 4.014 |
| NdGaO ₃ | Orthorhombic | Pbnm (62) | 3.851 |
| LaAlO ₃ | Cubic | Pm3m (221) | 3.791 |

 Table 2.2: A partial list of commercially available oxide substrates



Figure 2-5: Perovskite number line of common oxide film materials and commercially available substrates on adapted from Schlom *et.* al^{22}
One way to observe the strain in an epitaxial film is to measure the out-of-plane film lattice constant. When a material is compressed in one direction, it often expands in the directions perpendicular to the direction of the compression. In a commensurately strained film, the in-plane lattice spacing of the film is matched to that of the substrate. This change in the in-plane lattice constants also causes a change in the out-of-plane lattice constant according to Poisson's ratio (v). For a thin film with lattice constants (a_x , a_y , a_z), assuming z is the out-of-plane direction and x and y are in the film plane then the strains (ε_{ij}) can be described as follows:

$$\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$$

With strain related to stress (σ) by Hooke's law using the compliance tensor (*s*):

$$\varepsilon_{ij} = S_{ijkl} \sigma_{kl}$$

Expressed in terms of Young's modulus (E) and Poisson's ratio for an isotropic material:

$$\varepsilon_{xx} = \frac{1}{E} \left[\sigma_{xx} - v \left(\sigma_{yy} + \sigma_{zz} \right) \right]$$
$$\varepsilon_{zz} = \frac{1}{E} \left[\sigma_{zz} - v \left(\sigma_{xx} + \sigma_{yy} \right) \right]$$

With stress only applied to the film by the substrate:

$$\sigma_{xx} = \sigma_{yy} \& \sigma_{zz} = 0$$

$$\varepsilon_{xx} = \frac{1}{E} [\sigma_{xx} - v(\sigma_{xx})]$$

$$\varepsilon_{zz} = \frac{1}{E} [-v(2\sigma_{xx})]$$

$$\frac{\varepsilon_{xx}}{\varepsilon_{zz}} = \frac{[1-v]}{[-2v]}$$

Solving for v provides a method for calculating the film Poisson's ratio from the applied biaxial strain and resulting out-of-plane strain:

$$v = \frac{1}{1 - 2\frac{\varepsilon_{xx}}{\varepsilon_{zz}}}$$

This calculation is useful for determining if the film has a similar Poisson's ratio to a bulk crystal of the same material.

2.3 Molecular-Beam Epitaxy

Pioneered by J. R. Arthur and A. Y. Cho at Bell Labs in the 1960s,²³ molecular-beam epitaxy is a high-precision deposition method that is able to produce single-crystal thin films of substrate limited quality. Traditionally used for semiconductor materials, it can also be used in the deposition of metal oxide thin films.

The systems used in this work included an EPI 930 and a Veeco Gen 10. Figure 2-6 shows a Gen 10 cluster complete with a robotic transfer system. Samples are loaded into the load lock and then transferred into a growth module by the robotic.



Figure **2-6**: A Veeco Gen 10 cluster schematic including 3 growth modules and the cluster module. The film deposition takes place in the growth module while sample transfer is automated and done through the cluster module. (Courtesy of Veeco)

2.3.1 Components

The primary components that make up an MBE system are shown in Figure 2-7. These components including pumps, pressure gauges, pure elemental sources, shutters, a sample stage with substrate heater, and a reflection high-energy electron diffraction (RHEED) setup for in-situ monitoring of the deposition process. It is also useful to have a quartz-crystal microbalance or beam flux monitor in order to determine the elemental source fluxes prior to film growth as well as a residual gas analyzer to monitor what gas species are present in the chamber. Additional components may also include oxygen or gas inlet valve depending on the types of materials being grown. An ozone generating system or oxygen plasma source can particularly useful when growing oxide films since the MBE growth is limited to low background pressure in the chamber, which can cause films to be significantly reduced or oxygen deficient.

High vacuum is necessary in order to have atomic beams of atoms. Low pressure allows for a longer mean free path of the atoms used for deposition. The mean free path (λ) is related to Boltzman's constant (k_B), temperature (T), particle diameter (d), and pressure (p) by the following equation:

$$\lambda = \frac{k_{\rm B}T}{\sqrt{2} \pi \, d^2 p}$$

Turbo and cryo pumps are used to achieve this low pressure. Another reason high vacuum is important in MBE is to prevent source oxidation. Some source materials are extremely reactive with oxygen at the temperatures required for deposition.

Each element has different requirements for use as a source material. Two main factors to consider when installing a new elemental source are the temperature required to achieve the desired atomic flux, typically around 10¹³ atoms/cm²·s, and a chemically compatibility with crucible materials. Certain elements must be melted in order to achieve a usable flux for film

growth. This has the added danger of possibly cracking a crucible during freezing if the source is cooled.

| Table 2.3: Chambe | r pressure and | d approximate | particle mean | free path | length |
|-------------------|----------------|---------------|---------------|-----------|--------|
|-------------------|----------------|---------------|---------------|-----------|--------|

| Conditions | Pressure (torr) | Molecules per cm ³ | Mean free path (m) |
|-------------------|-------------------|-------------------------------|--------------------|
| Atmosphere | 760 | 10^{19} | 10-6 |
| Low vacuum | 10^{-3} | 10^{15} | 10 ⁻¹ |
| High vacuum | 10 ⁻⁷ | 10 ⁹ | 10^{3} |
| Ultra-high vacuum | 10 ⁻¹¹ | 10^{6} | 10^{7} |



Figure 2-7: A model of a EPI 930 with labeled components (a). A visualization of a molecularbeam incident on a substrate during a typical growth process is visualized in (b). The beams are controllable by shutters.²²

2.3.2 Reflection high-energy electron diffraction (RHEED)

The primary tool used to monitor thin film deposition by MBE is Reflection high-energy electron diffraction (RHEED). A 10kV potential is used to accelerate electrons in a beam that diffracts off the sample surface at grazing incidence, typically from 0.5-3 degrees. The non-relativistic equation for the wavelength of an electron with an accelerating potential (U) is related to Plank's constsant (h), the electron mass (m_0) and charge (e) by the following equation:

$$\lambda = \frac{h}{\sqrt{2m_0 eU}}$$

From this equation, the wavelength for 10keV electrons is approximately 12.3 pm.

This electron diffraction allows for the surface crystal structure of the sample to be observed during thin film deposition. The sample may be rotated to view diffraction along different azimuths. The specific RHEED used in this work is the kSA 400 shown in Figure 2-8. The [100] and [110] are the directions typically monitored for cubic systems. Example images from a SrTiO₃ surface are shown in Figure 2-9.



Figure 2-8: A kSA 400 Analytical RHEED by k-Space Associates. (http://www.k-space.com/)



Figure **2-9**: Typical RHEED patterns observed for the [100] and [110] directions for a SrTiO₃ film.

RHEED allows for feedback on the evolution of the sample surface during growth. It is clear if the film grows in a form that is single-crystal, polycrystalline or amorphous by the presence of spots/streaks, rings, or diffuse background respectively. When film growth becomes rough, the electrons pass through regions of the film resulting in a transmission diffraction pattern containing spots instead of a reflected diffraction pattern. These conditions are shown in Figure 2-10.



Figure 2-10: Electron diffraction from different crystal surfaces. Three common types of surfaces are (*a*) single crystal film with smooth surface, (*d*) single crystal film with islands, and (*g*) a polycrystalline film. The electron beam from these surfaces creates an Ewald sphere construction of electron scattering in these three cases in (*b*), (*e*) and (*h*). The corresponding diffraction patterns are shown in (*c*), (*f*) and (*i*), respectively.²⁴

During film growth, intensity oscillations can be observed in the diffraction spots from RHEED are due to changes in atomic layer completion during growth, which provides feedback that is critical to the growth of many layered structures. When an atomic layer is partially complete the intensity from surface diffraction is at a minimum while diffraction from a complete layer is at a maximum. These RHEED oscillations due to layer completion are shown in Figure 2-11.



Figure 2-11: RHEED intensity oscillations resulting from layer completion.²⁵

It is also possible, and often likely, that the diffraction spot intensity in films decreases over time. This occurs when the film becomes increasingly rough over time, shown in Figure 2-12.



Figure 2-12: STM and corresponding RHEED intensity oscillations from Fe films on Fe (001) substrates deposited at 20°, 180°, and 250° C.²⁶

A difference in diffraction spot intensity can also occur depending on the termination of the sample being observed. This is the case in the deposition of $SrTiO_3$ with SrO terminated layers having a higher intensity than the TiO_2 terminated surface. Because of this, it is possible to observe oscillations during growth corresponding to the terminating layer of the film. This

enables shuttered growth oscillations when growing films of SrTiO₃. *In-situ* RHEED allows for source shutter times to provide precise control over film thickness and composition.²⁷ This atomic layer control also enables the growth of super-lattices, such as the RP phases mentioned earlier.¹⁶ These shuttered growth oscillations are covered further in Chapter 3.

2.4 X-ray Diffraction (XRD)

The primary characterization technique used to determine film structure was x-ray diffraction (XRD). It provides information about thin film composition, crystal dimensions, and crystal quality. X-rays scatter primarily from atomic electron clouds. The wavelength (λ), incident angle (θ) and crystal spacing (d) are related by Bragg's law:



 $n \lambda = 2d \sin \theta$

Figure 2-13: A plane wave incident on a crystal lattice results in Bragg diffraction.

There are a number of useful scans that can be done using an x-ray diffractometer. The three primary scans used primarily in this work are scans over $\theta - 2\theta$, ω , and ϕ . $\theta - 2\theta$ scans provide phase identification and lattice constant information. Rocking curve measurements, where only the sample is rocked over ω , provide information on crystal quality. ϕ -scans are used in determining what the in-plane orientation of the film is relative to the substrate.

XRD has traditionally provided phase identification for powder samples in a θ -2 θ scan. This can also be useful for thin films. For example, in growing a multicomponent oxide film with iron as a constituent, expected impurity phases may include hemitite and magnetite. If either of these phases exist in the film and are polycrystalline, all diffraction peaks corresponding to the impurity phase will show up in a θ -2 θ scan. Often a preferred orientation may exist for a particular phase so that only one orientation of an impurity phase may be present. Most often as long as a scan is aligned to the substrate, any other phases aligned to the substrate show up in a θ -2 θ scan.

Out-of-plane lattice constant can be determined from a θ -2 θ scan using a Nelson-Riley fit.²⁸ This is useful for determining crystal quality and the degree to which a film is strained. After determining out-of-place lattice constant, an off-axis peak can be measured to extract the in-plane lattice constant.

Thickness fringes, or Kessig fringes, are an additional diffraction feature that occurs around film diffraction peaks in samples when there is a smooth interface between the film and substrate and a smooth film surface. The periodicity of these fringes corresponds to film thickness and can provide information on the film/substrate interface or the film surface. An alternative measurement called x-ray reflectivity (XRR) is performed at low angle and can provide thickness as well as surface roughness and electron density.

Rocking curve measurements are used for determining how well aligned a film is to the substrate. A narrower rocking curve indicates a better alignment of the crystal. A crystal with structural defects may have a rocking curve full-width at half-maximum (FWHM) of $> 1^{\circ}$ while a high quality crystal can have a rocking curve narrower than 0.01°. It is also possible to see if a strained film is commensurate with the substrate by comparing the rocking curve shape of the film with that of the substrate. Typically as a film relaxes, the rocking curve gets broader as the strain is accommodated by the formation of dislocations. The minimum achievable FWHM of the film is limited to by the substrate.

Typical θ -2 θ scans are unable to provide information about how the in-plane orientation of the film is relative to the substrate. ϕ -scans are necessary to determine what the film in-plane orientation is relative to that of the substrate. It can also show if multiple in-plane orientations exist, which can occur if a film has lower crystal symmetry than the substrate material on which it is grown.

The specific XRD equipment used for this work primarily consisted of a high-resolution Philips X'Pert Pro MRD diffractometer with a PreFix hybrid monochromator on the incident side and triple axis/rocking curve attachment on the diffracted side. The operating conditions were 45 kV and 40 mA. In order to collect meaningful data from this particular lab XRD setup, film thickness had to be at least 10nm, which corresponds to ~25 unit cells of SrTiO₃. Broadening of the film peak in 2θ makes it difficult to interpret results on samples that are much thinner.

References

- ¹ K. A. Müller and H. Burkard, Phys. Rev. B **19**, 3593-3602 (1979).
- ² J. Son, *et al.* **9**, 482-484 (2010).
- ³ J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Lett. **12**, 474-475 (1964).
- ⁴ K. S. Takahashi, *et al.* Nature **441**, 195-198 (2006).
- ⁵ K. Ueno, *et al.* Nature Mater. 7, 855-858 (2008).
- ⁶ M. S. Wrighton, *et al.* J. Am. Chem. Soc. **98**, 2774-2779 (1976).
- ⁷ F. T. Wagner and G. A. Somorjai, Nature **285**, 559-560 (1980).
- ⁸ R. G. Carr and G. A. Somorjai, Nature **290**, 576-577 (1981).
- ⁹ K. Nassau and A. E. Miller, J. Cryst. Growth **91**, 373 (1988).
- ¹⁰ H. W. Jang, A. Kumar, S. Denev, M. D. Biegalski, P. Maksymovych, C. W. Bark, C. T. Nelson, C. M. Folkman, S. H. Baek, N. Balke, C. M. Brooks, D. A. Tenne, D. G. Schlom, L. Q. Chen, X. Q. Pan, S. V. Kalinin, V. Gopalan, and C. B. Eom, Physical Review Letters 104, 1-4 (2010).
- ¹¹ K-H. Yang, T-Y. Chen, N-J. Ho, H-Y. Lu, J. Am. Ceram. Soc., **94**, 1811 (2011).
- ¹² J. Zhang, S. Walsh, C. Brooks, D. G. Schlom, L. J. Brillson, J. Vac. Sci. Technol. B. 26, 1466 (2008).
- ¹³ D. Balz and K. Plieth, Z. Elektrochem., **59** [6] 545-51 (1955).
- ¹⁴ S.N. Ruddlesden and P. Popper, Acta Cryst. 10, 538 (1957).
- ¹⁵ G. J. McCarthy, W.B. White, and R. Roy, J. Am. Ceram. Soc. **52**, 463 (1969).
- ¹⁶ J.H. Haeni, C.D. Theis, and D.G. Schlom, J. Electroceramics 4:2/3, 385-391 (2000).
- ¹⁷ Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, Nature 436, 1136-1138 (2005).
- ¹⁸ R. Rejman, T. Dhakal, P. Mukherjee, S. Hariharan, and S. Witanachchi, (Mater. Res. Soc. Symp. Proc. 1199, Pittsburgh, PA, 2009), F03-22.
- ¹⁹ J. Liu, Y. Wang, and J. Y. Dai, Thin Solid Films **518**, 6909-6914 (2010).
- ²⁰ W. Wang, Z. Gai, M. Chi, J. D. Fowlkes, J. Yi, L. Zhu, X. Cheng, D. J. Keavney, P. C. Snijders, T. Z. Ward, J. Shen, and X. Xu, Phys. Rev. B 85, 155411 (2012).
- ²¹ L.W. Martin, Y.-H. Chu, and R. Ramesh, Materials Science and Engineering: R: Reports 68, 89-133 (2010).
- ²² L.W. Martin and D. G. Schlom, Curr. Opin. Solid. St. M. 16, 199-215 (2012).
- ²³ A. Y. Cho and J. R. Arthur. *Prog.* Solid State Chem. **10**: 157–192 (1975).
- ²⁴ F. Tang, T. Parker, G-C. Wang, and T-M. Lu, J. Phys. D: Appl. Phys. **40** R427-R439 (2007).
- ²⁵ J. H. Neave and B. A. Joyce , Appl. Phys. A **31**, 1-8 (1983).
- ²⁶ J.A. Stroscio, D.T. Pierce, and R.A. Dragoset, Physical Review Letters 70, 3615-3618 (1993).
- ²⁷ J.H. Haeni, C.D. Theis, and D.G. Schlom, J. Electroceramics 4:2/3, 385-391 (2000).
 ²⁸ J.B. Nelson, D.P. Riley, Proc. Phys. Soc. 57, 160-177 (1945).

Chapter 3

Growth of homoepitaxial SrTiO₃ thin films by molecular-beam epitaxy

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Abstract

We report the structural properties of homoepitaxial (100) SrTiO₃ films grown by reactive molecular-beam epitaxy (MBE). The lattice spacing and x-ray diffraction (XRD) rocking curves of stoichiometric MBE-grown SrTiO₃ films are indistinguishable from the underlying SrTiO₃ substrates. Off-stoichiometry for both strontium-rich and strontium-poor compositions (i.e., Sr_{1+x}TiO_{3+*} films with -0.2< x <0.2) results in lattice expansion with significant changes to the shuttered reflection high-energy electron diffraction oscillations, XRD, and film microstructure. The dependence of lattice spacing on non-stoichiometry is significantly smaller for MBE-grown films than for homoepitaxial (100) Sr_{1+x}TiO_{3+*} films prepared by pulsed-laser deposition or sputtering.

Introduction

Homoepitaxial growth is a standard way of assessing the ability of a thin film growth technique to make a new material. Although this approach has been widely used to assess a multitude of techniques for the growth of semiconductors, it was largely bypassed in the drive to make thin films and heterostructures of complex oxides, e.g., oxide superconductors. Now, decades later, studies of homoepitaxial films of complex oxides are beginning to emerge with surprising results. For example, homoepitaxial SrTiO₃ films grown by pulsed-laser deposition (PLD) have been found to have compositions differing significantly from the stoichiometric targets from which they are ablated,^{1,2} to have extended lattice constants^{1- 2^3} that get even more extended following oxygen annealing,^{1,2} and even to be ferroelectric at room temperature⁴ in striking contrast to unstrained (bulk) SrTiO₃ itself which is not ferroelectric at any temperature. Only when grown with a very narrow range of laser fluence and ablation area do PLD-grown SrTiO₃ films appear to be stoichiometric with bulk lattice constants.² Studies for homoepitaixal SrTiO₃ films made by sputtering show similar features.⁵ The defect structure of highly nonstoichiometric homoepitaxial SrTiO₃ films grown by PLD has been studied.⁶ Here we study the structural properties of homoepitaxial $SrTiO_3$ films grown by reactive molecular-beam epitaxy (MBE), including the effect of changes in stoichiometry ($-0.2 \le x \le 0.2$) on the structural properties of the resulting homoepitaxial $Sr_{1+x}TiO_{3+x}$ films.

Experimental

250 unit-cell-thick $Sr_{1+x}TiO_{3+a}$ films, approximately 100 nm in thickness, were grown on (100) SrTiO₃ substrates in a Veeco 930 oxide MBE system at a substrate temperature of 650°C in a background pressure of 5.0×10^{-7} Torr of molecular oxygen. Two sets of five films were grown

with one set being grown in the additional presence of $\sim 10\%$ ozone. The strontium content of the $Sr_{1+x}TiO_{3+s}$ films ranged from -0.2 < x < 0.2. A Ti-BallTM was used as the titanium source⁷ and an effusion cell supplied strontium. Both sources were shuttered to deposit alternating monolayer doses of SrO and TiO₂.⁸ Shutter times were initially set based on flux measurements made using a quartz crystal microbalance, and then precisely tuned by optimizing shuttered RHEED intensity oscillations during deposition on a calibration sample immediately prior to the growth of the sample sets.^{8,9} These shuttered RHEED oscillations differ from typical RHEED growth oscillations and are more similar to the behavior seen in migration-enhanced epitaxy.¹⁰ A set of films was also grown using true codeposition with both shutters being open for the duration of the growth. The strontium and titanium elemental source fluxes were approximately 3×10^{13} atoms/($cm^2 \cdot s$), corresponding to shutter times of about 20 seconds and a film growth rate of 6 Å/min. Substrates were prepared using a termination recipe that provides a TiO_2 starting surface.¹¹ Growth temperature was verified by optical pyrometry. The film structure, including out-of-plane lattice constant, was examined by x-ray diffraction (XRD) using a high-resolution Philips X'Pert Pro MRD diffractometer with a PreFix hybrid monochromator on the incident side and triple axis/rocking curve attachment on the diffracted side.

Results

Figures 1(a) and 1(b) show the shuttered RHEED intensity as a function of time for the 10 streaks along the [011] azimuth at the beginning and middle of the growth of a 100 nm thick stoichiometric film of (100) SrTiO₃. The shuttered RHEED oscillations are stable and maintain intensity throughout the duration of the entire film deposition indicating both full monolayer dosage and 1:1 stoichiometry.⁸ Optimizing these oscillations is done prior to growth on a calibration sample by tuning computer-controlled shutter times.

Film composition was verified by Rutherford backscattering spectrometry (RBS). While there is some overlap in the signal, determining the homoepitaxial film composition from the substrate using RBS is possible and results confirm that all off-stoichiometric films are within 5% of expected compositions based on shutter time adjustments. Stoichiometric homoepitaxial films had less than a 1% difference in composition from the substrate.

RHEED oscillations from a $Sr_{1+x}TiO_{3+x}$ film deposited with excess strontium, x = 0.1, is displayed in Figs. 1(c) and 1(d). In the excess case the intensity reaches a maximum and then starts to decrease before the strontium shutter is closed and the titanium shutter is opened. At the start of growth (Fig. 1(c)) this maximum is surpassed by a larger amount for each subsequent layer before the strontium shutter is closed. This case eventually results in stable oscillations (Fig. 1(d)) of a different form to that of the stoichiometric, x = 0, case. Similar behavior is observed during the strontium cycle when the strontium excess is increased to x = 0.2 except the intensity goes down further after reaching its maximum before the closing of the strontium shutter. These shuttered RHEED oscillations also eventually stabilize into regular oscillations.

Figures 1(e) and 1(f) are of a strontium deficient film, x = -0.1. In this situation, the strontium shutter closes and the titanium shutter opens before the RHEED intensity reaches a maximum. This causes the peak maxima to decrease in intensity over time. During each cycle the strontium shutter is closed earlier than in the preceding oscillation. This eventually results in a beat frequency with a long period due to the accumulation of insufficient monolayer doses of strontium. Films that deviated further from stoichiometric composition were even more deficient in strontium and had correspondingly shorter periods for this oscillation envelope.

As shown in Fig 2, the non-stoichiometric films exhibit XRD peaks distinct and slightly offset to lower 2θ from the substrate peaks while the stoichiometric film peaks are indistinguishable from the substrate peaks. Intensity oscillations corresponding to the ~100 nm film thickness around film peaks are present in all films, including stoichiometric films,

indicating smooth interfaces between the film and substrate, but also suggesting differences between deposited film and substrate. The further away from stoichiometric composition the larger is the deviation between the 2θ position of the film peak and the substrate peak. The inplane lattice spacing of the $Sr_{1+x}TiO_{3+x}$ films were determined from XRD measurements of the 101 film peak in combination with the out-of-plane spacing determined from h00 peaks.¹² In all cases the in-plane lattice spacing was identical (within experimental error) to the underlying substrate. Figure 3 is a plot of the out-of-plane lattice constant as a function of strontium excess for the MBE grown films in this work and those deposited by other growth methods.^{2,5,6} All methods see an expansion of the lattice constant corresponding to the degree of off-stoichiometry. The largest lattice expansions occurred in films where PLD was the growth technique. Despite the MBE films being grown in low oxygen pressures (5×10^{-7} Torr), the lattice expansion was not measurable for the stoichiometric cases due to the overlap between film and substrate peaks. All non-stoichiometric film results show an expansion of the out-of-plane lattice constant regardless of growth technique or whether the films are excess or deficient in strontium. Strontium deficient MBE-grown films showed similar lattice expansion independent of whether they were deposited by true codeposition or alternately shuttered monolayers. For the strontium excess case, the codeposited films grown by MBE had larger lattice expansions than the films grown by alternately shuttered monolayers.

Figure 4 shows scanning transmission electron microscope (STEM) images of the set of five $Sr_{1+x}TiO_{3+s}$ films grown in the presence of 10% ozone in order of increasing strontium offstoichiometry, *x*, increasing from -0.2 to 0.2. The film microstructure seen is in general agreement with the microstructure seen in off-stoichiometric films prepared by PLD⁶ where excess SrO is incorporated as Ruddlesden-Popper planar faults¹³ and films deficient in strontium have a more disordered structure. The same features are visible despite the films in this study being much closer to stoichiometric composition. When the sample is deficient in strontium, the film appearance is visibly disordered from the lack of strontium throughout the film as shown in Figs. 4(a) and 4(b). The film and the substrate for the stoichiometric film, where x = 0, are nearly indistinguishable (Fig. 4(c)). For the strontium excess case, where x = 0.1 (Fig. 4(d)), the Ruddlesden-Popper planar faults¹³ appear as columns in the film. When the strontium excess reaches a higher value, x = 0.2 in Fig. 4(e), the planar faults no longer appear as columns but take on a mosaic structure similar to the x = 0.5 case in Suzuki *et al.*⁶

Conclusions

The precise control over composition provided by the MBE growth process for homoepitaxial SrTiO₃ films allows for the examination of slight deviations in film composition on film structure. These results highlight the sensitivity of SrTiO₃ film structure and out-of-plane lattice constant to even small changes in stoichiometry. Other material systems likely exhibit similar sensitivity to composition. The shuttered RHEED intensity behavior during the growth of off-stoichiometric films was shown to have unique forms for both the strontium excess and strontium deficient cases. The presence of ozone during growth had no observable effect on the out-of-plane lattice constant measurement by XRD or film microstructure observed by STEM. XRD film peaks are indistinguishable from substrate peaks for the stoichiometric homoepitaxial films.

Under optimized conditions sputtering, PLD, and MBE growth methods are able to achieve stoichiometric films with lattice constants close to bulk SrTiO₃. For a given amount of off-stoichiometry, however, the MBE growth process is able to deposit films much closer in lattice constant to bulk SrTiO₃ than films grown by higher energy growth methods such as PLD. If it is challenging to reproduce the structure and properties of the substrate when growing homoepitaxial films by a growth technique, then it becomes all the more important that additional care be taken with the growth and characterization of heteroepitaxial films.

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Figures



Figure 3-1: Shuttered RHEED oscillation behavior at the beginning ((a), (c), and (e)) and middle ((b), (d), and (f)) of the growth process of $Sr_{1+x}TiO_{3+d}$ films with stoichiometric composition (x = 0), (a) and (b), ~10% strontium excess (x = 0.1), (c) and (d), and ~10% strontium deficiency (x = -0.1), (e) and (f).



Figure 3-2: Out-of-plane x-ray diffraction data taken around the 200 peak of $Sr_{1+x}TiO_{3+d}$ films with x = -0.2 (a), -0.1 (b), 0 (c), 0.1 (d) and 0.2 (e). The vertical dashed line marks the 200 peak of the (100) SrTiO₃ substrate.



Figure 3-3: Comparison of out-of-plane lattice constant as a function of strontium excess, x, in $Sr_{1+x}TiO_{3+d}$ for sets of homoepitaxial films grown by MBE, PLD,^{2,6} and rf magnetron sputtering.⁵ The circles are from films grown by MBE in this study. The open circles were grown by codeposition, while the closed circles were grown by alternately shuttered monolayers.



Figure 3-4: STEM images of the interface between the (100) SrTiO₃ substrate and film for $Sr_{1+x}TiO_{3+d}$ films with x = -0.2 (a), -0.1 (b), 0 (c), 0.1 (d) and 0.2 (e). An arrow indicates the interface.



Figure **3-S1**: STEM images of the film-substrate interface for films deposited with excess strontium by both shuttered growth (a) and codeposition (b). More RP planar defects are observed to form in the shuttered case while the codeposited film seems to display a higher density of point defects.

References

- ¹ T. Ohnishi, M. Lippmaa, and T. Yamamoto, Appl. Phys. Lett. **87**, 241919 (2005)
- ² T. Ohnishi, K. Shibuya, T. Yamamoto, and M. Lippmaa, J. Appl. Phys. 103, 103703 (2008).
- ³ E.J. Tarsa, E.A. Hachfeld, F.T. Quinlan, J.S. Speck, and M. Eddy, Appl. Phys. Lett. **68**, 490 (1996).
- ⁴ Y. S. Kim, D. J. Kim, T. H. Kim, T. W. Noh, J. S. Choi, B. H. Park, and J.-G. Yoon, Appl. Phys. Lett. **91**, 042908 (2007)
- ⁵ D. Fuchs, M. Adam, P. Schweiss, S. Gerhold, S. Schuppler, R. Schneider, and B. Obst, J. Appl. Phys. **88**, 1844.
- ⁶ T. Suzuki, Y. Nishi, and M. Fujimoto, Philos. Mag. A. 80, 621 (2000).
- ⁷ C.D. Theis & D.G. Schlom, J. Vac. Sci. Technol. A 14, 2677 (1996).
- ⁸ J.H. Haeni, C.D. Theis, and D.G. Schlom, J. Electroceramics 4, 385 (2000).
- ⁹ J.H. Haeni, C.D. Theis, D.G. Schlom, W. Tian, X.Q. Pan, H. Chang, I. Takeuchi, and X.D. Xiang, Appl. Phys. Lett. **78**, 3292 (2001).
- ¹⁰ Y. Horikoshi, M. Kawashima, and H. Yamaguchi, Jpn. J. Appl. Phys., Part 1 **27**, 169 (1987).
- ¹¹ G. Koster, B. L. Keopman, G.J.H.M. Rijnders, D.H.A. Blank, and H. Rogalla, Appl. Phys. Lett. **73**, 2920 (1998).
- ¹² J.B. Nelson, and D.P. Riley, Proc. Phys. Soc. **57**, 160-177 (1945).
- ¹³ Ruddlesden and P. Popper, Acta Cryst. **10**, 538 (1957); **11**, 54 (1958)

Chapter 4

Reduced thermal conductivity in off-stoichiometric homoepitaxial SrTiO₃

(To be submitted)

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Abstract

We report on the effect of growth temperature, oxidation environment, and nonstoichiometry on the thermal conductivity of homoepitaxial $SrTiO_3$ films deposited by reactive molecular-beam epitaxy. The thermal conductivity decreases by 80%—from 11.5 W m⁻¹k⁻¹ for stoichiometric homoepitaxial $SrTiO_3$ to 2 W m⁻¹k⁻¹ for strontium-rich homoepitaxial $SrTiO_3$ films—by formation of Ruddlesden-Popper planar faults. Thermal conductivity was determined by time-domain thermoreflectance and scanning transmission electron microscopy was used to examine the formation of Ruddlesden-Popper planar faults in films with strontium excess.

Introduction

Improvements to oxide thermal barrier coatings and thermoelectrics hinge on the ability to engineer a thermally resistive oxide that is optimized in conjunction with other parameters such as thermal expansion, microstructure, or carrier mobility. Oxides with the perovskite structure have general formula ABO₃ and are known for their tunability since they are able to incorporate a majority of the stable elements in the periodic table, allowing for a wide range of tuning based on elemental selection. Due to this tunability and high-temperature stability, materials in the perovskite family hold promise for both thermal barrier coatings¹ and thermoelectric applications.^{2,3}

The quintessential perovskite oxide, SrTiO₃, exhibits many of the useful properties found in oxide materials and provides a rich experimental parameter space since defects are easily accommodated into the structure in the form of Ruddlesden-Popper (RP) defects.^{4,5,6,7} These RP phases have been suggested as a pathway to achieving effective thermal barrier coatings using SrTiO₃-based materials.⁸ N-type SrTiO₃ has itself been proposed as a candidate for hightemperature thermoelectric applications.⁹ Doped epitaxial films of SrTiO₃ have been reported to have a figure of merit (*ZT*) of 0.28 at 873 K.¹⁰ Strategies to lower the thermal conductivity without impacting the electrical conductivity or Seebeck coefficient are often employed to improve the ZT of thermoelectrics. This is often achieved by altering the microstructure of the material and the introduction of RP faults could be a route to ZT enhancement. Developing an understanding of how growth conditions affect the thermal behavior of SrTiO₃ has general implications for other perovskite systems.

When it comes to assessing the quality of semiconductor materials, transport properties are much more sensitive than structural properties. For this reason, electrical mobility at low temperature is commonly used to assess the quality of lightly doped semiconductors^{11,12} or two-

dimensional electron gasses.¹³ Thermal conductivity, another transport property, can be a useful metric for assessing the crystalline quality of thin films, with high-quality films reproducing the thermal conductivity observed in bulk single crystals. Indeed small deviations in growth conditions have been shown to have a strong influence on the thermal conductivity of epitaxial SrTiO₃ thin films.¹⁴ Superlattices and bulk RP phases exhibit reduced thermal conductivity compared with bulk stoichiometric SrTiO₃.¹⁵ RP planar defects have been seen to significantly decrease out-of-plane film thermal conductivity when aligned perpendicular to the growth direction. The effect of laser energy on thermal conductivity in SrTiO₃ films grown by pulsed-laser deposition by varying the laser energy, which also has an effect on the resulting film composition.¹⁶ The isolated effect that the film composition alone has on the film deposition process and the creation of RP defects, which serve to greatly reduce film thermal conductivity, remains unresolved.

In order to better understand how the thermal behavior of SrTiO₃ is affected by deposition conditions, we examined the effect of growth temperature, oxidation environment, and non-stoichiometry on the thermal conductivity in homoepitaxial films deposited by reactive molecular-beam epitaxy (MBE). We observe a reduction in the film thermal conductivity of non-stoichiometric SrTiO₃ films by as much as ~80% through intentionally depositing Sr-excess $Sr_{(x+1)}TiO_3$. This reduction occurs due to the formation of Ruddlesden-Popper (RP) planar faults^{4,5,6} perpendicular to the growth direction. In this work we also observe that the intentional ordering of these RP planar faults is not critical to achieving this five-fold decrease in thermal conductivity. This implies that the fabrication of low thermal conductivity strontium excess $Sr_{(1+x)}TiO_3$ does not specifically require ordering in the material to minimize film thermal conductivity and that such films may be readily achievable by other growth techniques.

Experimental

All films were grown using a Veeco GEN 10 molecular-beam epitaxy (MBE) system dedicated to the growth of oxides in a background pressure of $\sim 1.0 \times 10^{-6}$ Torr of molecular oxygen with $\sim 10\%$ ozone or distilled ozone. Sr_(1+x)TiO₃ samples with a range of compositions were deposited on (001) SrTiO₃ substrates at growth temperatures of 500°C, 750°C, and 900°C. Films were grown to a thickness of ~ 300 nm to ensure that the thermal measurements only probed the film. An effusion cell and a Ti-ball¹⁷ were used to provide elemental flux of strontium and titanium respectively. Elemental fluxes were measured using a quartz crystal microbalance (QCM) before growth. The titanium and strontium source fluxes were $\sim 2.0 \times 10^{13}$ atoms/cm²•s. More precise flux calibration was achieved using reflection high-energy electron diffraction (RHEED) oscillations¹⁸ while tuning the strontium source temperature to more precisely match strontium flux to the titanium flux. The strontium flux was then adjusted to achieve the desired film composition while depositing both sources simultaneously. These fluxes correspond to a growth rate of ~ 7.4 Å/min.

Rutherford backscattering spectrometry (RBS) was used to determine film composition. X-ray diffraction (XRD) was performed using a high-resolution Philips X'Pert Pro MRD diffractometer with a PreFix hybrid monochromator on the incident side and triple axis/rocking curve attachment on the diffracted side. Cross-sectional bright field scanning transmission electron microscopy (BF-STEM) images were recorded on a 200 keV FEI Tecnai F20-ST scanning transmission electron microscope. Thermal conductivity was studied by time domain thermoreflectance (TDTR).

Results

Stoichiometric films regardless of growth temperature do not exhibit film peaks distinct from the substrate peak by XRD, as displayed in Fig 1(a). The films with strontium excess deposited at 900°C are shown in Fig 1(b). The off-stoichiometric films all show film peaks at lower 2θ angle than the substrate peak, indicating an apparent expansion of the out-of-plane lattice constant of the film relative to the substrate. This is commonly seen in non-stoichiometric SrTiO₃ films.^{19,20} The apparent out-of-plane lattice constant for the films was calculated from the XRD results, shown in Fig 2. A large increase in this *c*-axis lattice constant is observed for strontium rich samples.

Bright-field images of the $Sr_{1.25}TiO_3$ film deposited at 900°C, shown in fig 3(a) and (b), reveal that the film has Ruddlesden-Popper planar faults that appear to primarily lie in the plane perpendicular to film growth. This alignment and ordering tendency occurs for films deposited at the highest temperature, as evidenced by the presence of super-lattice reflections in the XRD results, displayed in Fig. 1(c). This natural ordering perpendicular to the growth direction has been seen in films deposited at high-temperature by other techniques as well.²¹ A strontium deficient sample deposited at 500°C is shown in fig 3(c) and (d). No such ordering of defects is observed for strontium deficient samples. The disordered appearance in the Bright-field image is commonly observed in strontium deficient films.^{19,22}

The relationship between growth temperature and thermal conductivity in stoichiometric SrTiO₃ films is shown in fig 4(a). Since these films appear to have the same out-of-plane lattice constant by XRD, the variation of ~1 W/m·K on film thermal conductivity in these samples is not due to an observed defect strain imparted to the film by the growth process as in Wiedigen *et al.*²³ The stoichiometric film deposited in distilled ozone at 750°C shows the highest thermal conductivity, 11.5 W/m·K at room temperature, than the samples deposited in the

less oxidizing environment of 10% ozone. Post-growth annealing in 1 atm of O_2 at 700°C for 1 hour is unable to remove the defects accumulated due to this lack of oxygen during the growth process. Growing with ~10% ozone instead of distilled ozone resulted in a ~23% reduction in thermal conductivity. Reductions as high as ~32% have been observed in reduced bulk SrTiO₃.²⁴ The dependence of thermal conductivity on film composition is displayed in fig 4(b). The thermal conductivity for the Sr_{1.25}TiO₃ film is comparable to the n=4 Ruddlesden-Popper, while also sharing a similar overall film composition.(Che-Hui's work). Films deficient in strontium show a reduction in thermal conductivity of ~30% on average when compared with stoichiometric samples, similar to other studies.¹⁶

Conclusions

Even though the films in this study were grown by MBE, the growth conditions should be adaptable to other growth methods as well since it primarily depends on the presence of excess strontium and does not rely on features unique to MBE, such as individual source shuttering. This should allow for $Sr_{(1+x)}TiO_3$ films of low thermal conductivity to be deposited by alternative deposition methods. Additional steps may also be taken to increase conductivity of these samples, such as doping with oxygen vacancies and Nb or La.

We have shown the dependence of thermal conductivity on growth temperature and oxidation environment for stoichiometric SrTiO₃ films deposited by MBE, all of which display no detectable change in film lattice constant. We also observed a significant reduction of ~80% in thermal conductivity in Sr_(1+x)TiO₃ films (x = 0.25 - 0.5) through the introduction of a significant amount of Ruddlesden-Popper planar faults. Some evidence for the ordering of these faults is seen for films deposited at 900°C, but this ordering is not necessary to achieve the reduction in thermal conductivity. These results provide a path for minimizing thermal conductivity in films of

SrTiO₃ or related compounds for applications in areas such as thermal barrier coatings and high-temperature thermoelectrics.

Acknowledgements

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Figure 4-1: X-ray diffraction data for stoichiometric $SrTiO_3$ films deposited at different temperatures in 10% ozone and at 750°C in distilled ozone in (a). X-ray diffraction for strontium excess $Sr_{(1+x)}TiO_3$ films deposited at 900°C in (b). A wider range XRD scan reveals RP phase peaks that can be indexed for $Sr_5Ti_4O_{13}$ in (c).



Figure 4-2: The apparent out-of-plane or *c*-axis lattice constant for $Sr_{(1+x)}TiO_3$ films versus Sr:Ti stoichiometry ratio as determined by x-ray diffraction.



Figure 4-3: Bright field STEM images taken at different magnifications of the $Sr_{1.25}TiO_3$ at 900°C shown in (a) and (b) and the $Sr_{0.9}TiO_3$ sample deposited at 500°C shown in (c) and (d). The excess strontium is clearly seen to form layers perpendicular to the growth direction in (b).


Figure 4-4: Thermal conductivity for the same stoichiometric $SrTiO_3$ samples as shown in Fig 1a is displayed in (a). The dependence of thermal conductivity in relation to film composition is shown in (b) with excess strontium films showing the largest decrease. (c) shows the thermal resistively versus the apparent out-of-plane lattice constant of the film. The excess strontium is clearly seen to form layers perpendicular to the growth direction in (b).

References

- ¹ R. Vaßen, X-Q. Cao, F. Tietz, D. Basu, and D. Stöver, J. Am. Ceram. Soc. **83**, 2023-2028 (2000).
- ² J. W. Fergus, J. Eur. Ceram. Soc. 32, 525-540 (2012).
- ³ A. Widenkaff, R. Robert, M. Aguirre, L. Bocher, T. Lippert, and S. Canulescu, Renew. Energ. 33, 342-347 (2008).
 - ⁴ D. Balz and K. Plieth, Z. Elektrochem., **59** [6] 545-51 (1955).
- ⁵ S. N. Ruddlesden and P. Popper, Acta Cryst. 10, 538-539 (1957).
- ⁶ S. N. Ruddlesden and P. Popper, Acta Cryst., **11** [1] 54-5 (1958).
- ⁷ R. J. D. Tilley, J. Solid State Chem., **21** [4] 293-301 (1977).
- ⁸ A. Chernatynskiy, R. W. Grimes, M. A. Zurbuchen, D. R. Clarke, and S. R. Phillpot, Appl. Phys. Lett. **95**, 161906 (2009).
- ⁹ S. Ohta, T. Nomura, H. Ohta, and K. Koumoto, J. Appl. Phys. 97, 034106 (2005).
- ¹⁰ J. Ravichandran, W. Siemons, D.-W. Oh, J. T. Kardel, A. Chari, H. Heijmerikx, M. L. Scullin, A. Majumdar, R. Ramesh, and D. G. Cahill, Phys. Rev. B 82, 165126 (2010).
- ¹¹ G. E. Stillman and C. M. Wolfe, Thin Solid Films **31**, 69-88 (1976).
- ¹² T.L. Peterson, F. Szmulowicz, and P. M. Memenger, J. Cryst. Growth 106, 16-33 (1990).
- ¹³ D. G. Schlom and L. N. Pfeiffer, Nature Materials 9 (2010) 881-883.
- ¹⁴ D-W. Oh, J. Ravichandran, C-W. Liang, W. Siemons, B. Jalan, C. M. Brooks, M. Huijben, D. G. Schlom, S. Stemmer, L. W. Martin, A. Majumdar, R. Ramesh, and D. G. Cahill, Appl. Phys. Lett. **98** 221904 (2011).
- ¹⁵ K. H. Lee, Y. F. Wang, S. W. Kim, H. Ohta, K. Koumoto, Int. J. Appl. Ceram. Technol. 4, 326-331 (2007).
- ¹⁶ E. Breckenfeld, R. Wilson, J. Karthik, A. R. Damodaran, D. G. Cahill, and L. W. Martin, Chem. Mater. 24, 331-337 (2012).
- ¹⁷ C.D. Theis and D.G. Schlom, J. Vac. Sci. Technol. A 14, (1996).
- ¹⁸ J.H. Haeni, C.D. Theis, and D.G. Schlom, J. Electroceramics 4, 385-391 (2000).
- ¹⁹ C. M. Brooks, L. Fitting Kourkoutis, T. Heeg, J. Schubert, D. A. Muller, and D. G. Schlom, Appl. Phys. Lett. **94**, 162905 (2009).
- ²⁰ B. Jalan, R. Engel-Herbert, N. J. Wright, and S. Stemmer, J. Vac. Sci. Technol. A 27, 461 (2009).
- ²¹ K. Shibuya, S. Mi, C. Jia, P. Meuffels, and R. Dittmann, Appl. Phys. Lett. 92, 241918 (2008).
- ²² T. Suzuki, Y. Nishi, and M. Fujimoto, Philos. Mag. A, **80**, 621-637 (2000).
- ²³ S. Wiedigen, T. Kramer, M. Feuchter, I. Knorr, N. Nee, J. Hoffmann, M. Kamlah, C. A. Volkert, and C. Jooss, Appl. Phys. Lett. **100**, 061904 (2012).
- ²⁴ H. Muta, K. Kurosaki, and S. Yamanaka, J. Alloys, Compd. **392**, 306 (2005).

Chapter 5

Manipulating the band gap of SrTiO₃ with epitaxial strain

(To be submitted)

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Introduction

The family of crystal structures known as perovskites is able to accommodate nearly all elements as major constituents in a dense structure with numerous phase transitions. These phase transitions often accompany the many novel properties of perovskites including pyroelectricity, piezoelectricity, ferromagnetism, multiferroicity, non-linear optical effects, and superconductivity. The archetypal perovskite, SrTiO₃, exhibits many of these useful properties when suitably doped or strained, including superconductivity,¹⁻³ a high dielectric constant up to 20,000,⁴ ferroelectricity, ⁵ the highest mobility of any oxide (>30,000 cm²/V·s),⁶ photocatalysis for water splitting,⁷⁻⁹ and transparent conductivity.¹⁰ In this work we show that the band gap of SrTiO₃ can be altered by 10% (0.3 eV) by a ferroelectric phase transition or morphed from indirect to direct band gap through an antiferrodistortive phase transition. In agreement with theory,¹¹ both of these phase transitions can be manipulated using experimentally realizable biaxial strains providing a new means to accomplish band gap engineering of SrTiO₃ which may be expanded to related perovskites. Such band gap manipulation is relevant to applications in solar cells¹²⁻¹⁴, water splitting^{7-9,12}, transparent conducting oxides¹⁰, superconductivity¹⁻³

SrTiO₃ is already a well characterized, inexpensive, and non-hazardous material that is resistant to corrosion in water and has suitable band alignments for the photocatalytic splitting of water without any applied potential, thus making it nearly ideal with the exception of the band gap magnitude. Reducing the band gap of SrTiO₃ from the bulk value of 3.2 to below 3.0 eV would allow more efficient usage of the solar spectrum. Theory predicts that it is possible to modify the band gap of SrTiO₃ using epitaxial strain by more than this amount.¹¹ Importantly, it is the raising of the valence band maximum, dominated by oxygen 2*p* states, that is required in order to optimize the band structure for hydrogen production. A change in band gap with strain

has been seen experimentally in III-V systems,^{18,19} though the magnitude of the change is relatively small, up to ~30 meV. Changes at least an order of magnitude larger would be necessary in the case of SrTiO₃ and are indeed predicted to occur with experimentally realizable biaxial epitaxial strains $\leq 4\%$. Though the band gap magnitude when biaxial strain reshapes the unit cell of (001) oriented SrTiO₃ is predicted to decrease, strained SrTiO₃ also undergoes ferroic distortions that consistently serve to increase the band gap. Only in the case where the strain is applied perpendicular to [111] are the ferroic distortions suppressed and resulting decrease in band gap predicted with applied strain.¹¹

Experimental

A set of strained SrTiO₃ films were grown on a variety of substrates by EPI 930 MBE and Veeco Gen 10 systems dedicated to the growth of oxides a temperature of 650°C in a background pressure of 5.0 × 10⁻⁷ Torr of molecular oxygen and ~10% ozone. Films of both (100) and (111) orientation were deposited on substrates that provided a range of biaxial strain states ranging from 2.9% compressive strain to 2.6% tensile strain. The thicknesses of the films varied depending on the magnitude of epitaxial strain imposed by the substrate in order to avoid relaxation in the SrTiO₃ films from 5nm in the highest strain case to 100nm for the homoepitaxial case on SrTiO₃ substrate. An effusion cell supplied the strontium while a Ti-BallTM was used as the titanium source.²⁰ Films were by deposited with a constant Sr and Ti elemental flux incident on the substrate in the presence of oxygen. Source fluxes were initially calculated by using a flux monitoring quartz crystal microbalance (QCM), and fine-tuned by optimizing the RHEED intensity oscillations during a deposition of a calibration film prior to the growth of the samples by shuttering the Sr and Ti sources and adjusting the source temperature in order to flux-match the sources. The elemental source fluxes were approximately 2×10^{13} atoms/cm² • s, corresponding to shutter times of about 30 seconds and a film growth rate of 6 Å/min. The sample growth temperature was verified by optical pyrometry. The film structure, particularly out-of-plane lattice constant, was examined by x-ray diffraction (XRD) using a high-resolution Phillips X'Pert Pro MRD diffractometer with a PreFix Hybrid Monochrometer on the incident side and Triple Axis/Rocking Curve attachment on the diffracted side. The band gap of the SrTiO₃ films was determined by spectroscopic ellipsometer.²¹

Results

The θ -2 θ x-ray diffraction results for the strained films are displayed in figure 1. Out-ofplane lattice constant is extracted from this data using a Nelson-Riley fit.²² The structural change in the measured SrTiO₃ film lattice constant in response to epitaxial strain occurs as expected and is seen to increase with applied compressive strain and decrease with tensile strain. Figure 2 is a plot of the applied biaxial epitaxial strain imposed by the substrate versus the resultant strain in the out-of-plane direction as determined from XRD. A fitting of the strain in the out-of-plane direction as a function of in-plane strain results in a poisson's ratio, *v*, of 0.236 for the SrTiO₃, in accordance with the bulk value. A relaxed film that is not commensurately strained would exhibit an out-of-plane lattice constant closer to bulk SrTiO₃ and fall near the horizontal line formed in the zero strain case, at $e_{zz} = 0$. Film rocking curve full-width at half-maximum values for the (001)-oriented films indicate that the films are of equal quality to that of the substrate used, from 10 to 200 arcseconds depending on the substrate.

Both the direct and indirect band gaps of the SrTiO₃ films were determined over a spectral range from 0.8 to 6.5 eV at 4K and room temperature. Each film was measured at

multiple angles of incidence ($\Theta_i = 55^\circ$, 70°, and 85°) to obtain spectra in (Δ , ψ). The bulk layer thickness (d_b), the surface roughness thickness (d_s), and the complex dielectric function spectra $\varepsilon = \varepsilon_I + i \varepsilon_2$ is extracted using numerical inversion and artifact minimization.²³ The dielectric function spectra ε were then fit to a parameterized model in order to track the various dielectric function parameters as a function of strain in the SrTiO₃ film due to the substrate material. (αE)² and (αE)^{1/2} are extracted from the dielectric functions obtained from the numerical inversion/artifact minimization method and are plotted versus photon energy. An example of this band gap determination is displayed in figure 3. The extracted band gap values for the strained films as a function of epitaxial strain is shown in figure 4. The film band gap values are observed to change by as much as ~10% for the films in the (100)-oriented films while the change is as large as 20% for the (111)-oriented films.

Discussion

In accordance with predictions, a larger change in band gap is observed in the strained (111) oriented films likely due to the expected suppression of ferroic distortions seen in the (001) oriented films. This band gap tuning increases the usability of SrTiO₃ in practical water splitting application by expanding the usable light wavelengths into the visible range. In addition, strain is only one of many possible mechanisms enabling band gap manipulation. The band gap modifications presented in this work are solely in response to biaxial strain, thus allowing for further adjustments to the band structure by other methods such as doping. While these results are for SrTiO₃, they also may be generally relevant to other systems and serve as a proof-of-concept that then encourages the exploration of a similar strain related effect on band structure in other perovskite oxides.

Tables

| Substrate | Orientation | Sub. Lattice | Strain state (%) | Film thick. |
|---|-------------|--------------|------------------|-------------|
| | | const. (A) | | (nm) |
| LaAlO ₃ | (001) | 3.792 | -2.9 | 5 |
| $(NdAlO_3)_{0.3}$ - $(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ | (001) | 3.843 | - 1.6 | 10 |
| NdGaO ₃ | (110) | 3.863 | - 1.0 | 20 |
| $(LaAlO_3)_{0.3}$ - $(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ | (001) | 3.869 | - 0.9 | 20 |
| SrTiO ₃ | (001) | 3.905 | - | 100 |
| DyScO ₃ | (110) | 3.949 | 1.1 | 20 |
| TbScO ₃ | (110) | 3.959 | 1.4 | 20 |
| GdScO ₃ | (110) | 3.968 | 1.6 | 10 |
| SmScO ₃ | (110) | 3.987 | 2.1 | 10 |
| TbScO ₃ | (110) | 4.008 | 2.6 | 10 |

Table 5.1: Partial list of substrates and biaxial strain states for $SrTiO_3$ films. Lattice constant is a calculated average pseudocubic lattice parameter for the orthorhombic substrates.



Figure 5-1: X-ray diffraction results for the strained SrTiO₃ films



Figure 5-2: The plot displayed in (a) is of out-of-plane strain versus in-plane strain for the (100) oriented $SrTiO_3$ films. An example rocking curve measurement for the $SrTiO_3$ film on $GdScO_3$ is shown in (b).



Figure 5-3: The spectroscopic ellipsometry data is shown for epitaxially strained SrTiO₃ films on NdScO₃ and LaAlO₃ compared with bulk in (a). An example of the band gap extraction from $(\alpha E)^2$ and $(\alpha E)^{1/2}$ for a SrTiO₃ substrate is displayed in (b).



Figure 5-4: Band gap values for the various films versus the applied epitaxial strain for both (100) and (111) oriented films.

References

- ¹ Schooley, J. F., Hosler, W. R. & Cohen M. L. Superconductivity in semiconducting SrTiO₃. *Phys. Rev. Lett.* **12**, 474-475 (1964).
- ² Takahashi, K. S. *et al.* Local switching of two-dimensional superconductivity using the ferroelectric field effect. *Nature* **441**, 195-198 (2006).
- ³ Ueno, K. *et al.* Electric-field-induced superconductivity in an insulator. *Nature Mater.* **7**, 855-858 (2008).
- ⁴ Müller, K. A. & Burkard, H. SrTiO₃: An intrinsic quantum paraelectric below 4K. *Phys. Rev. B* **19**, 3593-3602 (1979).
- ⁵ Haeni, J. H. *et al.* Room-temperature ferroelectricity in strained SrTiO₃. *Nature* **430**, 758-761 (2004).
- ⁶ Son, J. *et al.* Epitaxial SrTiO₃ films with electron mobilities exceeding 30,000 cm² V⁻¹ s⁻¹. *Nature Mater.* 9, 482-484 (2010).
- ⁷ Wrighton, M. S. *et al.* Strontium titanate photoelectrodes. Efficient photoassisted electrolysis of water at zero applied potential. *J. Am. Chem. Soc.* **98**, 2774-2779 (1976).
- ⁸ Wagner, F. T. & Somorjai, G. A. Photocatalytic hydrogen production from water on Pt-free SrTiO₃ in alkali hydroxide solutions. *Nature* 285, 559-560 (1980).
- ⁹ Carr, R. G. & Somorjai, G. A. Hydrogen production from photolysis of steam adsorbed onto platinized SrTiO₃. *Nature* **290**, 576-577 (1981).
- ¹⁰ Reagor, D. W. & Butko, V. Y. Highly conductive nanolayers on strontium titanate produced by preferential ion-beam etching. *Nature Mater.* 4, 593-596 (2005).
- ¹¹ R. F. Berger, C. J. Fennie, J. B. Neaton, *Phys. Rev. Lett.* **107**, 146804 (2011)
- ¹² Glass, A. M., von der Linde, D. & Negran, T. J. High-voltage bulk photovoltaic effect and the photorefractive process in LiNbO₃. *Appl. Phys. Lett.* **25**, 233-235 (1974).
- ¹³ Grätzel, M. Photoelectrochemical cells. *Nature* **414**, 338-344 (2001).
- ¹⁴ Choi, T., Lee, S. Choi, Y. J., Kiryukhin, V. & Cheong, S.-W. Switchable Ferroelectric Diode and Photovoltaic Effect in BiFeO₃. *Science* **324**, 63-66 (2009).
- ¹⁵ Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* **427**, 423-426 (2004).
- ¹⁶ Mannhart, J., Blank, D. H. A., Hwang, H. Y., Millis, A. J. & Triscone, J.-M. Two-dimensional electron gases at oxide interfaces. *MRS Bull.* **33**, 1027-1034 (2008).
- ¹⁷ Mannhart, J. & Schlom, D. G. Oxide interfaces—an opportunity for electronics. *Science* **327**, 1607-1611 (2010).
- ¹⁸ G. H. Olsen, C. J. Nuese, and R. T. Smith, The effect of elastic strain on energy band gap and lattice parameter in III-V compounds, J. Appl. Phys. 49, 5523 (1978).
- ¹⁹ Ishikawa, et al. Appl. Phys. Lett. **82**, 13 (2003).
- ²⁰ C. D. Theis, D. G. Schlom, J. Vac. Sci. Technol. A 14(4), (1996).
- ²¹ J. Lee, P. I. Rovira, I. An, and R. W. Collins, Rev. Sci. Instrum. **69**, 1800 (1998).
- ²² J. B. Nelson, D. P. Riley, Proc. Phys. Soc. 57, 160-177 (1945).
- ²³ G. E. Jellison, Thin Solid Films 313, 33 (1998).

Chapter 6

The adsorption controlled growth of LuFe₂O₄ by molecular-beam epitaxy

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Abstract

We report the growth of single-phase (0001)-oriented epitaxial films of the purported electronically-driven multiferroic, LuFe₂O₄, on (111) MgAl₂O₄, (111) MgO, and (0001) 6H-SiC substrates. Film stoichiometry was regulated using an adsorption-controlled growth process by depositing LuFe₂O₄ in an iron-rich environment at pressures and temperatures where excess iron desorbs from the film surface during growth. Scanning transmission electron microscopy reveals reaction-free film-substrate interfaces. The magnetization increases rapidly below 240 K, consistent with the paramagnetic-to-ferrimagnetic phase transition of bulk LuFe₂O₄. In addition to the ~0.35 eV indirect band gap, optical spectroscopy reveals a 3.4 eV direct band gap at the gamma point.

Introduction

The quest for multiferroics, materials where magnetic order and ferroelectricity coexist, has been challenging due to the frequent incompatibility of the two phenomena.^{1,2} Reports that $LuFe_2O_4$ is simultaneously ferrimagnetic and ferroelectric below 250 K, the highest temperature of any known material,³ have resulted in significant interest in $LuFe_2O_4$. Of late, however, the multiferroic status of $LuFe_2O_4$ has become controversial.⁴⁻⁷ Unlike more traditional ferroelectrics, $LuFe_2O_4$ has been reported to develop a ferroelectric polarization from the charge ordering of Fe^{2+} and Fe^{3+} ions.³ This charge ordering mechanism would make $LuFe_2O_4$ an improper ferroelectric, free of a requisite polar displacement that often precludes the presence of magnetism.² On the other hand, recent experiments have shown that such charge ordering is absent in $LuFe_2O_4$,⁴ that it is not ferroelectric,⁵ and further that the antiferromagnetic order seen in some single crystals⁶ could imply the ferrimagnetic order seen in many samples is due to non-stoichiometry.

The ability to deposit single-crystal thin films of $LuFe_2O_4$ is a key stepping stone on the path to understanding and manipulating the properties of this material, for example with strain.^{8,9} There has been some success with growing thin films of $LuFe_2O_4$ by pulsed-laser deposition (PLD),¹⁰⁻¹² though so far this achievement is limited to polycrystalline films or films with impurity phases present, particularly at the interface. In these cases, the desired $LuFe_2O_4$ phase only forms with excess iron present during growth by PLD.¹¹ Primary challenges to the growth higher quality films include the sensitivity of the growth process to substrate temperature and oxygen pressure as well as a lack of suitable substrates.

In this work we report the deposition of $LuFe_2O_4$ thin films by molecular-beam epitaxy (MBE) using an adsorption controlled growth process to control the film composition. The growth method is inspired by that used in the growth of GaAs by MBE.¹³⁻¹⁵ This

thermodynamically driven process allows the composition of GaAs to self-limit to the stoichiometric value over a limited growth temperature range despite the substrate being supplied with excess arsenic. A similar process has also been employed as a method of composition-control in MBE-grown oxide thin films of compounds such as PbTiO₃ and BiFeO₃.^{16,17} In the case of oxides, oxygen background pressure and substrate temperature are the parameters that define the growth window where stoichiometric film deposition occurs. The growth of LuFe₂O₄ is analogous to that of InFe₂O₄, which has been achieved in a similar manner at lower temperature using PLD by making use of the volatility of indium at the growth conditions.¹⁸ Here we use the volatility of iron oxides to achieve phase-pure LuFe₂O₄ by adsorption-controlled growth.

Experimental

The first step towards achieving epitaxial deposition of $LuFe_2O_4$ films was uncovering a growth window. The thermodynamic properties of individual phases in the Fe-Lu-O system were developed by means of the CALPHAD method¹⁹ and the phase diagram was calculated using Thermo-Calc²⁰ with an oxygen partial pressure of 1 atm and a molar ratio of Fe:Lu of 2. These calculations provided the temperature and pressure region where the formation of LuFe₂O₄ is favorable, shown in Fig. 1.

Finding viable substrates providing a suitable template for single-phase epitaxial films of $LuFe_2O_4$ is also critical. Of commercially available substrates, we identified (111) MgO, (111) MgAl_2O_4, and (0001) SiC as candidates for the growth of (0001) LuFe_2O_4 films. The observed epitaxial relationship between (0001) LuFe_2O_4 and the various substrates is shown in Fig. 2(b). The lattice mismatch values for LuFe_2O_4 films on MgO, MgAl_2O_4, and SiC are -15.5, -4.25, and -12.0 percent respectively.²¹

Using the phase diagram in Fig. 1 as a guide to the adsorption-controlled regime, LuFe₂O₄ films were grown using a Veeco GEN 10 molecular-beam epitaxy (MBE) system dedicated to the growth of oxides at a growth temperature of 850 ± 20 °C as measured by optical pyrometry in a background pressure of $\sim 1.0 \times 10^{-6}$ Torr of molecular oxygen. Effusion cells were used to provide elemental fluxes of lutetium and iron. Epitaxial films of LuFe₂O₄ were successfully grown on (111) MgO, (111) MgAl₂O₄, and (0001) 6H-SiC single crystal substrates. Films were typically grown to a thickness of 50 nm and prepared with thicknesses up to 75 nm for optical measurements. In order to ensure the growth of a stoichiometric film, excess iron is required during the deposition process. At a growth temperature of 850°C much of the supplied iron is evaporated as Fe_xO_y species and is not incorporated into the resulting film. Source fluxes were determined using a quartz crystal microbalance prior to growth. Film structure was monitored periodically throughout the growth by reflection high-energy electron diffraction (RHEED). The lutetium and iron source fluxes were 6.0×10^{12} atoms/(cm² s) and 2.4×10^{13} atoms/(cm^2 s) respectively, corresponding to an overall lutetium-limited growth rate of ~ 3.2 Å/min. Although the amount of iron supplied is twice that required for the $LuFe_2O_4$ structure, the excess iron is not incorporated into the film. Rutherford backscattering spectrometry (RBS) was used to verify the Lu:Fe stoichiometry of the films is indeed 1:2 and that the sticking coefficient of iron is lower at high growth temperatures in the same oxygen background pressure used for the growth of LuFe₂O₄ films.

Four-circle x-ray diffraction (XRD) was performed using a high-resolution Philips X'Pert Pro MRD diffractometer with a PreFix hybrid monochromator on the incident side and triple axis/rocking curve attachment on the diffracted side. Cross-sectional high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded on a 100 keV Nion UltraSTEM. The magnetic properties were measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer in the temperature range from 1.8 to 350 K and magnetic fields up to 70 kOe. RHEED observations provided a convenient indication of proper LuFe₂O₄ phase formation during deposition. Undesired FeO_x phases are readily seen by RHEED in the form of spot patterns while the LuFe₂O₄ phase appears as streaks, indicating a smooth film surface. Since the film oxygen stoichiometry is difficult to quantify, the films may be oxygen deficient, which could affect properties as in the case with YFe₂O₄.²³

Results

The layered LuFe₂O₄ film structure was confirmed by XRD, displayed in Fig. 2, showing that the LuFe₂O₄ films are (0001) oriented and single phase. Despite excess iron being supplied during growth, no iron-rich phases are observed in the films when deposited at 850°C. Some of this excess iron has been observed by RBS to diffuse into the MgAl₂O₄ and MgO substrates. The LuFe₂O₄ film lattice constants and rocking curve results are reported in Table I. The epitaxial orientation relationships between the film and substrate were verified by f-scan of the 1014 LuFe₂O₄ film peak; the [100] LuFe₂O₄ was found to be parallel to [110] MgO, [211] MgAl₂O₄, [100] 6H-SiC.

Figure 3 shows the STEM images of the interface between the LuFe₂O₄ film and the MgAl₂O₄ substrate viewed down the [100] zone axis of the LuFe₂O₄ film. Notably, the film is single-phase and free of FeO_x impurity phases at the interface. Figure 3(b) shows a high-resolution image of the film, demonstrating the clear repetition of bright LuO_{1.5} layers (called U layers²⁴) with the darker Fe₂O_{2.5} layers (referred to as W layers²⁴), each of which contains two atomically resolved Fe-O planes.

Magnetization as a function of temperature, displayed in Fig. 4(a), shows that the samples exhibit a singular rapid increase in magnetization below 240 K that is consistent with the bulk paramagnetic to ferrimagnetic phase transition of $LuFe_2O_4$.²⁵ The samples also display hysteretic

behavior with magnetic field, as shown in Fig. 4(b). At 70 kOe, a magnetic moment of about 0.8, 0.3, and 0.1 μ_B per Fe is induced in the films on SiC, MgAl₂O₄, and MgO, respectively. The reduced magnetization in the LuFe₂O₄ film on MgAl₂O₄ and MgO compared to the film on SiC may be due to diffusion of Mg from the substrate into the film since Mg doping has been reported to have this effect.²⁶ The saturation magnetization in our films is lower than the reported bulk value of ~1.4 μ_B /Fe at 145 kOe.²⁷ While this difference in magnetic moment may be due to the strong dependence on field cooling observed in bulk LuFe₂O₄, other factors relating to the deposition process, such as the creation of oxygen vacancies, might be partially responsible. In addition, the samples do not exhibit superparamagnetism, which has been observed in films containing hexagonal LuFeO₃ impurities.¹²

Figure 5 displays the *ab*-plane optical response of LuFe₂O₄ in epitaxial thin film form on MgAl₂O₄ compared with bulk single crystal data.²⁸ Comparison with first principles calculations allows us to assign the observed excitations.²⁹ The band centered at ~4 eV and the rising higher energy absorption can be assigned as a combination of O $p \rightarrow$ Fe d and O $p \rightarrow$ Lu s charge transfer excitations. A plot of $(\alpha \cdot E)^2$ vs. energy places the direct band gap at ~3.4 eV. While the film is not fully commensurate, the average in-plane lattice constant of the film on MgAl₂O₄ from XRD is 3.42±0.02 Å, which is 0.6% smaller than the bulk value of 3.44 Å. This compressive strain blue-shifts the direct charge gap and the band maximum compared to similar structures in the single crystal. BiFeO₃ displays similar behavior.³⁰ Previous measurements on single crystalline LuFe₂O₄ also identified an indirect band gap at ~0.35 eV, a feature that is defined by the leading edge of the Fe²⁺ \rightarrow Fe³⁺ charge transfer excitations that occur in the W layer (the iron oxide double layer).²⁸ The film shows a similar, but somewhat leakier tendency in the ($\alpha \cdot E$)^{0.5} vs. energy plot, although due to limited optical density, our uncertainties are larger. Similar measurements on a film on SiC are less interpretable due to the 3.05 eV band gap of the substrate.

Conclusions

In summary we have identified a reliable method for depositing single-phase epitaxial $LuFe_2O_4$ films. This ability, combined with the knowledge that the charge-order transition temperature of $LuFe_2O_4$ is sensitive to pressure³¹ invites the use of thin film methods, e.g., strain or dimensional confinement through heterostructuring, to modify the structure and properties of this controversial multiferroic.

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Tables

Table 6.1: $LuFe_2O_4$ film lattice parameters and rocking curve full width at half maximum values determined from XRD data.

| Substrate | LuFe ₂ O ₄ film <i>c</i> -axis (Å) | LuFe ₂ O ₄ film <i>a</i> -axis (Å) | Rocking curve (°) |
|--|--|--|-------------------|
| (111) MgO | 25.42 ± 0.01 | 3.40 ± 0.02 | 1.13° |
| (111) MgAl ₂ O ₄ | 25.28 ± 0.01 | 3.42 ± 0.02 | 0.76° |
| (0001) 6H-SiC | 25.19 ± 0.01 | 3.44 ± 0.02 | 0.64° |

Figures



Figure 6-1: Arrhenius plot of oxygen partial pressure showing where $LuFe_2O_4$ is thermodynamically stable.



Figure 6-2: (a) Substrate model for MgO with the (111) growth plane highlighted. (b) The epitaxial orientation relationship of a LuFe₂O₄ lattice on (111) MgO, (111) MgAl₂O₄, and (0001) 6H-SiC lattices (see Ref. 21). (c) A model showing the alternating single layers of lutetium oxide (U layers) and double layers of iron oxide (W layers) in LuFe₂O₄. (d) θ -2 θ x-ray diffraction scans for three 50 nm thick LuFe₂O₄ films grown on (111) MgAl₂O₄, (111) MgO, and (0001) 6H-SiC. Asterisks (*) indicate XRD peaks from the substrates.



Figure 6-3: HAADF-STEM images of the same $LuFe_2O_4$ on $MgAlO_4$ film studied in Fig. 2(d) showing (a) the presence of a clean interface and (b) the well-ordered structure of $LuO_{1.5}$ U layers alternating with $Fe_2O_{2.5}$ W layers.



Figure 6-4: The magnetization as a function of temperature and magnetic field of the same $LuFe_2O_4$ films as in Fig. 2(d).



Figure 6-5: Optical response of a 75 nm thick (0001) $LuFe_2O_4$ film grown on (111) MgAl₂O₄ along with the *ab*-plane response of a $LuFe_2O_4$ single crystal²⁸ at 300 K. The film absorption was determined by a combination of direct calculation of absorption from transmittance (below ~ 3 eV) and a Glover-Tinkham analysis of both transmittance and reflectance to obtain absorption above 3 eV. The data were merged between 2.5 and 3 eV, where there was substantial overlap. The inset shows the indirect and direct band gap analysis.

References

- ¹ N. A. Hill, J. Phys. Chem. B **104**, 6694-6709 (2000).
- ² S.-W. Cheong and M. Mostovoy, Nat. Mater. **6**, 13-20 (2007).
- ³ N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, and H. Kito, Nature **436**, 1136-1138 (2005).
- ⁴ J. de Groot, T. Mueller, R. A. Rosenberg, D. J. Keavney, Z. Islam, J.-W. Kim, and M. Angst, Phys. Rev. Lett. **108**, 187601 (2012).
- ⁵ A. Ruff, S. Krohns, F. Schrettle, V. Tsurkan, P. Lunkenheimer, and A. Loidl, "Absence of Polar Order in LuFe₂O₄," arXiv:1204.1244v1 (2012).
- ⁶ J. de Groot, K. Marty, M. D. Lumsden, A. D. Christianson, S. E. Nagler, S. Adiga, W. J. H. Borghols, K. Schmalzl, Z. Yamani, S. R. Bland, R. de Souza, U. Staub, W. Schweika, Y. Su, and M. Angst, Phys. Rev. Lett. **108**, 037206 (2012).
- ⁷ X. S. Xu, J. de Groot, Q.-C. Sun, B. C. Sales, D. Mandrus, M. Angst, A. P. Litvinchuk, and J. L. Musfeldt, Phys. Rev. B **82**, 014304 (2010).
- ⁸ J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature **430**, 758-761 (2004).
- ⁹ K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005-1009 (2004).
- ¹⁰ R. Rejman, T. Dhakal, P. Mukherjee, S. Hariharan, and S. Witanachchi, *in: Multiferroic and Ferroelectric Materials, Mater. Res. Soc. Symp. Proc.*, Vol. 1199 (Materials Research Society, Pittsburgh, 2010) F03-22.
- ¹¹ J. Liu, Y. Wang, and J. Y. Dai, Thin Solid Films **518**, 6909-6914 (2010).
- ¹² W. Wang, Z. Gai, M. Chi, J. D. Fowlkes, J. Yi, L. Zhu, X. Cheng, D. J. Keavney, P. C. Snijders, T. Z. Ward, J. Shen, and X. Xu, Phys. Rev. B 85, 155411 (2012).
- ¹³ J. R. Arthur, J. Appl. Phys. **39**, 4032 (1968).
- ¹⁴ A. Y. Cho, J. Appl. Phys. **41**, 2780 (1970).
- ¹⁵ A. Y. Cho, J. Appl. Phys. **42**, 2074 (1971).
- ¹⁶ C. Theis and D. G Schlom, Thin Solid Films **325**, 107-114 (1998).
- ¹⁷ J. F. Ihlefeld, A. Kumar, V. Gopalan, D. G. Schlom, Y. B. Chen, X. Q. Pan, T. Heeg, J. Schubert, X. Ke, P. Schiffer, J. Orenstein, L. W. Martin, Y. H. Chu, and R. Ramesh, Appl. Phys. Lett. **91**, 071922 (2007).
- ¹⁸ M. Seki, T. Konya, K. Inaba, and H. Tabata, Appl. Phys. Expr. **3**, 105801 (2010).
- ¹⁹ Z. K. Liu, J. Phase Equilib. Diffus. **30**, 517-534 (2009).

- ²⁰ J. O. Andersson, T. Helander, L. Hoglund, P. Shi, and B. Sundman, CALPHAD 26, 273-312 (2002).
- ²¹ These mismatch values correspond to the observed epitaxial orientation relationship for these systems (described in Fig. 2), where we have assumed near-coincident site lattices (NCLS) with σ -boundary ratios at the interfaces of $\sigma_{Mg0}1: \sigma_{LuFe_2O_4}1, \sigma_{MgAl_2O_4}1: \sigma_{LuFe_2O_4}3$, and

 $\sigma_{SC} 1$: $\sigma_{LuFe_2O_4} 1$. The areas of the NCSL unit cells for these cases are 0.077 nm², 0.283 nm², and 0.081 nm², respectively. For additional information on NCSL see Ref. 22.

- ²² R. W. Balluffi, A. Brokman, and A. H. King, Acta Metall. **30**, 1453-1470 (1982).
- ²³ M. Inazumi, Y. Nakagawa, M. Tanaka, N. Kimizuka, and K. Siratori, J. Phys. Soc. Jpn. 50, 438-444 (1981).
- ²⁴ T. Sugihara, K. Siratori, N. Kimizuka, J. Iida, H. Hiroyoshi, and Y. Nakagawa, J. Phys. Soc. Jpn. 54, 1139-1145 (1985).
- ²⁵ J. Wen, G. Xu, G. Gu, and S. M. Shapiro, Phys. Rev. B **80**, 020403(R) (2009).
- ²⁶ Y. B. Qin, H. X. Yang, Y. Zhang, H. F. Tian, C. Ma, Y. G. Zhao, R. I. Walton, and J. Q. Li, J. Phys. Condens. Matter **21**, 015401 (2009).
- ²⁷ J. Iida, M. Tanaka, Y. Nakagawa, S. Funahashi, N. Kimizuka, and S. Takekawa, J. Phys. Soc. Jpn. 62, 1723-1735 (1993).
- ²⁸ X. S. Xu, M. Angst, T. V. Brinzari, R. P. Herman, J. L. Musfeldt, A. D. Christianson, D. Mandrus, B. C. Sales, S. McGill, J.-W. Kim, and Z. Islam, Phys. Rev. Lett. **101**, 227602 (2008).
- ²⁹ H. J. Xiang and M.-H. Whangbo, Phys. Rev. Lett. **98**, 246403 (2007).
- ³⁰ P. Chen, N. J. Podraza, X. S. Xu, A. Melville, E. Vlahos, V. Gopalan, R. Ramesh, D. G. Schlom, and J. L. Musfeldt, Appl. Phys. Lett. **96**, 131907 (2010).
- ³¹ X. Shen, C. H. Xu, C. H. Li, Y. Zhang, Q. Zhao, H. X. Yang, Y. Sun, J. Q. Li, C. Q. Jin, and R. C. Yu, Appl. Phys. Lett. **96**, 102909 (2010).

Chapter 7

Conclusions

This section provides a summary of the results of this dissertation along with suggestions for future directions for the different aspects of this research.

7.1 Summary

The film growth process of depositing an oxide thin film can have a pronounced effect on the resulting properties. Many growth methods involve high-energy kinetics that cause film properties to be significantly different than those observed in bulk. The experiments on homoepitaxial SrTiO₃ examined how structure changed in response to changes in film nonstoichiometry.

While it is meaningful to be able to understand how to reproduce bulk properties, as in the case of homoepitaxial $SrTiO_3$, in many cases it is useful to use defects introduced during growth in order to achieve a desired property. This is exemplified in the case where depositing $Sr_{(1+x)}TiO_3$ excess SrO results in an 80% decrease in film thermal conductivity. These results with the $SrTiO_3$ system are applicable to other perovskite systems that can form Ruddlesden-Popper planar faults. It is possible to use these results have general implications for other thin-film deposition methods.

Experimental evidence of a significant change (>10%) in the band gap of $SrTiO_3$ from epitaxial strain for both (100) and (111) oriented $SrTiO_3$ films provides an additional control mechanism for band gap engineering. Band gap manipulation is useful for water-splitting applications and results that show a change in band gap of ~10% in $SrTiO_3$ with strain has implications for other oxide systems as well. This thesis presented the first results of phase-pure thin films of $LuFe_2O_4$ and should assist in achieving a better understanding of the charge ordering and magnetic behavior in $LuFe_2O_4$. The ability to deposit thin films of $LuFe_2O_4$ and hexagonal $LuFeO_3$ also allow these materials to be strained or modified in other ways unique to thin films.

7.2 Future Work

The work contained within this thesis has numerous possible future directions available. These many options branch into two main categories: basic research on growth influence in other material systems as a comparison or further application specific development. The following list covers possible directions for future research for each major component in this thesis.

- 1. Growth studies on SrTiO₃
 - Exploration into how the homoepitaxial depositions of other oxides behave and accommodate defects introduced by the growth process. This could be done for other technologically interesting perovskite oxides or systems with other crystal structures as long as bulk single-crystal substrates are available.
 - Enhancing the ability of large-area or lower-cost deposition methods to get closer to achieving the quality seen in films deposited by molecular-beam epitaxy.
- 2. Thermal conductivity in SrTiO₃
 - Exploration of how the thermal conductivity in other material systems layer similar to SrTiO₃. These could include CaTiO₃ and BaTiO₃. Solid solutions of (Ca, Sr, Ba)TiO₃ could also provide an additional tuning knob for thermal behavior.
 - Development and testing of an actual thermal barrier coating by deposition methods ideally suited for such applications making use of excess strontium to form Ruddlesden-Popper defects to achieve a coating with low thermal conductivity.
 - Testing of a possible thermoelectric device setup using *n*-type $Sr_{(1+x)}TiO_3$ by introducing oxygen vacancies combined with layered Ruddlesden-Popper defects to reduce thermal conductivity on a conducting substrate, possibly silicon.

- 3. SrTiO₃ band gap manipulation
 - Explore how the biaxial epitaxial strain modifies the band gap in other oxide systems. This direction would combine well with theoretical predictions.
 - Test strained SrTiO₃ films for photocatalysis applications by measuring hydrogen production on exposure to a range of illumination conditions.
- 4. Growing LuFe₂O₄
 - Adsorption controlled growth of LuFe₂O₄ is possible due to evaporation of iron oxide. The ability to deposit other iron containing oxide systems may be achievable by a similar mechanism.
 - Since a possible defect seen in LuFe₂O₄ films is a missing layer of iron, which if grown continuously is hexagonal LuFeO₃, it may be possible to achieve films that combine the two phases in a supper-lattice that has tunable magnetic and ferroelectric properties based on the layering frequency.

It has been proposed that the development of oxides may follow a similar path set by semiconductors, with ZnO and SrTiO₃ being analogous to Si and GaAs.¹ If oxides manage to achieve even a fraction of the historical impact on society that semiconductors have then there is a bright future for oxides indeed.

References

¹ Y. Tokura and H. Y. Hwang, Nat. Mater. 7, 694 (2008).

Appendix

Additional Techniques

This section provides an overview of the primary characterization techniques used for this thesis work. These include Rutherford backscattering spectrometry (RBS), Time-domain thermoreflectance (TDTR), spectroscopic ellipsometry, and magnetic measurements by superconducting quantum interference device (SQUID).

A1.1 Rutherford backscattering (RBS)

Rutherford backscattering spectrometry (RBS) can be used to determine the composition of thin films by measuring the backscattered high-energy ions from a sample. Typically the ion source is alpha particles. The energy loss of the backscattered ion depends on the cross-section of the sample nuclei, which is related to mass and atomic number, and a gradual loss due to interactions with electron density, which is related to the distance traveled in the sample by the ions. So RBS is able to provide elemental composition information throughout the sample thickness. A sample RBS spectra is shown for multiple $SrTiO_3$ films from Chapter 3 of different compositions in Fig A-1. For homoepitaxial films the uncertainty in the compositional measurement is quite large (~ 5%).



Figure A-1: RBS spectra for off-stoichiometric SrTiO₃ films on SrTiO₃ substrate.

A1.2 Time-doamin thermoreflectance (TDTR)

Measuring the thermal conductivity of a thin film can be done using Time-domain thermoreflectance (TDTR), which is a pump-probe optical technique making use of two coaligned laser beams. For this technique, a laser beam operating at a specified frequency, typically around 10MHz, locally heats the sample surface while the surface temperatures are measured by the change in reflected intensity of a probe laser beam by the piezo-optic effect. Each layer can be modeled by the following parameters: thermal conductivity Λ_n , thermal diffusivity D_n , and layer thickness L_n .¹



Figure A-2: Time-domain thermoreflectance (TDTR) setup.²

A1.3 Spectroscopic Ellipsometry (SE)

Spectroscopic ellipsometry is an optical technique that is sensitive to thin films and can be used to determine layer thickness, surface or interface roughness, and optical constants. The change in polarization of light as it is reflected off the surface of a sample is measured. It is most useful when examining a sample that is homogeneous with well-defined layering. The two parameters measured, $Psi(\Psi)$ and $Delta(\Delta)$, are related to the in-plane-of-incidence (r_p) and outof-plane-of-incidence (r_s) reflection coefficients by: ³

$$Tan(\Psi)e^{i\Delta} = \rho = \frac{r_p}{r_s}$$

A diagram showing the measurement geometry is shown in figure A-3.



Figure A-3: Diagram of an ellipsometry setup.³

For spectroscopic ellipsometry, which uses white light, the band gap extraction is based on the absorption coefficient.

The direct gap is related to the light frequency by the following equation:

$$\alpha \propto A^* \sqrt{hv - E_{\rm g}}$$

The indirect gap is related to the light frequency by the following equation:

$$\alpha \propto \frac{\left(hv - E_{\rm g} + E_{\rm p}\right)^2}{\exp\left(\frac{E_{\rm p}}{kT}\right) - 1} + \frac{\left(hv - E_{\rm g} - E_{\rm p}\right)^2}{1 - \exp\left(-\frac{E_{\rm p}}{kT}\right)}$$

a: absorption coefficient *h*: Plank's constant *v*: light frequency E_g: band gap energy E_p: phonon energy *k*: Boltzman's constant T: temperature

A1.4 SQUID

A superconducting quantum interference device (SQUID) is a highly sensitive magnetometer used to measure minute magnetic fields, such as those present in thin film samples. The use of superconducting Josephson junctions enables the detection of fields below 10⁻¹⁰ G. SQUID measurement can be very used to determine magnetic transition temperatures in very thin films. While the measurement component used in a SQUID can be very small, typically the entire apparatus is quite large for insulation purposes since the superconducting material requires low temperatures to function, achieved through use of liquid helium. A basic diagram of SQUID device is shown in figure A-4.



Figure A-4: The components that make up a SQUID magnetometer.⁴

References

¹ D. G. Cahill, Rev. Sci. Instrum. **75**, 5119-5122 (2004).

⁴ J. E. Lenz, P. IEEE **78**, 973-989 (1999).

² D. G. Cahill, W. K. Ford, K. E. Goodson, G. D. Mahan, A. Majumdar, H. J. Maris, R. Merlin, and S. R. Phillpot, J. Appl. Phys. **93**, 793-818 (2003).

³ J. A. Woollam, B. Johs, C. M. Herzinger, J. Hilfiker, R. Synowicki, and C. L. Bungay, Proc. SPIE **72**, 29 (1999).
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J. A. Mundy, Q. Mao, C. M. Brooks, D. G. Schlom, D. A. Muller, "Atomic-resolution chemical imaging of oxygen local bonding environments by electron energy loss spectroscopy", Appl. Phys. Lett. **101**, 42907 (2012).

H. W. Jang, A. Kumar, S. Denev, M. D. Biegalski, P. Maksymovych, C. W. Bark, C. T. Nelson, C. M. Folkman, S. H. Baek, N. Balke, C. M. Brooks, D. A. Tenne, D. G. Schlom, L. Q. Chen, X. Q. Pan, S. V. Kalinin, V. Gopalan, and C. B. Eom, "Ferroelectricity in strain-free SrTiO₃ thin films," Phys. Rev. Lett. **104**, 197601 (2010)

D. Nuzhnyy, J. Petzelt, S. Kamba, P. Kuzel, C. Kadlec, V. Bovtun, M. Kempa, J. Schubert, C. M. Brooks, and D. G. Schlom, "Soft mode behavior in SrTiO₃/DyScO₃ thin films: Evidence of ferroelectric and antiferrodistortive phase transitions" Appl. Phys. Lett. **95**, 232902 (2009).

C. M. Brooks, L. Fitting Kourkoutis, T. Heeg, J. Schubert, D.A. Muller, and D.G. Schlom, "Growth of homoepitaxial SrTiO₃ thin films by molecular-beam epitaxy," Appl. Phys. Lett. **94**, 162905 (2009).

J. Zhang, S. Walsh, C. Brooks, D. G. Schlom, and L. J. Brillson, "Depth-resolved cathodoluminescence spectroscopy study of defects in SrTiO₃," J. Vac. Sci. Technol. B **26**, 1466 (2008).

A. Tselev, C. M. Brooks, S. M. Anlage, H. Zheng, L. Salamanca-Riba, R. Ramesh, and M. A. Subramanian, "Evidence for power-law frequency dependence of intrinsic dielectric response in the $CaCu_3Ti_4O_{12}$," Phys. Rev. B **70**, 144101 (2004).