NANOENGINEERING OF RUDDLESDEN-POPPER PHASES USING MOLECULAR BEAM EPITAXY

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by
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Abstract

Epitaxial films including superlattices of the $A_{n+1}B_nO_{3n+1}$ Ruddlesden-Popper homologous series with $A = \text{Sr}$ and $\text{Ba}$ and $B = \text{Ti}$ and $\text{Ru}$ have been grown by reactive molecular beam epitaxy (MBE) on $(\text{LaAlO}_3)_{0.3}(\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$ (LSAT), $\text{SrTiO}_3$, $\text{DyScO}_3$ and Si substrates. The strict composition control necessary for the synthesis of these phases was achieved through the use of reflection high-energy electron diffraction (RHEED) intensity oscillations. By monitoring changes in the RHEED intensity oscillations as appropriate doses of elemental beams of these constituents are sequentially deposited to grow monolayers of $AO$ and $BO_2$, the $\text{Sr:Ti}$, $\text{Ba:Ti}$ or $\text{Sr:Ru}$ ratio can be adjusted to within 1% of stoichiometry. Furthermore, the presence of a beat frequency in the intensity oscillation envelope allows the adjustment of the $A$ and $B$ elemental fluxes so that a complete $AO$ or $BO_2$ monolayer is obtained with each shuttered dose of the $A$ or $B$ elemental constituent in a continuous flux of oxygen or ozone.

Epitaxial $\text{SrTiO}_3$ thin films grown on $\text{DyScO}_3$ and LSAT substrates show dramatically different dielectric properties, as measured with interdigitated electrodes. On $\text{DyScO}_3$, $\text{SrTiO}_3$ is under biaxial tensile strain, while on LSAT it is strained in biaxial compression in the plane of the substrate / film interface. The film under biaxial tensile strain shows significant room temperature tunability and a sharp Curie-Weiss peak at 293 K. Under biaxial compressive strain, the $\text{SrTiO}_3$ exhibits negligible room temperature tunability. The figure of merit for the $\text{SrTiO}_3$ / $\text{DyScO}_3$ films make them well suited for application to room temperature microwave devices.

Epitaxial $\text{SrTiO}_3$ / $\text{BaTiO}_3$ short period superlattices were grown with codeposition and sequential deposition of the $A = \text{Sr,Ba}$ and $B = \text{Ti}$ elemental fluxes. The structure and microstructure of the films were investigated by x-ray diffraction,
transmission electron microbeam diffraction, and high-resolution transmission electron microscopy (HRTEM) in combination with computer image simulations. Both diffraction and HRTEM studies revealed that the superlattices have nearly atomically-abrupt interfaces that are maintained even after annealing to high temperature. In addition, cross-sectional TEM reveals that all superlattice periods grown are coherently strained to the underlying (001) SrTiO$_3$ and (001) LSAT substrates.

The first five members of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ and the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series, i.e., Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$, Sr$_4$Ti$_3$O$_{10}$, Sr$_5$Ti$_4$O$_{13}$, and Sr$_6$Ti$_5$O$_{16}$, and Sr$_2$RuO$_4$, Sr$_3$Ru$_2$O$_7$, Sr$_4$Ru$_3$O$_{10}$, Sr$_5$Ru$_4$O$_{13}$, and Sr$_6$Ru$_5$O$_{16}$, respectively, were grown with layer-by-layer deposition. X-ray diffraction and HRTEM images confirm that these films are epitaxially oriented and nearly free of intergrowths. Dielectric measurements indicate that the dielectric constant tensor coefficient $\varepsilon_{33}$ of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ series increases from a minimum of 44±4 in the $n = 1$ (Sr$_2$TiO$_4$) film to a maximum of 263±2 in the $n = \infty$ (SrTiO$_3$) film.

Sr$_2$TiO$_4$ / SrTiO$_3$ heterostructures have been investigated as a possible candidate system for the formation of a two-dimensional electron gas in oxides. X-ray photoelectron spectroscopy was used to measure the valence band offset between Sr$_2$TiO$_4$ and SrTiO$_3$. In addition, powder reflectance was used to measure the bandgap of Sr$_2$TiO$_4$. These measurements indicate a type II interface between the two materials, with a valence band offset of -0.40 ± 0.02 eV, and a conduction band offset of -0.2 ± 0.02 eV, suggesting that appropriately doped heterostructures of these compounds may result in the formation of an accumulation layer at the interface of the materials.

Epitaxial SrRuO$_3$ layers were grown on Si (100) on which a thin epitaxial (Ba,Sr)O/SrSi$_2$ buffer layer was first grown. Vertical transport measurements show that
the SrRuO$_3$ forms a conductive contact with the silicon substrate, although cross-section TEM indicates there is a thin, amorphous interfacial Sr-Si-O layer at the substrate / film interface. This metallic perovskite SrRuO$_3$ film was used as a template for the subsequent growth of an epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_3$ / PbZr$_{0.6}$Ti$_{0.4}$O$_3$ / La$_{0.5}$Sr$_{0.5}$CoO$_3$ stack. Through epitaxy, this ferroelectric stack was oriented in a direction maximizing its remanent polarization. It also exhibited excellent fatigue-free ferroelectric properties up to $10^{10}$ cycles.
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FIG. 9.3. Measurement of the three independent dielectric tensor coefficients for DyScO$_3$ allows the full tensor to be calculated. (a) Three-dimensional representation of the dielectric constant of DyScO$_3$ (b) dielectric constant in the $a$-$b$ plane (c) dielectric constant in the $a$-$c$ plane (d) dielectric constant in the $b$-$c$ plane.

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The number of coauthors on the papers in this thesis is indicative of the number of collaborators who directly contributed to my thesis work. In particular, I would like to thank Mari-anne Rosario, Beth Hutchinson, Ling Zou, and Ying Liu for their assistance with all transport measurements on my films. The beautiful TEM work of Wei Tian and X. Pan have added a powerful visual impact to our results.

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1.0 Introduction

Since the discovery that copper and tin could be combined to make a hardened alloy known as bronze by solid state synthesis\(^1\) researchers have realized the potential benefit of artificially engineered materials. Recently, a wide range of technologies have been developed with the goal of fabricating materials that are difficult to make with conventional synthesis techniques. These are capable of fabricating materials under extreme conditions or even engineering materials at the atomic level. While these technologies are applicable to a variety of different crystal systems, oxide materials are particularly interesting based on their broad range of physical and electrical properties. Oxides exhibit a tremendous range of functionality including superconductivity, ferroelectricity, and magnetic ordering making them exciting for both fundamental studies and for application in a variety of electronic devices.

The search for new materials has led many researchers to explore the growth of compounds that do not appear on an equilibrium phase diagram, but are theoretically predicted to exist. The discovery of high temperature superconductivity in layered oxides that belong to a class of materials known as perovskites\(^2\) resulted in an explosion of research investigating the growth of metastable layered oxide structures. Tremendous success was achieved in the growth of these compounds and in the realization of improved electronic properties. Recently, the growth of metastable layered perovskites exhibiting other functional properties, such as ferroelectricity, magnetism, and non-conventional transport phenomena, has also been explored. Several techniques have been employed for the growth of these compounds, including solid state reactions under
extreme ambients, soft chemical reactions, and a variety of thin film deposition techniques.

There are two strong driving forces for the growth of these oxides in an epitaxial, thin film form. First, because these compounds are highly layered structures, their intrinsic properties often vary dramatically in different crystallographic directions. Controlling the orientation of these materials, through epitaxial growth, allows these anisotropic properties to be studied and fully utilized. In addition, the functional properties of these compounds are applicable to a variety of microelectronic devices. The processing, design, and size of many device architectures requires integration of materials in thin film form.

This thesis focuses on the use of a thin film deposition technique, known as molecular beam epitaxy, for the growth of a family of perovskite compounds. The two main objectives that motivate this research are 1) to grow thin films of materials previously only grown in single crystalline or polycrystalline form; and 2) to engineer new compounds of materials which are thought to possess promising properties but which have not be grown by solid state or single crystal growth techniques. Achieving the epitaxial thin film growth of these compounds should help to facilitate the understanding of their fundamental properties and enable their utilization in microelectronic devices, while the growth of new compounds could lead to the discovery of materials with unique, novel, or improved properties.

Specifically, this work focuses on the growth of a family of oxides crystals, known as the $(\text{Sr, Ba})_{n+1}(\text{Ti, Ru})_n\text{O}_{3n+1}$ Ruddlesden-Popper Homologous Series. While these compounds all contain a nearly identical crystal structure, their fundamental
properties vary dramatically. By changing the composition of a single layer, or by modifying the layering sequence, they can switch from insulators to metals, diamagnets to ferromagnets, or linear dielectrics to ferroelectrics. While the crystal chemistry of these compounds suggests that an infinite number of layering sequences should theoretically exist, the energetics and thermodynamics of the system have thus far allowed just of few of these compounds to be grown and studied. The growth of new members of this crystal family, or the combination of existing members in a unique order, is an obvious step in the search for new materials with unique or functional properties.

Because the different members of this series of compounds contain different layering sequences along certain crystallographic directions, a growth technique capable of delivering elements in a layer-by-layer fashion is ideal for their growth. Molecular beam epitaxy is one of the few thin film deposition techniques that offers such capabilities, and it has been used for the growth of all films described in this thesis. By supplying the constituent elements in a sequential order, the desired phase can be built one atomic layer at a time. The layering sequence used during growth provides the driving force for the formation of the desired phase which is often metastable, where an overall thermodynamic driving force is no longer available.

While the range of properties in oxides give them the potential to reach or surpass the functionality possessed by conventional semiconductors, commercial utilization of this functionality depends on their ability to be integrated with standard silicon integrated circuit technology. In essence, this means: can these oxides be grown on silicon in a way that preserves their intrinsic properties and facilitates the design and realization of an integrated circuit? This question is also explored in this thesis; with the atomic scale
layering capabilities of molecular beam epitaxy an essential element for the integration of crystalline oxide materials on silicon substrates.

This hybridization of a study of the fundamental physics and materials science of these materials and concern for issues involving their commercial application presented in this thesis, aptly reflects the current state of oxide materials research. Progress on both of these fronts should lead to the better understanding and utilization of an exciting class of oxide materials.
REFERENCES

1. Sometime before 3000 B.C.
2.1 Molecular Beam Epitaxy

The desire to engineer materials at increasingly smaller levels has led to the development of several thin film growth techniques capable of controlling the deposition of materials on an atomic scale. Molecular beam epitaxy (MBE) is a thin film growth technique relying on the evaporation of elements from individual sources in a high vacuum environment. Its unique layering capabilities, capable of depositing monolayer doses of several different elements in rapid succession, are difficult to reproduce with other thin film deposition techniques such as sputtering, pulsed laser deposition (PLD), or chemical vapor deposition, and have made it the technique of choice for the deposition of complex heterostructures in a variety of crystal systems.\textsuperscript{1-3} In addition, unlike traditional single source sputtering and laser ablation, MBE does not require the fabrication of a target of the desired compound, instead relying on evaporation from elemental source materials. This allows the growth of many metastable compounds and structures that cannot be realized by bulk synthesis techniques.

MBE has been successfully used for years for the deposition of a variety of conventional semiconducting materials and devices.\textsuperscript{4} In particular, MBE is the primary tool used for the deposition of III-V semiconductors, such as GaAs and InP, employed in a variety of optoelectronic devices. Growth techniques utilizing the volatility of the group V elements (e.g. As and P) have been a key enabler of the stoichiometric growth of these compounds\textsuperscript{4} but have limited the development of composition control technologies. In general, ion gauges, mass spectrometers, and reflection high energy electron diffraction (RHEED) are the common flux calibration tools utilized in III-V MBE machines.
Oxide MBE is a relatively new field in comparison, initially used for the growth of layered perovskite superconductors\textsuperscript{5,6} after the discovery of high temperature superconductivity in oxides.\textsuperscript{7} The growth of multicomponent oxides by MBE offered many unique challenges, with hardware compatibility in an oxidizing environment and composition control of the constituent elements a primary limitation. While some multicomponent oxides are suitable for absorption controlled growth,\textsuperscript{8-11} many contain two or more elements with little or no volatility, requiring precise flux control to ensure the stoichiometric deposition of the desired phase. The demands of oxide MBE have led to the development of several real time \textit{in situ} composition control techniques\textsuperscript{12} including conventional and laser atomic absorption spectroscopy,\textsuperscript{13,15-17} quartz crystal microbalances, and RHEED. Currently, composition control continues to be one of the primary limitations in the growth of complex oxide heterostructures and high quality multicomponent oxides compounds by MBE.

\subsection{2.2 Reflection-High Energy Electron Diffraction}

RHEED is one of the most common real time, \textit{in situ} analysis techniques utilized during MBE growth. Typical RHEED geometry involves a beam of high energy (10-30 KeV) electrons striking the surface of the sample at a low angle of incidence ($< 1 \, ^\circ$) and diffracting toward a phosphorous detector screen. Because of the shallow angle of incidence, the penetration depth of the electrons is small and RHEED is extremely surface sensitive providing information on the top few monolayers of the deposited film. In addition, the small angle of incidence allows for the monitoring of highly insulating oxide materials without the common charging problems associated with normal incidence electron probe techniques, such as low energy electron
diffraction (LEED). Extensive information on the characteristics of the surface of a film can be obtained from a RHEED image including its crystallinity, roughness, in-plane lattice constant, and phase purity. In addition, analysis of the RHEED intensity oscillations during the growth of a film can be used for composition control and flux calibration.

Several different RHEED techniques have been employed for MBE composition control. RHEED oscillations are routinely used to measure the film growth rate during the deposition of either single component materials (e.g. Si, Be, Pt) or two-component materials with a volatile constituent (e.g. GaAs, ZnSe, SrO, etc.). In multicomponent systems with two or more nonvolatile constituents adjusting the ratio of incident fluxes in response to the appearance of identifiable impurity phase spots in the RHEED pattern has been successfully used for composition control.\textsuperscript{18,19} In addition, RHEED oscillations have been used during the deposition of the binary oxides CaO and SrO\textsuperscript{20}, and the co-deposition of multicomponent oxides\textsuperscript{21,10,22,23} to determine when a full monolayer coverage has been obtained. Prior to the work in this thesis, however, there has been no report of the use of these oscillations for the composition control of multicomponent oxides. Chapter 3 of this thesis describes the development of RHEED intensity oscillations as a highly sensitive composition control method for the growth of multicomponent oxides of the \((\text{Sr,Ba})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}\) Ruddlesden-Popper Series of compounds.

2.3 Thin film growth of Metastable Superlattices and Oxide Homologous Series:

Research efforts focusing on the growth of thin films of metastable oxides exploded with the discovery of high temperature superconductivity in a variety of layered oxide
perovskite structures. Since then, much progress has been made in growing some superconducting homologous series phases by molecular beam epitaxy (MBE). Prior to this thesis, however, little work has focused on the growth of metastable thin films of intermediate members of dielectric, ferroelectric and magnetic homologous series. MBE and PLD have been utilized for the growth of the \( n = 4, 5, \) and 6 member of the \((\text{Bi}_2\text{O}_2)(\text{Sr,Bi})_{n-1}\text{Ti}_n\text{O}_{3n+1}\) and \((\text{Pb}_2\text{O}_2)(\text{Sr,Pb})_{n-1}\text{Ti}_n\text{O}_{3n+1}\) ferroelectric Aurivillius phases. In addition, the \( n = 2 \) member of the \((\text{La,Sr})_2\text{Mn}_2\text{O}_7\) Ruddlesden-Popper Phase has been synthesized in epitaxial, thin film form by PLD. Although x-ray diffraction indicates that these superconducting and ferroelectric metastable films contain a majority of the desired layered phase, most of the studies that involve detailed TEM analysis indicate that some intergrowths of other phases exist in these samples. Chapter 6 and 8 of this thesis describe the growth of intermediate members of both the \(\text{Sr}_n\text{Ti}_n\text{O}_{3n+1}\) and \(\text{Sr}_n\text{Ru}_n\text{O}_{3n+1}\) Ruddlesden-Popper series of compounds.

Extensive work has been reported on the deposition of metastable oxide superlattice structures by MBE and PLD. Metastable oxide superlattices that have been grown include \(\text{SrTiO}_3 / \text{LaAlO}_3\), \(\text{SrTiO}_3 / \text{BaTiO}_3\), \(\text{SrTiO}_3 / \text{SrRuO}_3\), \(\text{SrTiO}_3 / \text{LaTiO}_3\), \(\text{SrTiO}_3 / \text{PbTiO}_3\), \(\text{KTaO}_3 / \text{KNbO}_3\), \(\text{PbTiO}_3 / \text{Pb}_{1-x}\text{La}_x\text{TiO}_3\), \(\text{LaFeO}_3 / \text{La(Mn,Cr)O}_3\) and \(\text{BaTiO}_3 / \text{BaZrO}_3\). These superlattice structures have been used for studying size effects in magnetic or ferroelectric systems, studying strain effects on the dielectric and ferroelectric properties of thin films, reducing leakage in ferroelectric films, and as charge modulation layers. Investigation of the intrinsic properties of these structures, however, is complicated by the possibility of solid solution mixing at the interface of each superlattice layer. Mixing can result from surface
roughness, the deposition of incomplete monolayer doses of the constituent compounds, or from interlayer diffusion occurring at elevated growth temperatures. This solid solution mixing can complicate measurement of intrinsic superlattice properties. Chapter 5 of this thesis utilizes the RHEED composition control techniques described in chapter 3 to grow nearly atomically abrupt short period BaTiO$_3$ / SrTiO$_3$ superlattices. In particular, the structure of these superlattices is carefully examined through TEM and x-ray diffraction studies to quantify and to limit the amount of interfacial mixing.

2.4 (Sr,Ba)$_{n+1}$(Ti,Ru)$_n$O$_{3n+1}$ Ruddlesden Popper Homologous Series:

The $n = \infty$ members of the (Sr,Ba)$_{n+1}$(Ti,Ru)$_n$O$_{3n+1}$ Ruddlesden-Popper series, $^{47}$ SrTiO$_3$, BaTiO$_3$, and SrRuO$_3$, have been extensively studied in single crystal, polycrystalline, and thin film forms. Although their crystal structures are identical, each of these end members has dramatically different properties.

SrTiO$_3$ is a quantum paraelectric material that exhibits an increase in dielectric constant as it is cooled, but does not undergo a phase transition to a ferroelectric state. When doped with Nb, Ta, La, or by reduction SrTiO$_3$ exhibits metallic conduction and superconductivity. $^{48}$ It has been extensively studied as a substrate for perovskite oxides and for application in tunable dielectric devices, $^{49,50}$ dynamic random access memory (DRAMs), and recently, as an alternative gate oxide in metal oxide semiconducting field effect transistors (MOSFETs). $^{51,52}$

BaTiO$_3$, the $n = \infty$ member of the Ba$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden Popper series, is the first ceramic material in which ferroelectricity was observed. Since then, it has been the focus of numerous studies, and has been utilized in a variety of different devices in single crystal, thin film, and polycrystalline forms. BaTiO$_3$ has a bulk $T_c$ of 130 °C, which
makes it an attractive candidate for room temperature applications utilizing its extremely high room temperature permittivity ($\varepsilon_r = 2000 – 10,000$), and piezoelectric and pyroelectric coefficients. It is currently used in capacitors, phase shifters, memory storage devices, and actuators.

In addition to their application as pure materials, the solid solution mixture of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ is of great commercial interest. The functionality of this solid solution is based on the fact that the paraelectric/ferroelectric transition point can be adjusted almost linearly from nearly 0 K for pure $\text{SrTiO}_3$ ($x = 1$) to 400 K for pure $\text{BaTiO}_3$ ($x = 0$). For room temperature memory applications, the ferroelectric compounds ($x < 0.25$) are suitable for nonvolatile FRAMs, while the paraelectric compositions ($x > 0.25$) are well suited for dynamic random access memory applications. For tunable dielectric devices, which require that the film be used in a highly non-linear region of its paraelectric state, $\text{SrTiO}_3$ is typically used for cryogenic applications, while $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ is typically used for room temperature devices. Chapter 4 of this thesis investigates the use of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ for room temperature tunable dielectric devices. However, rather than utilizing the typical $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ($x = 0.5$) solid solution mixture to obtain maximum room temperature tunability, we utilize strain from the substrate to accomplish the same goal with pure $\text{SrTiO}_3$ ($x = 1$).

The desire to grow a variety of perovskite ferroelectric materials on an epitaxial conducting electrode has led to the extensive investigation of $\text{SrRuO}_3$. Single crystalline $\text{SrRuO}_3$ is a metallic conductor with a paramagnetic to ferromagnetic phase transition at 160 K. Epitaxial thin films of $\text{SrRuO}_3$ have been grown by sputtering, pulsed laser deposition, metal organic chemical vapor deposition, and molecular beam epitaxy.
on SrTiO$_3$ and LaAlO$_3$ substrates. These epitaxial thin films have been shown to be excellent electrodes for the growth of several ferroelectric compounds, including BaTiO$_3$ and PbZrTiO$_3$. In addition to its perovskite crystal structure and lattice constant of $a = 3.925^{62}$ which provide excellent structural compatibility with these ferroelectric materials, SrRuO$_3$ has been shown to significantly reduce fatigue in these materials, $a$ a serious advantage over metal electrodes. $^{64}$ The growth of SrRuO$_3$ on silicon for use as an epitaxial template for the growth of ferroelectrics is the focus of chapter 10 of this thesis. In addition, the ability to grow high quality SrRuO$_3$ by MBE was a prerequisite for the growth of the $n = 1 - 5$ members of the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ Ruddlesden-Popper series, described in chapter 8 of this thesis.

While SrRuO$_3$ is an excellent electrode for the growth of a variety of ferroelectrics materials, its lattice constant is significantly smaller than many ferroelectric compounds. The growth of BaRuO$_3$ thin films, with a psuedocubic lattice constant of $a = 4.01$ Å, would provide an excellent electrode material for many of these larger materials. $^{65}$ The stable form of BaRuO$_3$ is a hexagonal structure with plane sharing octahedra, $^{66}$ however, and not well suited for the subsequent growth of the ferroelectric compound. The growth of metastable, cubic BaRuO$_3$ has been attempted by several groups using pulsed laser deposition and sputtering with no success. $^{67,68}$ It is possible that layer-by-layer MBE growth of BaRuO$_3$ on the appropriate substrate could help stabilize the cubic phase, but the growth of this material is not covered in this thesis.

The $n = 1$ members of the (Sr,Ba)$_{n+1}$(Ti,Ru)$_n$O$_{3n+1}$ series, Sr$_2$TiO$_4$, Ba$_2$TiO$_4$, Sr$_2$RuO$_4$, and Ba$_2$RuO$_4$ exhibit interesting dielectric, magnetic and superconducting properties. The tetragonal crystal structure of these phases involve a double SrO rocksalt layer
separating the titania octahedral along the $c$-axis. As a result, these compounds exhibit many anisotropic properties.

Before the work in this thesis, Sr$_2$TiO$_4$ had only been grown in polycrystalline form. Several studies have been done on the properties of polycrystalline Sr$_2$TiO$_4$ indicating that it has an average dielectric constant of 38, has a lower dielectric loss than SrTiO$_3$, $^{69-71}$ and shows no sign of metallic conduction when doped with La, Nb, and Ta. $^{72,73}$ Unlike SrTiO$_3$, however, Sr$_2$TiO$_4$ is a tetragonal compound and the study of polycrystalline samples does not allow its anisotropic properties to be investigated. The single crystal growth of Sr$_2$TiO$_4$ is complicated (if not prohibited) by a phase transition at 1550 °C and a peritectic decomposition at 1860 °C. $^{74}$ Using the floating zone technique, the incongruent melting of the Sr$_2$TiO$_4$ was not an obstacle to the initial single crystal growth of Sr$_2$TiO$_4$. However, upon cooling, a distinct line is observed in the crystal as it cools through its $\alpha$ to $\beta$ reconstructive phase transition temperature (Fig. 2.1). The resulting material was polycrystalline, single phase Sr$_2$TiO$_4$.

Thin films of Sr$_2$TiO$_4$ have previously not been reported. Attempts by our group to grow codeposited Sr$_2$TiO$_4$ by MBE resulted in the growth of double SrO layers in several different directions. $^{75}$ X-ray diffraction of these films reveals no $c$-axis spacing expected from the Sr$_2$TiO$_4$ phase (Fig. 2.2 (a)), while TEM images of these samples clearly show horizontal and vertical double SrO layers (Fig. 2.2 (b)). It is likely, although not experimentally verified, that a similar morphology would occur for a thin film deposited from a Sr$_2$TiO$_4$ target using pulsed laser deposition. Layer-by-layer deposition of this
FIG. 2.1. Floating zone growth of a Sr$_2$TiO$_4$ single crystal from a polycrystalline Sr$_2$TiO$_4$ feed rod. The arrow points to a clear line on the crystal as it cools through its $\alpha$ to $\beta$ phase transition at 1550 °C. The resulting material is single phase, polycrystalline Sr$_2$TiO$_4$. 
FIG. 2.2. (a) $\theta$-2$\theta$ x-ray diffraction pattern of a Sr$_2$TiO$_4$ film grown by codeposition of the Sr and Ti cations. Although the Sr and Ti ions were deposited in a 2:1 ratio, no evidence of Sr$_2$TiO$_4$ peaks can be seen in the x-ray diffraction pattern. (b) A cross-sectional TEM reveals that no c-axis lattice spacing consistent with Sr$_2$TiO$_4$ is present. The excess SrO was incorporated into the film by forming double SrO layers in random orientation. Layer-by-layer deposition allows the orientation of the double SrO layers to be controlled.
compound by MBE allows the directionality of the double SrO layer to be controlled and is the focus of chapter 6 in this thesis.

$\text{Sr}_2\text{RuO}_4$ has been synthesized in single crystalline form using the floating zone technique.\textsuperscript{76} It is the only copper-free layered oxide superconductor with a $T_c$ of 1.5 K. Superconductivity in $\text{Sr}_2\text{RuO}_4$ is extremely sensitive to a host of defects and can be suppressed by grain boundaries in polycrystalline films,\textsuperscript{76} defects in epitaxial films,\textsuperscript{77} and low level impurities in single crystalline material.\textsuperscript{78} The only epitaxial films reported to date have been grown by PLD and do not exhibit superconductivity.\textsuperscript{79-81} The growth of $\text{Sr}_2\text{RuO}_4$ films by MBE may be a way to achieve superconducting films by reducing the structural defects and chemical impurities in the films. Chapter 8 describes the MBE growth of $\text{Sr}_2\text{RuO}_4$ epitaxial films, although superconductivity in these films has yet to be achieved.

Unlike $\text{Sr}_2\text{TiO}_4$ and $\text{Sr}_2\text{RuO}_4$, the tetragonal form of $\text{Ba}_2\text{TiO}_4$ and $\text{Ba}_2\text{RuO}_4$ are not the thermodynamically stable phases.\textsuperscript{82} A metastable structure of $\text{Ba}_2\text{RuO}_4$ has been synthesized under extreme pressures (65,000 atm) in polycrystalline form\textsuperscript{83} and in epitaxial thin film form by utilizing epitaxial stabilization.\textsuperscript{84} It may be possible to grow the tetragonal $\text{Ba}_2\text{TiO}_4$ phase in this same manner, but to our knowledge this has not been attempted. Some evidence of $\text{Ba}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper phases have been reported on the surface of polycrystalline $\text{BaTiO}_3$ samples,\textsuperscript{85,86} indicating that the higher formation energies of these compounds may be able to be overcome with epitaxial stabilization. The growth of both $\text{Ba}_2\text{TiO}_4$ and $\text{Ba}_2\text{RuO}_4$ are not investigated in this thesis, although it is believed that the same growth techniques used for the successful
growth of Sr$_2$TiO$_4$ and Sr$_2$RuO$_4$ could be effectively applied to the growth of these compounds.

The growth of intermediate members (i.e. $1 < n < \infty$) of the $(\text{Sr,Ba})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}$ Ruddlesden Popper series are difficult because of the introduction of unwanted intergrowths of other members within the crystal framework. Only the $n = 2$ member of the Sr$_n$Ru$_{n+1}$O$_{3n+1}$ series, Sr$_3$Ru$_2$O$_7$, has been synthesized in single crystal form, although intergrowths of other phases exist in small quantities in these samples. These Sr$_3$Ru$_2$O$_7$ crystals are paramagnetic but are not superconducting. Polycrystalline $n = 2$ and 3 samples have been made of the Sr$_n$Ti$_n$O$_{3n+1}$ series by solid state techniques but little is known about their anisotropic dielectric properties. Prior to the work in this thesis, no reports of thin films of intermediate phases of any of the $(\text{Sr,Ba})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}$ Ruddlesden Popper series have been reported. More recently, multi-target PLD has also been used for the successful growth of the $n = 5$ member of the Sr$_n$Ti$_n$O$_{3n+1}$ Ruddlesden Popper series. Chapters 6 and 8 describe the growth of intermediate members of both the Sr$_n$Ti$_n$O$_{3n+1}$ and the Sr$_n$Ru$_n$O$_{3n+1}$ Ruddlesden Popper series by MBE.

2.5 Substrate Choice

The growth of high quality epitaxial materials requires that substrates with structural and chemical compatibility with the desired film are used. Chemical incompatibility can lead to a variety of interfacial reaction layers or interdiffusion of unwanted elements into the films. Structural incompatibility, typically manifested through substrate lattice constants with different values than the film, or large differences in thermal expansion between the film and substrate, can have a dramatic effect on the structural and electrical properties of a film. Structural defects, including dislocations, cracking, or even a
complete loss of epitaxy are common when the film and substrate are not well lattice matched. In addition, several experimental and theoretical studies have shown that strain can have a dramatic effect on the electrical properties of dielectric, ferroelectric, and superconducting thin films. For example, these have been shown to include shifting in the curie temperature in ferroelectric $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ and $\text{BaTiO}_3$, introduction of ferroelectricity and improved dielectric tunability in $\text{SrTiO}_3$, and increasing the superconducting transition temperature in $(\text{LaSr})_2\text{CuO}_4$. Clearly, characterization of the intrinsic properties of thin films without consideration of their strain state is not possible.

The choice of substrate is also important when the growth of metastable structures is desired. Choosing a substrate with lattice constants better matched to the metastable structure is an effective technique to frustrate the growth of a poorer lattice matched stable structure. As discussed above, this is particularly applicable in the $(\text{Sr,Ba})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}$ Ruddlesden Popper series, where the cubic, and tetragonal form of the $\text{BaRuO}_3$, and $\text{Ba}_2(\text{Ti,Ru})\text{O}_4$, members, respectively, are not the stable structures.

The $(\text{Sr,Ba})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}$ Ruddlesden Popper series compounds have lattice constants ranging from 3.88 Å to 4.1 Å and substrates with a similar range of values are desired for their growth. Figure 2.3(a) shows a schematic of all the commercially available substrates as a function of their lattice constant. While several substrates, including $\text{LaAlO}_3$, LSAT, $\text{NdGaO}_3$, and $\text{LaSrGaO}_4$, are available with lattice constants between 3.79 Å and 3.9 Å, a noticeable gap exists between $\text{SrTiO}_3$ ($a = 3.905$ Å) and $\text{KTaO}_3$ ($a = 3.99$ Å). Chapter 9 describes the single crystal growth and measurement of the dielectric constant and bandgap of the perovskite crystals, $\text{ReScO}_3$. Although this chapter focuses on these materials for application to alternative gate dielectrics, they are
FIG. 2.3. Lattice constant of commercially-available oxide substrates (bottom of axis) compared with several perovskite films (top of axis). (a) a significant gap between SrTiO$_3$ and KTaO$_3$ existed in available substrates before the work in this thesis (b) magnified region between 3.9 and 4.1 Å showing the lattice constants of several ReScO$_3$ crystals grown in this thesis.
equally applicable as oxide substrates with lattice constants between 3.93 Å and 4.03 Å (Fig. 2.3(b)). The growth of these compounds has enabled the study of the effect of strain on the dielectric tunability of SrTiO$_3$ thin films as described in Chapter 4. In addition to strained SrTiO$_3$, several other members of the Ruddlesden Popper phases are well lattice matched with these scandate crystals including, BaTiO$_3$ ($a = 3.992$ Å), SrRuO$_3$ ($a = 3.925$ Å), tetragonal Ba$_2$RuO$_4$ ($a = 3.99$ Å),$^{65}$ and cubic BaRuO$_3$ ($a = 4.01$ Å). The growth of these compounds on these new scandate substrates will be the focus of future work.

2.6 Integration with Silicon

The desire to integrate the functional properties of crystalline oxides with silicon has led to the development of a variety of innovative growth techniques to achieve this goal. The primary obstacle to the growth of crystalline oxides on silicon is the propensity of silicon to form an amorphous surface layer of SiO$_2$ in an oxidizing ambient. Formation of this amorphous layer before epitaxial growth of the oxide has begun prevents the subsequent deposition of an epitaxial oxide layer. The first researchers to successfully address this problem utilized vapor phase epitaxy to grow MgAl$_2$O$_4$ epitaxially on silicon.$^{100}$ Subsequent attempts have used a variety of transition layers in an attempt to transition from the silicon to the oxide without the formation of SiO$_2$ and loss of epitaxy. The first report of epitaxial perovskites grown on silicon utilized an MgAl$_2$O$_4$ buffer layer for the subsequent growth of PbTiO$_3$.$^{101}$ In 1991, epitaxial BaTiO$_3$ was reported on silicon with the use of a BaO/BaSi$_2$ buffer layer.$^{102}$ Significant progress in this field has been achieved recently with the goal of using epitaxial oxides as a replacement for SiO$_2$ as the gate dielectric in Si MOSFETs. SrTiO$_3$ has been the epitaxial
perovskite studied in most detail, however, its inability to withstand a 1000 °C anneal and its minimal conduction band offset with Si pose significant challenges for its use as an alternative gate dielectric material. Other multicomponent oxides, however, are believed to be thermodynamically stable in contact with silicon and possess a significant band offset to prevent leakage. Unfortunately, little data on the dielectric constants or bandgap of many of these compounds exists; data that is crucial in the selection of appropriate materials for study as possible alternative gate dielectrics. Chapter 9 of this thesis describes the single crystal growth and dielectric and optical characterization of many of these multicomponent oxide perovskites for potential application as gate dielectric materials.

Although the work on the epitaxial growth of SrTiO$_3$ on Si may not be suitable for the gate dielectric application, it has opened the door to the growth of a variety of functional epitaxial compounds on Si for other applications. In particular, the epitaxial SrTiO$_3$ layer has been used effectively as a template for the growth of GaAs on Si and for the growth of a variety of ferroelectric compounds on silicon.

While the insulting properties of SrTiO$_3$ and MgAl$_2$O$_4$ provide suitable template layers for many applications, the growth of an epitaxial metallic buffer layer in direct contact with Si would enable many useful design architectures. Recently, La-doped SrTiO$_3$ has been effectively used to provide a fully conductive pathway to the underlying silicon. However, donor-doped SrTiO$_3$ is a notoriously unreliable conductor when subject to highly oxidizing conditions at elevated temperatures. Similar difficulties exist with conductive TiN, which has been used as a suitable epitaxial buffer layer for some perovskites, but whose inability to withstand the oxidizing conditions and
elevated temperatures necessary for the growth of many ferroelectric oxides is a considerable limitation.\textsuperscript{112}

As mentioned above, SrRuO$_3$ has emerged as the electrode of choice for the growth of a variety of ferroelectric, dielectric, and piezoelectric materials on oxide substrates because its lattice constant is well matched to many perovskites, it prevents fatigue in many ferroelectric materials, and it is able to withstand a wide range of demanding oxidizing and temperature conditions. Epitaxial integration of SrRuO$_3$ with silicon would provide an ideal conducting template for the subsequent growth of ferroelectrics.

Attempts to grow SrRuO$_3$ directly on silicon have resulted in a variety of interfacial reaction layers with the ultimate growth of a polycrystalline SrRuO$_3$ film.\textsuperscript{113} Epitaxial SrRuO$_3$ has been grown with a (110) orientation on (100) Si using a thick (800Å) YSZ buffer layer.\textsuperscript{114,115} While (110) oriented SrRuO$_3$ is well suited for the growth of some ferroelectrics, such as SrBi$_2$Nb$_2$O$_9$, it is not favorable for exploiting the maximum polarizability in a variety of other ferroelectrics such as Pb$_{1-x}$Zr$_x$TiO$_3$, and BaTiO$_3$, where the polarization lies completely in the c-axis. The growth of (100) oriented SrRuO$_3$ has been reported with the use of a TiAlN/Pt buffer layer, although electrical contact to the substrate was not measured.\textsuperscript{116} Chapter 10 of this thesis investigates the growth of epitaxial SrRuO$_3$ on Si by means of a thin (Ba,Sr)O buffer layer for use as a conducting, epitaxial template for the subsequent growth of ferroelectric materials.
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CHAPTER 3

RHEED Intensity Oscillations for the Stoichiometric Growth of SrTiO₃ Thin Films by Reactive Molecular Beam Epitaxy

RHEED Intensity Oscillations for the Stoichiometric Growth of SrTiO$_3$ Thin Films by Reactive Molecular Beam Epitaxy

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Abstract The growth of high quality multicomponent oxide thin films by reactive molecular beam epitaxy (MBE) requires precise composition control. We report the use of in situ reflection high-energy electron diffraction (RHEED) for the stoichiometric deposition of SrTiO$_3$ (100) from independent strontium and titanium sources. By monitoring changes in the RHEED intensity oscillations as monolayer doses of strontium and titanium are sequentially deposited, the Sr:Ti ratio can be adjusted to within 1% of stoichiometry. Furthermore, the presence of a beat frequency in the intensity oscillation envelope allows the adjustment of the strontium and titanium fluxes so that a full monolayer of coverage is obtained with each shuttered dose of strontium or titanium. RHEED oscillations have also been employed to determine the doping concentration in barium- and lanthanum-doped SrTiO$_3$ films.

Keywords: SrTiO$_3$, RHEED, Molecular Beam Epitaxy (MBE), Composition Control, Sequential Deposition

3.1. Introduction

The primary obstacle in the growth of many oxide thin films by reactive molecular beam epitaxy (MBE) is precise composition control. Often, even 1-2% variation in monolayer doses results in impurity phases or intergrowths [1,2]. High quality films grown by this technique require that both the stoichiometry of the cations is maintained, and that each cation is supplied in a full monolayer dose.

Several in situ monitoring techniques have been employed in the growth of multicomponent oxides for composition control with varying degrees of success [3]. Atomic absorption spectroscopy (AA) offers better than 1% composition control of many elements [4-6]. Unfortunately, the absorption of the AA signal for some elements (e.g., titanium) is weak and compositional control of better than 5-10% is not possible using conventional hollow cathode AA sources. Laser atomic absorption offers better
sensitivity than traditional AA, but is restricted to elements with absorption in wavelengths achievable with tunable lasers and has not been widely implemented due to its high cost [7,8].

Another in situ monitor that has been used for composition control in oxide MBE systems is reflection high-energy electron diffraction (RHEED). RHEED oscillations are routinely used to measure the film growth rate during the growth of either single component materials (e.g. Si, Be, Pt) or two-component materials with a volatile constituent (e.g. GaAs, ZnSe, SrO, etc.). However, in multicomponent oxides where two or more components are not growing in an adsorption-controlled regime, measurement of the RHEED oscillation period is insufficient for composition control as there are multiple unknowns. While adjusting the ratio of incident fluxes in response to the appearance of identifiable impurity phase spots in the RHEED pattern has been used for composition control of some multicomponent oxides [9], it lacks the necessary sensitivity for the phase-pure growth of many multicomponent oxide thin films because it only alerts the grower to composition errors after an unwanted impurity phase has been nucleated. In some systems these unwanted impurities can be dissolved, but in others they cannot. Another technique, called RHEED difference, can alert the grower sooner to stoichiometry errors, but also is inherently sensitive only after unwanted impurities have been formed and begin to diffract [10].

This work focuses on the development of RHEED oscillations as a highly sensitive composition control method for the growth of multicomponent oxides. Previously, RHEED oscillations have been used during the deposition of the binary oxides CaO and SrO [11], and the co-deposition of multicomponent oxides [12],
including SrTiO$_3$ [10,13,14] to determine when a full monolayer coverage has been obtained. RHEED oscillations have also been observed during the sequential deposition of many oxide films [15], including SrTiO$_3$ [10,13], but to our knowledge there has been no report of the use of these oscillations for the composition control of multicomponent oxides. We find that composition control based on RHEED oscillations during the shuttered deposition of SrTiO$_3$ is more accurate than AA to control the titanium flux and ensure that a complete monolayer of each cation is deposited in each shutter cycle.

3.2. Experimental

All films were grown in an MBE system (EPI 930) designed for and dedicated to the growth of oxides (Fig. 3.1) [16]. The strontium flux was produced by sublimating elemental strontium contained in an alumina crucible using a low-temperature effusion cell. The strontium flux was monitored by an AA system (Intelligent Sensor Technology model ATOMICAS) with closed-loop real-time feedback to the MBE shutter (WeckTech MicroCrystal software). A Ti-Ball™ titanium sublimation pump powered by a precision power supply (HP model 6673A) was used as a stable ($\pm 2\%$ per hour) alternative to an effusion cell or electron beam source to supply titanium flux [17]. A RHEED gun (Staib model EK-15-RMG) operated at 10 kV and an incident angle of 1-2° supplied the electron beam to the substrate surface. The RHEED pattern was monitored with a CCD camera and real-time analysis software (k-Space model 400). Molecular beams of strontium and titanium were shuttered in a sequential manner (Fig. 3.2) to deliver alternating monolayer doses of each cation onto well oriented ($\pm 0.3^\circ$) SrTiO$_3$ (100) and LSAT (100) substrates. Before growth, the SrTiO$_3$ substrates were etched with a buffered-HF solution to achieve a TiO$_2$-terminated surface [18]. The average flux of both
the strontium and titanium sources was $1.0 \times 10^{14}$ atoms/cm$^2$·s for all growths. The RHEED intensity oscillations are relatively insensitive to both substrate temperature and background oxygen pressure. During growth, the substrate temperature was typically held at 750 °C as measured by an optical pyrometer, although similar results have been obtained for substrate temperatures as low as 550 °C. The substrate was immersed in a continuous flux of molecular oxygen, yielding a background pressure of $2 \times 10^{-7}$ Torr. The oxygen pressure at the substrate surface is about 20× higher than the measured background pressure [19].

3.3. Results and Discussion

3.3.1 Optimizing the Sr:Ti Ratio

To achieve the optimal ratio of Sr:Ti two complementary techniques are employed. AA has a high sensitivity to the strontium molecular beam and is used to control the deposition of exactly one monolayer during growth. Before growth, a quartz crystal microbalance (QCM) is utilized to calibrate the AA signal. The QCM is located approximately 3 cm directly in front of the substrate, so a correction factor (or tooling factor) is needed to relate the flux measured by the QCM to the flux reaching the substrate. This tooling factor is determined by measuring the periodicity of the specularly-reflected RHEED oscillations as several monolayers of SrO are deposited onto a SrTiO$_3$ substrate. The period of the RHEED intensity oscillations corresponds to the deposition of one monolayer of SrO [11]. The RHEED oscillations are done on a hot substrate, so in addition to geometric differences, the tooling factor (0.87) also includes sticking coefficient differences between the water-cooled QCM and the hot substrate. Once the AA flux vs. absorption calibration curve is established, the QCM is retracted,
allowing strontium to reach the substrate. To deposit one monolayer of strontium, the shutter is opened and the AA signal is converted to a flux using the AA vs. flux calibration curve. This flux is integrated until the desired one monolayer dose is delivered to the substrate at which time the strontium shutter is closed. Using these techniques, a full monolayer of strontium can reproducibly be supplied to the substrate in each shutter cycle.

Although AA provides the required composition control for strontium, it is quite insensitive to the titanium molecular beam and monolayer to monolayer variations in excess of 5% are common. For this reason, we have developed a method based on shuttered RHEED intensity oscillations to determine the correct titanium dose. Figure 3.3 shows a series of shutter-driven RHEED oscillations that occur during the deposition of homoepitaxial SrTiO$_3$. The intensity plotted is the average total diffracted intensity of the 00 streak of the zeroth Laue zone with the RHEED beam incident along the SrTiO$_3$ [011] azimuth. The pattern achieves a maximum intensity following the deposition of one monolayer of SrO and a minimum intensity following the deposition of one monolayer of TiO$_2$. If a full monolayer of titanium is deposited, the maximum intensity of the pattern remains constant after the deposition of several SrO layers (Fig. 3.3(a)). However, if excess titanium is deposited, the maximum intensity of the pattern will decrease with each succeeding monolayer (Fig. 3.3(b)). If an insufficient dose of titanium is deposited, the maximum intensity of the pattern will increase, and often a double peak can be seen (Fig. 3(c)). For clarity, Fig. 3.3 demonstrates these changes for a 3% change in flux; changes of < 1% are less pronounced, but are noticeable. The fundamental reasons behind this behavior are unclear, but numerous growths of members
of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series [2], whose phase pure growth is very sensitive to stoichiometry, have confirmed the validity of this growth technique. Section 3.3.3 also presents evidence confirming the validity of this method.

The behavior of the intensity oscillations of the diffracted portion of the RHEED pattern is more reproducible than those of the specular reflection. The diffracted portion of the 00 and 01 streaks exhibit similar behavior regardless of the incident angle of the RHEED beam and the miscut of the substrate. The oscillations of the specular spot are much less predictable, however. In fact, the two previous studies of shuttered RHEED oscillations report conflicting behavior of the intensity oscillations of the specular spot. Iijima et al. [13] report an increase in the intensity with the deposition of SrO (which matches our results for the diffracted intensity), while Bodin et al. [10] report an increase in intensity during the deposition of TiO$_2$. Both of these phenomena have been observed in different growths (or even at different times in the same growth), with the specular beam oscillating in-phase and out-of-phase with the diffracted intensity (Fig. 3.4(a), 3.4(b), and 3.4(c)). This type of behavior has been observed during the MBE growth of GaAs by codeposition where the phase shift is linked to the angle of incidence of the RHEED beam [20]. A direct correlation between the angle of the incident beam and the phase of oscillation of the specular reflection for the growth of SrTiO$_3$ by sequential deposition has not been established. A “double peak” behavior where an intensity maximum is reached after the deposition of both the SrO and TiO$_2$ layers has also been observed (Fig. 3.4(d)). This may be the result of the sensitivity of the specular reflection to the surface roughness of the film. After the deposition of a complete monolayer of SrO or TiO$_2$, the surface is the smoothest and the specularly reflected intensity is at a
maximum. The roughest film surface occurs with the deposition of a half monolayer of each cation, corresponding to the reflected intensity minimum. This behavior has not been observed for all growths and more work must be done to fully understand the relationship between the specular oscillations and variables such as substrate miscut and the angle of incidence of the RHEED beam.

3.3.2 Determination of Doping Levels

This technique is also useful when a high level (e.g., 1-20%) of a substitutional dopant or solid solution constituent is desired in a SrTiO$_3$ film. For instance, we commonly use La-doped SrTiO$_3$ as a bottom electrode for the growth of overlying epitaxial perovskite films; barium is often added to SrTiO$_3$ to modify its dielectric properties. Because both of these dopants substitute onto the Sr-site in the lattice, it is common to codeposit the strontium and dopant species. AA is insensitive to the low dopant flux levels desired in these films and it is most common to estimate the doping percentage by extrapolation from an Ahrenius plot of the flux vs. reciprocal temperature of the effusion cell. This is an imprecise method with up to 50% discrepancy in the calculated doping level and the actual amount of dopant incorporated into the film.

Using RHEED oscillations the doping levels in these films can more accurately be specified. To grow a doped SrTiO$_3$ film, the correct titanium dose must first be determined using the methods described above. The strontium dose is then decreased by the desired doping level and both the dopant and strontium are deposited simultaneously. If excess dopant is deposited, the RHEED intensity pattern will increase as in Fig. 3.3(c). If insufficient dopant is added, the pattern will decrease as in Fig. 3.3(b). In this manner, the dopant’s effusion cell temperature (or codeposition time) is adjusted until a sufficient
flux is achieved to compensate for the strontium deficiency, and a stoichiometric RHEED pattern is again reached.

3.3.3. Incomplete Monolayer Coverage

It is possible to confirm that the methods described above achieve full monolayer coverage of each cation by monitoring the intensity of the RHEED pattern over many supply cycles. If the Sr:Ti ratio is correct and a full monolayer of each cation is being deposited, no fluctuation in the maximum or minimum intensity of the pattern is observed (Fig. 3.5(c)). However, if the Sr:Ti ratio is maintained constant but the dose of each is increased or decreased beat frequencies are observed. Figure 5(c) shows the RHEED intensity oscillations as 20 monolayers of stoichiometric SrTiO$_3$ are deposited in full monolayer doses. For the deposition of 1.15 and 0.85 monolayers per dose, there is an overall maximum and minimum intensity in the oscillations every 6-7 monolayers (Fig. 3.5(a) and 3.5(e)). Similarly, the deposition of 1.1 or 0.9 monolayers results in a beat frequency of 10 monolayers (Fig. 3.5(d) and 3.5(b)). This result is identical to results obtained during the shuttered deposition of GaAs films at low temperatures, where fractional coverage resulted in a modulation of the RHEED intensity oscillation envelope [21]. This beat frequency is evident in the intensity oscillations of the diffracted 00 streak and 10 streak of the zeroth Laue zone, as well as the reflected specular spot (Fig. 3.6).

3.4. Conclusions

The use of shuttered RHEED oscillations in conjunction with AA for the stoichiometric deposition of SrTiO$_3$ thin films by MBE has been demonstrated. This technique has also been utilized to correctly determine the doping levels in lanthanum and barium doped
SrTiO$_3$ films. The presence of a beat frequency in the RHEED intensity oscillation envelope occurs when incomplete monolayer doses are supplied, providing a confirmation of the effectiveness of this technique, as well as a means to monitor the deposition of complete monolayers. This technique has enabled the growth of the first five members of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper series and provides an effective alternative to other more costly systems for the precise control of titanium.
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FIG. 3.1. A schematic diagram of the oxide MBE system used for the deposition of multicomponent oxide thin films.
FIG. 3.2. Timing diagram of the sequential deposition of strontium and titanium atoms during the growth of SrTiO$_3$. Oxygen is continuously supplied to the substrate during growth.
FIG. 3.3 RHEED intensity oscillations of the central diffracted streak as the strontium and titanium are deposited in a sequential manner. (a) Stoichiometric full monolayers of both strontium (SrO) and titanium (TiO$_2$) deposited. (b) Strontium dose held constant but titanium dose increased by 3% from a full monolayer. (c) Strontium dose held constant but titanium dose decreased by 3% from a full monolayer.
FIG. 3.4. RHEED intensity oscillations with the RHEED beam incident along the SrTiO$_3$ [011] azimuth during different growths of SrTiO$_3$ by sequential deposition. (a) average diffracted intensity of the 00 streak. (b) specular spot oscillating in-phase with the diffracted intensity, (c) specular spot oscillating 180° out of phase with diffracted intensity. (d) specular spot intensity “double peak” with peaks occurring at the termination of both the SrO and TiO$_2$ layers.
FIG. 3.5. Beat frequency observed during the deposition of incomplete monolayers of strontium and titanium where the incomplete monolayers contain the correct stoichiometry (i.e., Sr:Ti = 1). (a) 0.85 monolayers of each cation supplied with each shutter cycle; beat frequency = 6-7 oscillations. (b) 0.90 monolayers of each cation supplied with each shutter cycle; beat frequency = 10 oscillations. (c) Complete monolayer of each cation supplied with each shutter cycle; no beat frequency observed. (d) 1.10 monolayers of each cation supplied with each shutter cycle; beat frequency = 10 oscillations. (e) 1.15 monolayers of each cation supplied with each shutter cycle; beat frequency = 6-7 oscillations.
FIG. 3.6. Beat frequency during the deposition of 0.90 monolayers of each cation with the RHEED beam incident along the [011] azimuth of SrTiO$_3$. (a) RHEED pattern of the SrTiO$_3$ [011] azimuth, (b) average intensity of the entire 10 streak, (c) average intensity of the specular reflection, (d) average intensity of the diffracted portion of the 00 streak.
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Chapter 4

Improved Room Temperature Dielectric Tunability in Strained SrTiO₃ Thin Films

To be submitted to *Applied Physics Letters*
Improved Room Temperature Dielectric Tunability in Strained SrTiO$_3$ Thin Films

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Abstract
Epitaxial SrTiO$_3$ thin films have been grown by MBE on both DyScO$_3$ and LSAT substrates. On DyScO$_3$, SrTiO$_3$ is under tensile stress, while on LSAT it is compressively strained. The dielectric properties of these films, as measured with interdigitated electrodes, are dramatically different. The films under biaxial tensile stress show significant (83%) room temperature tunability and a sharp Curie-Weiss peak at 293 K. Under biaxial compressive stress, the SrTiO$_3$ exhibits no room temperature tunability. The loss and tunability of the SrTiO$_3$ / DyScO$_3$ films make them well suited for application to room temperature microwave devices.
SrTiO$_3$ and Ba$_{1-x}$Sr$_x$TiO$_3$ have emerged as leading materials for application to a variety of tunable microwave devices. Efficient operation of these devices requires that the active material is used in a highly non-linear region of its paraelectric state, thereby maximizing the tunability without the increased loss associated with operation in the ferroelectric state. Ba$_{1-x}$Sr$_x$TiO$_3$ is well suited for such application as the temperature of its paraelectric to ferroelectric phase transition can be varied as a function of composition from nearly 0 K for pure SrTiO$_3$ ($x = 1$) to 400 K for pure BaTiO$_3$ ($x = 0$). Typically, this dictates that SrTiO$_3$ be used for low temperature applications, while Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ be used for room temperature devices. Although the dielectric properties of bulk SrTiO$_3$ and Ba$_{1-x}$Sr$_x$TiO$_3$ samples have been well studied, the properties of thin films have been shown to be quite different, and to vary widely depending on processing conditions and substrate choice. In particular thin film loss values are higher than in single crystals, and the width of the Curie-Weiss peak is broader than in bulk samples. Substrate induced strain has been shown to be an important factor in these anomalous thin film properties. In particular, strain has been theoretically predicted, and experimentally shown, to shift the $T_c$ and change the permittivity in Ba$_x$Sr$_{1-x}$TiO$_3$ samples. While SrTiO$_3$ is intrinsically a quantum paraelectric material, it has been forced into its ferroelectric state by the application of uniaxial strain and biaxial compressive strain in single crystal and thin film samples, respectively. Non-uniform strain is also believed to contribute to the broadening of the Curie-Weiss peak, as $T_c$ varies within the sample based on the local strain state of the material.

Experimentally, the growth and measurement of the anisotropic dielectric properties in uniformly strained SrTiO$_3$ films is difficult. Typically, epitaxial films for microwave applications have been grown with thicknesses exceeding their critical thickness, and the strain results from thermal expansion differences between the substrate and film. The strain state in these films can be difficult to analyze quantitatively, however, due to the inherent dislocations present in the film. Alternatively, coherently strained films can be
grown, utilizing lattice mismatch between substrate and film, to impose uniform strain on films that do not exceed their critical thickness.

Several substrates, such as LSAT, LaAlO$_3$, NdGaO$_3$, LaSrGaO$_4$ have lattice constants ranging from 3.79 Å – 3.88 Å and offer excellent templates for the growth of compressively strained SrTiO$_3$. Unfortunately, few can be made conductive with doping, and a bottom electrode is needed for capacitor structures to be measured. La$_{0.5}$Sr$_{0.5}$CoO$_3$ is an oxide compatible electrode with lattice constants of 3.8 Å, however, its significant lattice mismatch with SrTiO$_3$ leads to an extremely thin critical thickness. Recently, the growth of strained LaAlO$_3$/SrTiO$_3$ superlattices on La$_{0.5}$Sr$_{0.5}$CoO$_3$ has allowed the dielectric properties along the $c$-axis of biaxially compressively strained SrTiO$_3$ to be measured.$^{12}$ These films demonstrated improved room temperature dielectric tunability and showed no ferroelectric switching at room temperature. YBCO has also been used as a bottom electrode for the growth of ferroelectric SrTiO$_3$ films with a dielectric constant that reaches a maximum of 5000 with 20% tunability ($\pm$ 3 V) at 80 K, and a $T_c$ of 90 K.$^{12}$ However, these films are not believed to be coherently strained to the substrate.

Interdigitated electrodes have been widely used to measure the dielectric properties of a variety of materials without the need for a bottom electrode. Interdigitated electrodes predominantly measure the in-plane dielectric properties of the materials, however, and the growth and measurement of SrTiO$_3$ in tensile strain is difficult. KTaO$_3$ is one of the few commercially available substrates suitable for such a growth, but again, its lattice constant of 3.98 Å quickly leads to dislocations in the SrTiO$_3$ film. We have grown and utilized a new substrate material, DyScO$_3$, as well as the widely used substrate LaAlO$_3$—Sr$_2$AlTaO$_6$ (LSAT), for the growth and characterization of SrTiO$_3$ films under uniform biaxial tensile and compressive strain.

DyScO$_3$ is an orthorhombic crystal with lattice constants $a = 5.43$, $b = 5.71$, and $c = 7.89$ Å. It can be considered to have a pseudocubic cell with lattice constant of $a = 3.93$ Å.$^{13}$ resulting in a 0.6% lattice mismatch ($((a_{\text{sub}}-a_{\text{film}})/a_{\text{film}})$ with SrTiO$_3$. It is
stable when heated to growth temperatures (~700 °C) in an oxidizing or reducing
environment, and shows no signs of chemical reaction with the overlying SrTiO$_3$ film.
LSAT has a double perovskite structure with lattice constant of $a = 7.737$ Å, resulting in
a -0.9% lattice mismatch with SrTiO$_3$. The low dielectric constant of both DyScO$_3$
($\varepsilon_{11} = 22.0, \varepsilon_{22} = 18.8,$ and $\varepsilon_{33} = 35.5$)$^{14}$ and LSAT ($\varepsilon_r = 22.5$)$^{15}$ reduce field
penetration in the substrate and facilitate modeling of the films dielectric constant.

An oxide MBE system was used for the growth of the SrTiO$_3$ films. Monolayer
doses ($6.6 \times 10^{14}$ atoms/cm$^2$) of Sr and Ti were deposited in a sequential manner on
DyScO$_3$ (001) and LSAT (001) substrates. The average flux of both the Sr and Ti sources
was $1.0 \times 10^{14}$ atoms/cm$^2$·s for all growths. Reflection high-energy electron diffraction
(RHEED) intensity oscillations were used to adjust the stoichiometry of the Sr and Ti
molecular beams and ensure that a complete monolayer of each cation was deposited in
each shuttered cycle.$^{16}$ During growth, the substrate temperature was 650 °C as measured
by an optical pyrometer. The substrate was immersed in a continuous flux of molecular
oxygen mixed with 10% ozone, yielding a background pressure of $5.0 \times 10^{-7}$ Torr. A
series of films, with thicknesses of 100 Å, 200 Å, 500 Å and 1000 Å were grown on
both LSAT and DyScO$_3$ substrates. After growth, the samples were annealed for 0.5
hours at 700 °C in atmosphere. In addition to the annealed samples, one additional 500 Å
film on each substrate was grown and measured without a post growth anneal.

X-ray $\theta$-2$\theta$ and $\phi$-scans were performed on all samples before and after anneal.
These measurements revealed no shift in peak position in any of the samples after anneal,
indicating that little, if any, relaxation occurred during heating. The $\theta$-2$\theta$ scans reveal that
the $c$-axis lattice constant is compressed in the films grown on DyScO$_3$ and extended in the
films on LSAT, as would be expected from the tensile and compressive stain, respectively,
imparted by the substrates (Fig. 4.1). The $c$-axis lattice constant of these films as determined by a Nelson-Riley analysis of the diffraction peak positions is $3.88 \pm 0.01 \, \text{Å}$ for the films grown on DyScO$_3$ and $3.93 \pm 0.01 \, \text{Å}$ for the films grown on LSAT. No variation of in- or out-of-plane lattice constants was seen for the 200 – 1000 Å films on LSAT or on DyScO$_3$. Accurate lattice constant calculations could not be performed on the 100 Å films because of insufficient resolution between the film and substrate peak positions. X-ray $\phi$-scans of the 321 peak indicated epitaxial, $c$-axis films with orientation (001) SrTiO$_3 \parallel$ (001) LSAT (DyScO$_3$) and [100] SrTiO$_3 \parallel$ [100] LSAT (DyScO$_3$). In-plane lattice constants of $3.89 \pm 0.01 \, \text{Å}$ and $3.90 \pm 0.01 \, \text{Å}$ for the 200, 500, and 1000 Å films on LSAT and DyScO$_3$, respectively, indicate that these films may not be coherently strained to the in-plane lattice constants of the substrate. High-resolution cross-sectional TEM studies are currently being performed to quantitatively characterize the strain state of these films with more precision, and allow comparison between our experimental dielectric properties and those expected from first principle calculations.

Dielectric measurements were made on these films from –40 to 40 volts using 1 – 2 μm thick Ag interdigitated electrodes deposited by e-beam evaporation. Room temperature measurements were made using electrodes with 80 μm finger length and 6 μm finger gap while temperature dependent measurements were made with smaller electrodes of 40 μm finger length and 12 μm finger gap to facilitate integration with a 100 μm picoprobe. Measurements were made from 1 - 20 GHz using an HP 8510 C network analyzer. Capacitance and loss values were obtained using a parallel resistor-capacitor model.

The dielectric properties exhibited by these films are dramatically different. The room temperature permittivity of the as-grown 500 Å SrTiO$_3 /$ DyScO$_3$ film is 6000,
while the film grown on LSAT is 310, in close agreement with its single crystal value of 328. In addition, the film grown on DyScO$_3$ exhibits 83% dielectric tunability from -40 to 40 volts while the sample grown on LSAT exhibits essentially no tunability in the same voltage range (Fig. 4.2). The dielectric constant of the film on DyScO$_3$ has a rather sharp peak at 0 volts, with a small field tunability (-5 to 5 V) of 37%. The dielectric quality factor ($Q$), defined as

$$Q = \frac{1}{\tan \delta},$$  \hspace{1cm} (1)

was low for both the as-grown film on LSAT and DyScO$_3$, with an average value of 10. The reasons for this high loss are not known, although a comparison of the as-grown and annealed 500 Å DyScO$_3$ samples showed no significant difference in the $Q$ factor, indicating that oxygen vacancies are most likely not the primary loss mechanism. The annealed sample did show a significant decrease in dielectric constant, however, with a room temperature dielectric constant of 2000 and 50% tunability at -40 Volts. The reason for this change is not known, and is somewhat surprising considering the identical lattice constants of the pre- and post- annealed sample.

The dielectric constants of the annealed 100, 200, 500, and 1000 Å SrTiO$_3$ / DyScO$_3$ films were similar, although variation in tuning was observed as a function of film thickness. The 100 Å SrTiO$_3$ / DyScO$_3$ had a significantly reduced tunability of 10%, while the 200 Å, 500 Å, and 1000 Å annealed samples exhibited tunability of 50%, 50%, and 65%, respectively (Fig. 4.3). It is possible that the 100 Å film is the only film in the series with a thickness under the critical thickness restricting the atomic displacement amplitude and thus reducing the tuning.

The temperature dependent dielectric permittivity of the SrTiO$_3$ / DyScO$_3$ film shows Curie-Weiss behavior with a peak at 293 K (Fig. 4.4). Unlike previous reports of ferroelectric SrTiO$_3$ films, which have broad peaks and show anomalously high permittivity in the ferroelectric regime,$^{9,18}$ the temperature dependence of our film agrees
quite well with theoretical Curie-Weiss behavior, exhibiting a sharp peak around $T_c$. We believe that the narrow peak observed in this samples may be a result of the largely uniform strain in the samples.

The location of the paraelectric to ferroelectric phase transition slightly below room temperature makes the SrTiO$_3$ films on DyScO$_3$ well suited for application to room temperature devices. Despite the low $Q$ of the films, an overall figure of merit, $(K)$, defined as $(Q \times$ tuning ratio) is comparable to some of the best materials we have measured to date. The significant tuning at small fields also makes these films well suited to a variety of low power applications.

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FIG. 4.1. θ-2θ x-ray diffraction scans of 500 Å SrTiO$_3$ films grown on LSAT and DyScO$_3$ substrates. Substrate peaks are labeled with a (*), and the plots are offset for clarity. Nelson-Riley analysis of the out-of-plane lattice constant, and off-axis scans to determine the in-plane lattice constant reveal that the SrTiO$_3$ is tetragonally distorted with an elongated out of plane lattice constant ($c = 3.93$ Å) on the LSAT substrate and shortened out of plane lattice constant ($c = 3.88$ Å) on the DyScO$_3$ substrate. In-plane lattice constants of 3.89 Å and 3.91 Å were measured for the films grown on LSAT and DyScO$_3$, respectively.
FIG. 4.2. Dielectric tunability of the as-grown 500 Å SrTiO$_3$ film grown on a DyScO$_3$ and LSAT substrate. The film grown on DyScO$_3$ shows 83% tunability for the application of ± 40 V at room temperature. The film grown on LSAT exhibits ~ 0% tunability with application of ± 40 V at room temperature.
FIG. 4.3. Dielectric tunability of annealed 100 Å, 200 Å, 500 Å, and 1000 Å SrTiO$_3$ / DyScO$_3$ films. The tuning ratio of the films generally decreases with film thickness, with ratios of 10%, 50%, 50%, and 65% for the 100 Å, 200 Å, 500 Å, and 1000 Å films, respectively. The 500 Å SrTiO$_3$ / DyScO$_3$ film shows a reduced dielectric constant and tuning ratio as compared to the as-grown 500 Å SrTiO$_3$ / DyScO$_3$ film (Fig. 4.2).
FIG. 4.4. Temperature dependent dielectric constant of the as-grown 500 Å SrTiO$_3$ film grown on DyScO$_3$. The film grown on DyScO$_3$ exhibits a sharp Curie-Weiss peak with $T_c = 293$ K. Plots are shown for applied voltages of 0, 10, 20, 30, and 40 volts.
REFERENCES

13. Pseudocubic indexing is used throughout this manuscript for DyScO$_3$.
CHAPTER 5

Growth and Characterization of Strained SrTiO$_3$ / BaTiO$_3$
Superlattices

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Growth and Characterization of Strained SrTiO$_3$ / BaTiO$_3$ Superlattices

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Epitaxial SrTiO$_3$ / BaTiO$_3$ short period superlattices were synthesized on (001) SrTiO$_3$ and (001) LSAT substrates by reactive molecular beam epitaxy. Both codeposition and sequential deposition of the Sr / Ti and Ba / Ti cations were used and reflection high-energy electron diffraction oscillations were utilized as a real time composition control technique. The structure and microstructure of the films were investigated by x-ray diffraction, transmission electron microbeam diffraction, and high-resolution transmission electron microscopy (HRTEM). Both diffraction and HRTEM studies revealed that the superlattices have nearly atomically abrupt interfaces that are maintained even after high temperature anneal. In addition, cross-sectional TEM reveals that all superlattice periods grown are coherently strained to the substrate.

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I. INTRODUCTION

Oxide superlattice structures have recently been shown to possess several enhanced functional properties. For instance, many studies have shown that strain can have a dramatic effect on the properties of ferroelectric materials. The lattice mismatch between cubic SrTiO$_3$ ($a = 3.905$ Å) and tetragonal BaTiO$_3$ ($a = 3.992$ Å, $c = 4.036$ Å) make SrTiO$_3$ / BaTiO$_3$ superlattices an excellent vehicle for investigation of strain effects on the dielectric properties of these compounds. In short-period superlattices grown on SrTiO$_3$ substrates, where the thickness of the individual BaTiO$_3$ layers do not exceed its critical thickness, BaTiO$_3$ will grow in biaxial compressive strain with in-plane lattice constants equal to those of SrTiO$_3$.\(^1\) Biaxial compressive strain has been experimentally demonstrated to increase the tunability,\(^2\) dielectric permittivity\(^3,4\) and remanent polarization\(^5\) in BaTiO$_3$ / SrTiO$_3$ superlattices as compared to their solid solution equivalents.

In addition to the possibility for enhanced dielectric properties that may result from strain in these superlattices, several studies have shown that certain atomic ordering in ferroelectric systems can produce unique electrical and structural effects. For instance, in some ferroelectric materials, novel atomic ordering obtained by compositional grading has been shown to produce a positive or negative charge translation of the hysteresis loop.\(^6\) In addition, it has been calculated that compositional grading in certain perovskite alloys may lead to enhanced electromechanical response.\(^7\) Superlattices offer an excellent route to digitally grade composition in ferroelectric systems by changing the shuttering sequences during the course of a growth. Digital grading has been used
successfully in compound semiconductor devices, such as quantum well structures, for years but to our knowledge has not been demonstrated in oxide superlattice structures.

In addition to composition profiles, several theoretical\(^8\) and experimental studies\(^9\) have recently suggested that superlattice periodicities that break the inversion symmetry of the superlattice structure may cause an asymmetry in the ferroelectric double well potential and provide a driving force for the growth of self-poling materials.\(^8\) Although asymmetric inversion symmetry structures are not investigated in this study, growing these structures is a natural extension of this work.

One of the primary obstacles to the study of these effects in SrTiO\(_3\)/BaTiO\(_3\) superlattices is the thermodynamic driving force for the formation of interfacial solid solution regions at the interface of the individual SrTiO\(_3\) and BaTiO\(_3\) layers. Mixing can result from surface roughness, the deposition of incomplete monolayer doses of SrTiO\(_3\) or BaTiO\(_3\), or from diffusion of Sr and Ba occurring at elevated growth temperatures. This solid solution mixing can complicate measurement of intrinsic superlattice properties. Few of the superlattice studies performed to date have sufficiently characterized the interfacial structure through high resolution TEM or careful x-ray diffraction studies.

We have investigated several different BaTiO\(_3\)/SrTiO\(_3\) superlattice periods, including compositionally graded structures, with particular attention to the relation between growth conditions and the structural quality as determined by x-ray diffraction and HRTEM.

**II. EXPERIMENTAL**

An MBE system (EPI 930)\(^{10}\) was used for the growth of all superlattices.\(^{11}\) Molecular beams of strontium, barium, and titanium were generated using a conventional
“low-temperature” effusion cell\textsuperscript{10} for strontium and barium metal (99.95% purity)\textsuperscript{12} and a Ti-Ball\textsuperscript{TM},\textsuperscript{13} heated by a precision power supply, for titanium.\textsuperscript{14} A homoepitaxial SrTiO\textsubscript{3} buffer layer about 2-6 nm thick was grown on the bare SrTiO\textsubscript{3} or LSAT substrates prior to the deposition of the SrTiO\textsubscript{3} / BaTiO\textsubscript{3} superlattice layers. Growth of this SrTiO\textsubscript{3} buffer layer allowed the shutter timing needed to provide stoichiometric monolayer doses of SrO and TiO\textsubscript{2} to be adjusted with an accuracy of 1\% using reflection high energy electron diffraction (RHEED) intensity oscillations.\textsuperscript{15} The Sr and Ba fluxes were measured with a quartz crystal microbalance before growth and timed wait statements were used for all elements during growth. Background oxygen pressures of $2 \times 10^{-7}$ Torr were used during growth resulting in the strong reduction of the substrate and film. Superlattices were grown on well oriented ($\pm 0.1^\circ$) SrTiO\textsubscript{3} (001) and LaAlO\textsubscript{3}—Sr\textsubscript{2}AlTaO\textsubscript{6} (LSAT) (001) substrates. The average flux of the strontium, barium and titanium sources was $1.0 \times 10^{14}$ atoms/cm$^2$·s for all growths. During growth, the substrate temperature was held at 680 °C.

TEM specimens were prepared by conventional cross-sectional TEM techniques. The cross-sectional slices were obtained by cutting BaTiO\textsubscript{3} / SrTiO\textsubscript{3} samples along the [100] or [010] direction of the (001) SrTiO\textsubscript{3} substrate. The slices were then glued face-to-face by joining the BaTiO\textsubscript{3} / SrTiO\textsubscript{3} surfaces together to make SrTiO\textsubscript{3} / [BaTiO\textsubscript{3} / SrTiO\textsubscript{3}] / SrTiO\textsubscript{3} sandwiches. Cross-sectional TEM specimens were then fabricated by mechanical grinding, polishing, and dimpling, followed by final Ar-ion milling of the sandwiches in a Gatan Precision Ion Polishing System (PIPS\textsuperscript{TM}, Model 691) at 4.5 kV to electron transparency. HRTEM studies were carried out using a JEOL
4000EX operated at 400 kV, which has a point-to-point resolution of 0.17 nm. Computer simulation was conducted using the EMS software package.

III. RESULTS/DISCUSSION

A. \([(\text{BaTiO}_3)_2 / (\text{SrTiO}_3)_2]_{20} \text{ superlattice:}\]

The shuttered deposition of the Sr, Ba, and Ti cations produced strong RHEED oscillations during the growth of all superlattice structures. Figure 5.1 shows the RHEED oscillations during the growth of a \([(\text{BaTiO}_3)_2 / (\text{SrTiO}_3)_2]_{20} \text{ superlattice on a LSAT substrate. The intensity oscillations of the BaTiO}_3 \text{ and SrTiO}_3 \text{ layers in the superlattice structure are nearly identical to the oscillations observed during the growth of single layers of SrTiO}_3 \text{ or BaTiO}_3 \text{ on LSAT or SrTiO}_3 \text{ substrates.}\]

An increase in the RHEED intensity is observed during the deposition of the Sr and Ba layers and a decrease is observed during the deposition of the Ti layer. In addition, an overall increase in the maximum intensity of the oscillations is observed during the deposition of the SrTiO$_3$ layer. Figure 5.2(a) shows the x-ray $\theta$-2$\theta$ scan with all superlattice reflections labeled. The in-plane orientation relationship between the film and the underlying substrate is \[100\] \([(\text{BaTiO}_3)_2 / (\text{SrTiO}_3)_2]_{20} \parallel [100] \text{ LSAT as determined by an x-ray $\phi$-scan of the 104 peaks of the same film (Fig. 5.2(b)). Figure 5.3 shows a high-resolution cross-sectional TEM image of the superlattice structure. Analysis of the atomic positions reveal that both the BaTiO$_3$ and SrTiO$_3$ are coherently strained to the lattice parameter of the LSAT (cubic, \(a = 7.737 \text{ Å}\)) substrate and are therefore in a biaxial compressive strain state. Unlike the other superlattice periods examined, however, the $2 \times 2$ superlattice shows
some regions where solid solution mixing occurred. This indicates that intermixing is most likely present in all superlattice structures on the order of ~ 1 unit cell.

**B. \([(\text{BaTiO}_3)_6 / (\text{SrTiO}_3)_5]\)_{20} superlattice:**

The RHEED oscillations during the growth of a \([(\text{BaTiO}_3)_6 / (\text{SrTiO}_3)_5]\)_{20} superlattice can be seen in Fig. 5.4. In this case, 1.2 monolayers of Ba and Ti were deposited in each supply cycle resulting in the growth of a \((\text{BaTiO}_3)_6 / (\text{SrTiO}_3)_5\) superlattice with a shuttering cycle of \((\text{BaTiO}_3)_5 / (\text{SrTiO}_3)_5\). During the homoepitaxial growth of SrTiO$_3$ a RHEED intensity oscillation envelope has been observed when more than a full monolayer dose of each cation was deposited in each shutter cycle.\(^{15}\) This envelope was not observed during the growth of this superlattice, however, presumably masked by the change in the maximum RHEED intensity present during the transition from the SrTiO$_3$ to BaTiO$_3$ layers. A series of superlattice growths with different fractions of a monolayer deposited during the BaTiO$_3$ deposition indicated that when ratios were used that did not end in full monolayer coverage at the completion of the BaTiO$_3$ cycle (e.g. 1.1 monolayers deposited for 5 cycles resulting in 5 1/2 unit cells) significantly fewer superlattice reflections were observed in the $\theta$-2$\theta$ x-ray diffraction pattern. This is most likely a result of increased interfacial mixing occurring at the interface of the incomplete layers.

Figure 5.5(a) shows the $\theta$-2$\theta$ x-ray diffraction scan of a \([(\text{BaTiO}_3)_6 / (\text{SrTiO}_3)_5]\)_{20} superlattice with nearly all superlattice reflections present for $2\theta < 55^\circ$. The presence of these superlattice reflections is indicative of sharp interfaces between the SrTiO$_3$ and BaTiO$_3$ layers, as well as a consistency in BaTiO$_3$ and SrTiO$_3$ layer thickness throughout
the superlattice structure. The in-plane orientation relationship between the film and the underlying substrate is [100] \([(BaTiO_3)_6 / (SrTiO_3)_5]_{20} \parallel [100] \) SrTiO_3 as determined by an x-ray φ-scan of the 10\overline{1}1 peaks of the same film (Fig. 5.5(b)). Figure 5.6 shows a cross-sectional HRTEM image of the same superlattice structure. Nearly atomically abrupt interfaces between the BaTiO_3 and SrTiO_3 layers are evident. An analysis of the atomic position in the BaTiO_3 indicate that it has lattice constants with a \(c/a\) ratio of 1.049±0.006 nm, with \(c = 0.4096±0.0005 \) nm and \(a = 0.3905±0.0005 \) nm. The \(c/a\) ratio for bulk BaTiO_3 is 1.011 indicating that confining the BaTiO_3 to the in-plane lattice parameters of SrTiO_3 has caused a significant tetragonal distortion in the lattice. A discussion of the effect this distortion has on the polarization of BaTiO_3, as determined by quantitative HRTEM analysis and first principle atomic position calculations will be published elsewhere.\(^{18}\)

In addition to variation of the shutter cycle doses, a comparison was also made between superlattices layers grown by sequential and codeposition. Figure 5.7 shows a θ-2θ x-ray diffraction scan of a \([(BaTiO_3)_6 / (SrTiO_3)_5]_{20} \) superlattice grown by codeposition of the Sr and Ti cations during the SrTiO_3 layers and the Ba and Ti cations during the BaTiO_3 layers. Like the superlattice grown by sequential deposition, nearly all of the expected superlattice reflections are present in this scan. High-resolution TEM images of the film indicate that it is also coherently strained and has sharp interfaces. This comparison indicates that for the specific case of SrTiO_3 and BaTiO_3, sequential or codeposition can be used successfully for the deposition of high quality superlattices.

C. Compositionally Graded \([(BaTiO_3)/(SrTiO_3)] \) superlattices:
A schematic of the compositionally graded structure grown in this study is shown in Fig. 5.8. The composition of this superlattice is digitally varied from pure SrTiO$_3$ to pure BaTiO$_3$. The grading is accomplished by increasing the number of BaTiO$_3$ unit cells ($x$) in each of 10 successive iterations of a ten unit cell (SrTiO$_3$)$_{10-x}$ / (BaTiO$_3$)$_x$ repeat structure. In other words, the growth begins with $x = 0$, containing 10 unit cells of SrTiO$_3$, continues with $x = 1$ containing 9 unit cells of SrTiO$_3$ and 1 unit cell of BaTiO$_3$, and proceeds until $x = 10$ contains 10 unit cells of BaTiO$_3$. RHEED oscillations during the growth of a portion of this structure can be seen in Fig. 5.9. Figure 5.10 shows a low magnification TEM image of the entire structure where the layering sequence can clearly be seen as it transitions from pure SrTiO$_3$ to pure BaTiO$_3$. HRTEM of the same film indicates that like the [(BaTiO$_3$)$_6$ / (SrTiO$_3$)$_5$]$_{20}$ superlattice, it contains sharp interfaces and is coherently strained to the SrTiO$_3$ substrate. The absence of dislocations in the 10 unit cell thick BaTiO$_3$ layer suggests that the critical thickness of BaTiO$_3$ on SrTiO$_3$ is $> 40$ Å. HRTEM studies we have performed on single layers of BaTiO$_3$ grown on SrTiO$_3$ indicate that partial relaxation has begun to occur in 60 Å films. Combining these studies indicates that the critical thickness for the SrTiO$_3$ / BaTiO$_3$ system is between 40 and 60 Å, thinner than some previously reported values obtained by RHEED and x-ray diffraction studies, but consistent with more recent RHEED studies. 

D. Effect of High Temp (1000 °C) Anneal:

The presence of a thermodynamic driving force for the formation of the solid solution Ba$_{1-x}$Sr$_x$TiO$_3$ compound from these metastable SrTiO$_3$ / BaTiO$_3$ superlattice structures makes a study of their stability under high temperatures interesting. Although prolonged exposure to high temperatures would be expected to promote interdiffusion of
the solid solution components, it has recently been shown that anneals at certain temperatures can also be used to improve the sharpness of the interface in other oxide superlattice structures.\textsuperscript{22}

Figure 5.11(a) and (b) shows a HRTEM image of the digitally graded superlattice before, and after, a 2 hour, 1000 °C oxygen anneal. No significant degradation of the interface structure is apparent in the cross-sectional images, suggesting that the interdiffusion of these solid solution components is relatively slow, even at elevated temperatures. Limited diffusion in the annealed film is evident, however, in an analysis of the sharpness of the superlattice reflections in a selected area electron diffraction image taken along the \([100]\) zone axis. Figure 5.12(a) shows distinct separation between the superlattice satellite peaks for the as-grown film, while more diffuse diffraction spots are evident in the annealed film (Fig. 5.12(b)).

These structural effects are magnified when a longer anneal time is used, giving more time for interdiffusion to occur. Figures 5.13(a) and (b) show a cross-sectional HRTEM image of the \([\text{(BaTiO}_3\text{)}_6 / \text{(SrTiO}_3\text{)}_3]_{20}\) superlattice before and after a 13 hour, 1000 °C anneal. While limited degradation of the interface can been seen in these cross-sectional images, selected area diffraction again shows a significant blurring of the satellite peaks in the annealed film (Fig. 5.14 (a) and (b)). These studies suggest that although interdiffusion is occurring between the SrTiO\textsubscript{3} and BaTiO\textsubscript{3} layers, these structures are relatively stable at elevated temperatures and should be able to withstand high temperature anneals that may be necessary to reduce oxygen vacancies and leakage current or the demanding processing conditions that may be necessary for device fabrication.
V. CONCLUSIONS

In conclusion, [(BaTiO$_3$)$_2$ / (SrTiO$_3$)$_2$]$_{20}$, [(BaTiO$_3$)$_6$ / (SrTiO$_3$)$_5$]$_{20}$ and digitally graded superlattices were synthesized by reactive MBE and were studied by x-ray diffraction and HRTEM. X-ray diffraction indicated that all of the superlattices grew epitaxially with a $c$-axis orientation on (001) SrTiO$_3$ and (001) LSAT substrates. In addition, nearly all of the expected superlattice reflections were present, indicating highly regular superlattice periodicities. HRTEM images reveal nearly atomic abrupt interfaces between the BaTiO$_3$ and SrTiO$_3$ layers, with interfacial mixing limited to ~1 unit cell. All superlattices were coherently strained to the SrTiO$_3$ substrate, causing significant tetragonal distortion in the BaTiO$_3$ crystal structure. High temperature anneals had limited effect on the structural quality of these superlattice, indicating that interdiffusion of the cations is relatively slow in this system. This work indicates that MBE can be used to grow oxide superlattice with comparable quality to what can be obtained in compound semiconductor systems.

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FIG. 5.1. RHEED oscillations during the growth of a [(SrTiO$_3$)$_2$ / (BaTiO$_3$)$_2$)$_{20}$ superlattice grown by the sequential deposition of Sr, Ba, and Ti. An increase in the RHEED intensity is seen during the deposition of the Sr and Ba cations, while a decrease is seen during Ti deposition.
FIG. 5.2. X-ray diffraction scans of the same \([(\text{SrTiO}_3)_2 / (\text{BaTiO}_3)_2]_{20}\) superlattice whose RHEED oscillations are shown in Fig. 5.1. (a) $\theta$-$2\theta$ x-ray diffraction scan showing several superlattice reflections. Substrate peaks are marked by asterisks (*). FWHM values in $2\theta$ of 0.36° and in $\omega$ of 0.3° were measured for the 007 peak, approaching the instrumental resolution of our picker 4-circle x-ray diffractometer. (b) X-ray $\phi$-scan of the \([(\text{SrTiO}_3)_2 / (\text{BaTiO}_3)_2]_{20}\) 104 peak showing the film is epitaxial with an in-plane orientation relationship of [100] \([(\text{SrTiO}_3)_2 / (\text{BaTiO}_3)_2]_{20}\) || [100] LSAT; $\phi = 0^\circ$ is aligned to be parallel to the [100] in-plane direction of the (001) LSAT substrate. Together these scans indicate that the lattice parameters of this \([(\text{SrTiO}_3)_2 / (\text{BaTiO}_3)_2]_{20}\) film are $a = b = 3.91 \pm 0.05$ Å and $c = 16.10 \pm 0.02$ Å.
FIG. 5.3. HRTEM image of the same \([(\text{SrTiO}_3)^2 / (\text{BaTiO}_3)^2]\) film whose x-ray diffraction pattern is shown in Fig. 5.2 taken along the [100] zone axis of the (001) LSAT substrate. Although the film is predominantly the \([(\text{SrTiO}_3)^2 / (\text{BaTiO}_3)^2]\) desired structure, some regions of \(\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3\) intermixing are also evident.
FIG. 5.4. RHEED oscillations during the growth of a [(SrTiO$_3$)$_6$ / (BaTiO$_3$)$_5$]$_{20}$ superlattice grown by the sequential deposition of Sr, Ba, and Ti. A schematic of the shuttering sequence used during growth can be seen under the oscillations, with shutters open during the same interval as the corresponding RHEED oscillation shown above. A dose of 1.2 monolayers of Ba and Ti were deposited in each shutter cycle, resulting in 6 unit cells of BaTiO$_3$ from 5 shuttering cycles.
FIG. 5.5. X-ray diffraction scans of the same [(SrTiO$_3$)$_5$/(BaTiO$_3$)$_6$]$_{20}$ superlattice whose RHEED oscillations are shown in Fig. 5.4. (a) $\theta$-2$\theta$ x-ray diffraction scan showing several superlattice reflections. Substrate peaks are marked by asterisks (*). FWHM values in $2\theta$ of 0.26° and in $\omega$ of 0.22° were measured for the 1020 peak, approaching the instrumental resolution of our picker 4-circle x-ray diffractometer. (b) X-ray $\phi$-scan of the [(SrTiO$_3$)$_5$/(BaTiO$_3$)$_6$]$_{20}$ 1011 peak showing the film is epitaxial with an in-plane orientation relationship of $[100]$ [(SrTiO$_3$)$_5$/(BaTiO$_3$)$_6$]$_{20}$$\parallel$$[100]$ SrTiO$_3$; $\phi = 0^\circ$ is aligned to be parallel to the [100] in-plane direction of the (001) SrTiO$_3$ substrate. Together these scans indicate that the lattice parameters of this [(SrTiO$_3$)$_5$/(BaTiO$_3$)$_6$]$_{20}$ film are $a = b = 3.88 \pm 0.05$ Å and $c = 44.01 \pm 0.02$ Å.
FIG. 5.6. HRTEM image of the same [(SrTiO$_3$)$_5$/(BaTiO$_3$)$_6$]$_{20}$ film whose x-ray diffraction pattern is shown in Fig. 5.5, taken along the [100] zone axis of the (001) SrTiO$_3$ substrate. Abrupt interfaces between the SrTiO$_3$ and BaTiO$_3$ layers can be seen. The BaTiO$_3$ layers are coherently strained to the in-plane lattice constant of SrTiO$_3$, causing an elongation of the $c$-axis BaTiO$_3$ lattice constant ($c = 0.4096 \pm 0.0005$ nm).
FIG. 5.7. \(\theta-2\theta\) x-ray diffraction scan of a \([(\text{SrTiO}_3)_5 / (\text{BaTiO}_3)_6]_{20}\) superlattice where both the SrTiO\(_3\) and the BaTiO\(_3\) layers were deposited by codeposition. Similar structural quality is observed to that seen in the sequentially deposited superlattice (Fig. 5.5(a)), with nearly all superlattice reflections present. Substrate peaks are marked by asterisks (*)..

SrTiO$_3$ Substrate

Homoepitaxial SrTiO$_3$
Buffer Layer

FIG. 5.8. Schematic structure of the compositionally graded superlattice structure grown by digitally varying the composition from pure SrTiO$_3$ to pure BaTiO$_3$. 
FIG. 5.9. Reflection High-Energy Electron Diffraction oscillations during the growth of a digitally graded superlattice where Sr, Ba, and Ti were all deposited sequentially. The number of SrTiO$_3$ layers varies from 4 to 1 as the number of BaTiO$_3$ layers subsequently increases from 7 to 9.
FIG. 5.10. A low-magnification TEM micrograph of the same superlattice whose RHEED oscillations are shown in Fig. 5.9 taken along the [100] zone axis of the (001) SrTiO$_3$ substrate. The composition profile can clearly be seen transitioning from SrTiO$_3$ to BaTiO$_3$ in ten unit cell increments.
FIG. 5.11. HRTEM image of the same graded superlattice structure shown in Fig. 5.10 (a) before and (b) after a 2 hour 1000 °C oxygen anneal. The BaO monolayers in each unit cell of BaTiO$_3$ are marked with arrows. Minimal difference in the interface structure of the as–grown and annealed structure can be seen, indicating that interdiffusion of the compounds is slow even at elevated temperatures.
FIG. 5.12. Selected-area electron diffraction pattern taken along the [100] zone axis of the (a) as-grown and (b) annealed digitally graded superlattice structures shown in Fig. 5.11. Analysis of the intensity of the superlattice reflections (bottom right) reveal a more diffuse pattern in the annealed film, indicative of some interdiffusion at the interface of the SrTiO$_3$ and BaTiO$_3$ layers.
FIG. 5.13. HRTEM image of the same [(SrTiO$_3$)$_5$ / (BaTiO$_3$)$_6$]$_{20}$ superlattice structure shown in Fig. 5.6(a) before and (b) after a 10 hour 1000 °C oxygen anneal. The BaO monolayers in each unit cell of BaTiO$_3$ are marked with arrows. Minimal difference in the interface structure of the as-grown and annealed structure can be seen, indicating that interdiffusion of the compounds is slow even at elevated temperatures.
FIG. 5.14. Selected-area electron diffraction pattern taken along the [100] zone axis of the (a) as grown and (b) annealed [(SrTiO$_3$)$_5$ / (BaTiO$_3$)$_6$]$_{20}$ superlattice structures shown in Fig. 5.13. Analysis of the intensity of the superlattice reflections (bottom right) reveal a more diffuse pattern in the annealed film, indicative of some interdiffusion at the interface of the SrTiO$_3$ and BaTiO$_3$ layers.
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CHAPTER 6

Epitaxial growth of the first five members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$
Ruddlesden-Popper homologous series

Epitaxial growth of the first five members of the Sr\(_{n+1}\)Ti\(_n\)O\(_{3n+1}\) Ruddlesden-Popper homologous series

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Abstract

The first five members of the Sr\(_{n+1}\)Ti\(_n\)O\(_{3n+1}\) Ruddlesden-Popper homologous series, i.e., Sr\(_2\)TiO\(_4\), Sr\(_3\)Ti\(_2\)O\(_7\), Sr\(_4\)Ti\(_3\)O\(_{10}\), Sr\(_5\)Ti\(_4\)O\(_{13}\), and Sr\(_6\)Ti\(_5\)O\(_{16}\), have been grown by reactive molecular beam epitaxy (MBE). A combination of atomic absorption spectroscopy (AA) and reflection high-energy electron diffraction (RHEED) intensity oscillations were used for the strict composition control necessary for the synthesis of these phases. X-ray diffraction and high-resolution transmission electron microscope images confirm that these films are epitaxially oriented and nearly free of intergrowths. Dielectric measurements indicate that the dielectric constant tensor coefficient \(\varepsilon_{33}\) increases from a minimum of 44±4 in the \(n = 1\) (Sr\(_2\)TiO\(_4\)) film to a maximum of 263±2 in the \(n = \infty\) (SrTiO\(_3\)) film.

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The controlled synthesis of a wide variety of homologous oxide crystal systems offers tremendous potential for tailoring the superconducting, ferroelectric, and dielectric properties of materials. Although much progress has been made in growing some superconducting homologous series phases by molecular beam epitaxy (MBE), intergrowths continue to prohibit the phase-pure growth of many of these systems. These intergrowths inhibit the identification of the electrical properties of individual members of these series. Similarly, intergrowths are seen in many dielectric homologous series and prevent the investigation of dielectric constant, dielectric loss, and dielectric tunability in the higher order members.

The \( n = \infty \) member of the \( \text{Sr}_{n+1} \text{Ti}_n \text{O}_{3n+1} \) Ruddlesden-Popper homologous series, \( \text{SrTiO}_3 \), exhibits a wide range of electrical properties from a high dielectric constant tunable paraelectric in its undoped form, to a metallic superconductor when doped with a variety of elements. It has been extensively studied as a substrate for perovskite oxides and for application in tunable dielectric devices, dynamic random access memory (DRAMs), and recently as an alternative gate oxide in metal oxide semiconducting field effect transistors (MOSFETs).

This broad range of physical properties and applications of \( \text{SrTiO}_3 \) make the investigation of the properties of other members of this homologous series (Fig. 1) an obvious step in the search for new materials with improved properties. For example, polycrystalline samples of \( \text{Sr}_2\text{TiO}_4 \) (\( n = 1 \)) and \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) (\( n = 2 \)) exhibit lower dielectric loss than \( \text{SrTiO}_3 \). Unfortunately, the study of these phases has been limited by several factors. First \( \text{SrTiO}_3 \) is the only member of the series that melts congruently. The single crystal growth of \( \text{Sr}_2\text{TiO}_4 \) is complicated (if not prohibited) by a phase transition at 1550 \( ^\circ \text{C} \) and a peritectic decomposition at 1860 \( ^\circ \text{C} \). \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) has a peritectoid decomposition at 1580 \( ^\circ \text{C} \), which prohibits growth of single crystals of this phase from the melt.
Conventional solid state techniques have been successful in making (polycrystalline) samples of only the \( n = 1 - 3 \) members. Previous attempts to synthesize intermediate \( (3 < n < \infty) \) members of this series have been unsuccessful. This has been explained by lattice energy calculations performed by several groups. The results of the calculations from all groups are in agreement that there is no driving force to form single-phase samples with intermediate \( n \). Due to the slight differences in calculated energies, however, there is some disagreement as to which phases are stable and which are metastable. For example, McCoy et al. concluded that \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) and \( \text{SrTiO}_3 \) are the only stable \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) phases, whereas Noguera concluded that \( \text{Sr}_2\text{TiO}_4 \), \( \text{Sr}_3\text{Ti}_2\text{O}_7 \), and \( \text{SrTiO}_3 \) are the only stable phases.

We have used MBE to overcome these challenging barriers to the synthesis of these materials. Each of the unit cells of this series is made up of different sequences of \( \text{SrO} \) and \( \text{TiO}_2 \) layers (Fig. 6.1). \( \text{SrTiO}_3 \) has the perovskite crystal structure with alternating \( \text{TiO}_2 \) and \( \text{SrO} \) layers; we refer to the combination of these two layers as a perovskite sheet. The \( n = 1 \) \( (\text{Sr}_2\text{TiO}_4) \) compound has an additional \( \text{SrO} \) layer (making a double \( \text{SrO} \) layer) disrupting each perovskite sheet along the \( c \)-axis. Subsequent members of the series have an increasing number of perovskite sheets separated by the double \( \text{SrO} \) layers. By changing the shuttering sequence of Sr and Ti ions to match the layering sequence of the desired phase, we have grown epitaxial films of these phases despite the fact that they melt incongruently, have structural transitions, and have energetically-degenerate driving forces for formation.

The growth of the \( n = 1 - 5 \) members of this series was achieved using an oxide MBE system. Before growth, the substrates were etched with a buffered HF solution to achieve a \( \text{TiO}_2 \)-terminated surface. Monolayer doses \((6.6\times10^{14} \text{ atoms/cm}^2)\) of Sr and Ti were deposited in a sequential manner on well oriented \((\pm 0.1^\circ)\) \( \text{SrTiO}_3 \) (001) substrates. For the double \( \text{SrO} \) layers in these structures, a dose corresponding to twice the monolayer
dose was delivered. The average flux of both the Sr and Ti sources was $1.0 \times 10^{14}$ atoms/cm$^2$·s for all growths. During growth, the substrate temperature was 750 °C as measured by an optical pyrometer. The substrate was immersed in a continuous flux of molecular oxygen, yielding a background pressure of $2 \times 10^{-7}$ Torr. The thicknesses of the films were 470 Å, 410 Å, 565 Å, 540 Å, and 590 Å, for the $n = 1 - 5$ films, respectively.

A combination of reflection high-energy electron diffraction (RHEED) intensity oscillations and atomic absorption spectroscopy (AA) was used to adjust the stoichiometry of the Sr and Ti molecular beams and ensure that a complete monolayer of each cation was deposited in each shuttered cycle. A series of growths revealed that the phase-pure synthesis of these compounds required that both the stoichiometry and absolute monolayer doses not be off by more than about 1%. The absolute dose required for one monolayer of Sr was determined by RHEED oscillations during the growth of SrO on SrTiO$_3$. During growth, AA was used to determine the shutter time needed to deposit this predetermined full-monolayer Sr dose. While AA provides the required composition control for Sr, it is less sensitive to the Ti molecular beam and monolayer-to-monolayer variations of 5% are common for our AA system and growth conditions. To overcome this problem, a method to adjust the Sr to Ti ratio was developed based on the change of the maximum intensity of the RHEED oscillations during the deposition of several monolayers of homoepitaxial SrTiO$_3$. The shutter time of the Ti source was adjusted until there was no increase or decrease in the maximum intensity of the RHEED oscillations, indicating a stoichiometric mixture of Sr and Ti. Once this shutter time was known, reproducible, stoichiometric, full monolayer doses of Ti and Sr could be delivered during the subsequent deposition of the higher $n$ phases.

Films grown outside this narrow composition window (i.e., where the stoichiometry or absolute monolayer doses are off by more than 1%) show clear evidence of intergrowths.
within the desired phase when examined by x-ray diffraction. A non-periodic stacking sequence in the c-direction (intergrowths) causes certain x-ray peaks to split, broaden, or shift in 2θ.\textsuperscript{21,22} The monolayer-by-monolayer deposition of films with the correct stoichiometry resulted in single-phase films whose x-ray peaks show narrow widths and the correct 2θ positions (Fig. 6.2). The c-axis lattice constant of these phases as determined by a Nelson-Riley\textsuperscript{23} analysis of the diffraction peak positions is 12.46±0.02 Å, 20.35±0.05 Å, 28.1±0.2 Å, 35.6±0.2 Å, and 43.5±1.0 Å for the \(n=1\) - 5 phases, respectively. This compares to the bulk reported lattice constants of 12.601 Å, 20.38 Å, and 28.1 Å for the \(n=1\) - 3 phases, respectively.\textsuperscript{7} X-ray φ-scans of the 103, 105, 107, 109, and 10\textsuperscript{11} peaks of the \(n=1\) - 5 films, respectively, indicated epitaxial, c-axis films with orientation (001) \(\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} || (001) \text{SrTiO}_3\) and [100] \(\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} || [100] \text{SrTiO}_3\). The φ-scans of the \(n=1\) - 5 films look identical; one example is shown in Fig. 6.3. The in-plane lattice constants determined from the x-ray measurements ranged from 3.83 ± 0.05 Å to 3.94 ± 0.05 Å.

A JEOL 4000EX high-resolution transmission electron microscope (HRTEM) operated at 400 kV was used to examine the local nanostructure of these films.\textsuperscript{24} Figure 6.4 is a cross-sectional HRTEM image showing the interface of each of these phases with the \(\text{SrTiO}_3\) homoepitaxial buffer layer. Equal spacing between the double SrO layers (light lines) indicates a single-phase film. All of the imaged areas of the \(n=1\) - 3 films look similar to the region shown in Fig. 6.4 with no intergrown regions observed. However, some intergrowths of higher \(n\) phases were observed in localized regions of the \(n=4\) and 5 films. In addition, defects consisting of vertical SrO double layers (see Fig. 6.4) were commonly seen adjacent to an intergrowth.\textsuperscript{24} Such vertically running SrO double layers have also been seen in bulk \(\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}\) samples and have been shown to have low-energy interfaces.\textsuperscript{17} They have also been observed in other perovskite
The intergrowths in these samples are most likely the result of slight monolayer-to-monolayer composition fluctuations during the deposition of the films. These (<1%) fluctuations are present in all of the growths, but the higher \( n \) phases seem to be more sensitive to them, as manifested by the more frequent intergrowths. We believe that theoretically there is no limit to the \( n \) value of these \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) phases that can be synthesized with MBE. In reality, we are limited by the composition control limits of the AA system and RHEED technique. An attempt to synthesize the \( n = 10 \) phase resulted in an x-ray diffraction pattern with some diminished and broadened peaks, indicating significant intergrowths.\(^{21}\)

The growth of epitaxial films allowed the \( \varepsilon_{33} \) dielectric constant tensor coefficient to be measured in these anisotropic materials. Previous measurements of polycrystalline \( \text{Sr}_2\text{TiO}_4 \) and \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) samples reported the average dielectric constant (\( \varepsilon_r \)) to be 38 and 50, respectively.\(^{11}\) Room temperature dielectric measurements were made on the \( n = 1, 2, \) and \( \infty \) members of this series with a scanning evanescent microwave microscope (SEMM)\(^{28,29}\) at 1 GHz and in a parallel plate capacitor structure with an HP 4284A at 1 kHz. The films measured with the SEMM were 1000 Å thick and grown directly on a (001) \( \text{LaAlO}_3—\text{Sr}_2\text{AlTaO}_6 \) (LSAT) substrate. LSAT (cubic, \( a = 7.737 \) Å)\(^{30}\) has an excellent lattice match with these phases and was used instead of \( \text{SrTiO}_3 \) because its low dielectric constant (\( \varepsilon_r = 22.5 \))\(^{31}\) did not interfere with the measurement. The capacitor structure was made by the MBE growth of a 1000 Å \( \text{Sr}_{0.85}\text{La}_{0.15}\text{TiO}_3 \) bottom electrode and a 1000 Å \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) film, followed by the \textit{ex situ} evaporation of 0.3 mm diam \text{Cr/Au} top electrodes.

Both of these techniques show excellent agreement for the values of \( \varepsilon_{33} \). The first member of this series, \( \text{Sr}_2\text{TiO}_4 \), has a dielectric constant tensor coefficient \( \varepsilon_{33} \) of 44±4, while \( \text{Sr}_3\text{Ti}_2\text{O}_7 \) has an \( \varepsilon_{33} \) of 86±6. The dielectric loss (\( \tan \delta \)) of all films measured was
lower than the detection limit of the SEMM (less than 1.5%). The magnitude of $\varepsilon_{33}$ makes these low $n\ Sr_{n+1}Ti_nO_{3n+1}$ phases not only of interest for tunable dielectric devices, but also for alternative gate oxides in MOSFETs. $Sr_2TiO_4$ has several potential advantages over $SrTiO_3$ in this application including its 38% better lattice match with Si, higher bandgap\textsuperscript{18} (to reduce leakage), lower thermodynamic driving force for reaction with Si, and greater stability against reduction.

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FIG. 6.1. Schematic of the crystal structure of a unit cell of the $n = 1$ (Sr$_2$TiO$_4$), $n = 2$ (Sr$_3$Ti$_2$O$_7$), $n = 3$ (Sr$_4$Ti$_3$O$_{10}$), $n = 4$ (Sr$_5$Ti$_4$O$_{13}$), $n = 5$ (Sr$_6$Ti$_5$O$_{16}$), and $n = \infty$ (SrTiO$_3$) members of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series. Circles represent Sr atoms, while Ti atoms are at the center of the octahedra (coordination polyhedra) with oxygen atoms at each apex.
FIG. 6.2. $\theta$-$2\theta$ x-ray diffraction scans of the first five members of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series grown on SrTiO$_3$ (001) substrates. Substrate peaks are labeled with a (*), and the plots are offset for clarity. The narrow peaks at the correct $2\theta$ positions indicate that each of the films is single phase.
FIG. 6.3. X-ray $\phi$-scan of the Sr$_2$TiO$_4$ 103 peak showing that the film is epitaxial with an in-plane orientation relationship of [100] Sr$_2$TiO$_4$ $\parallel$ [100] SrTiO$_3$. The full width at half-maximum (FWHM) of the peaks in $\phi$ is 0.38°, comparable to the instrumental resolution of our Picker 4-circle diffractometer. The $\phi$-scans of all the members of this homologous series grown look identical.
FIG. 6.4. Cross-sectional HRTEM images (from left to right) of the $n = 1$ ($\text{Sr}_2\text{TiO}_4$), $n = 2$ ($\text{Sr}_3\text{Ti}_2\text{O}_7$), $n = 3$ ($\text{Sr}_4\text{Ti}_3\text{O}_{10}$), $n = 4$ ($\text{Sr}_5\text{Ti}_4\text{O}_{13}$), and $n = 5$ ($\text{Sr}_6\text{Ti}_5\text{O}_{16}$) films. A model of the crystal structure of the $n = 1$ and $n = 5$ members are adjacent to the corresponding images showing the position of the SrO double layers and perovskite layers. The arrows mark the position of the interface of the films with the homoepitaxial SrTiO$_3$ buffer layer.
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CHAPTER 7

Band Structure of $\text{Sr}_2\text{TiO}_4 / \text{SrTiO}_3$ Heterojunctions

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Band Structure of $\text{Sr}_2\text{TiO}_4 / \text{SrTiO}_3$ Heterojunctions

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Abstract

$\text{Sr}_2\text{TiO}_4 / \text{SrTiO}_3$ heterojunctions have been grown by molecular beam epitaxy for investigation as a candidate system for the formation of a two-dimensional electron gas in oxides. We have used x-ray photoelectron spectroscopy to measure the valence band offset between $\text{Sr}_2\text{TiO}_4$ and $\text{SrTiO}_3$. In addition, diffuse reflectance was used to measure the bandgap of $\text{Sr}_2\text{TiO}_4$ powder. These measurements indicate a type II band alignment between the two materials, with a valence band offset of $-0.40 \pm 0.1$ eV, and a conduction band offset of $-0.2 \pm 0.1$ eV, suggesting that appropriately modulation doped heterostructures of these compounds may result in the formation of an accumulation layer at the interface of the materials.
The recent report of fractional quantum hall effect in tetracene\cite{1} has renewed interest in the investigation of similar phenomena in other unconventional semiconductor systems significantly different than group IV or compound semiconductors. One particular class of materials with properties drastically different than conventional semiconductors are perovskite semiconductors. The perovskite SrTiO$_3$, for example, has an effective mass \((m^*_e = 5m_0)^{2,3}\) and dielectric constant \((\varepsilon_r = 20,000\) at 4 K\)\cite{4} orders of magnitude higher than conventional semiconductors and the highest mobility \((\mu_{\text{bulk}} = 22,000\text{ cm}^2/\text{V} \cdot \text{s at } 2\text{ K})^5\) of any known oxide material. This completely different regime of semiconducting properties, coupled with the occurrence of superconductivity in appropriately electron-doped SrTiO$_3$, makes the study of the behavior of a two-dimensional electron gas (2DEG) in SrTiO$_3$ of great interest. The desire to study a 2DEG in SrTiO$_3$ was recognized long ago,\cite{6} but it remains to be achieved experimentally.

The intrinsic properties of SrTiO$_3$, the \(n = \infty\) end member of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper series, are well known, and it has been extensively studied for application to tunable dielectric devices,\cite{7,8} dynamic random access memory (DRAMs), and as an alternative gate oxide in metal-oxide-semiconductor field-effect transistors (MOSFETs).\cite{9,10} It is a metallic superconductor when doped with Nb, Ta, La, or by reduction,\cite{11} and has a bandgap of 3.2 eV.\cite{12} Unfortunately, unlike many conventional semiconductors systems, the band offset of many potential high bandgap barrier layers with SrTiO$_3$ is unknown, making the design of an optimal 2DEG structure difficult. We have investigated Sr$_2$TiO$_4$ / SrTiO$_3$ heterojunctions, the \(n = 1\) and \(n = \infty\) endmembers of the Sr$_{n+1}$Ti$_n$O$_{3n+1}$ Ruddlesden-Popper Homologous series, respectively, as a possible system for the formation of a 2DEG in SrTiO$_3$. Sr$_2$TiO$_4$ is a particularly attractive candidate due to its excellent chemical compatibility and lattice match with SrTiO$_3$,\cite{13} as well as its theoretically predicted bandgap that is 0.2 eV larger than SrTiO$_3$.\cite{14} In this study we
demonstrate the growth of epitaxial Sr$_2$TiO$_4$/SrTiO$_3$ heterojunctions and use x-ray photoelectron spectroscopy (XPS) and diffuse reflectance to experimentally determine the band offset between SrTiO$_3$ and Sr$_2$TiO$_4$ as well as the bandgap of Sr$_2$TiO$_4$.

An oxide MBE system was used for the growth of Sr$_2$TiO$_4$/SrTiO$_3$ heterostructures. Details on the growth and structure of these epitaxial Sr$_2$TiO$_4$ films have been described previously.$^{15,16}$ For this study, four epitaxial Sr$_2$TiO$_4$ films, with thicknesses of 24 Å, 30 Å, 36 Å, and 150 Å, were grown on a 150 Å SrTiO$_3$ homoepitaxial buffer layer on a buffered HF etched SrTiO$_3$ substrate.$^{17}$ All films were grown with sequential shuttering of the elemental strontium and titanium sources in a constant background pressure of 5.0×10$^{-7}$ O$_3$ at 650 °C. In addition to these heterostructures, one 150 Å homoepitaxial SrTiO$_3$ film was grown to obtain a reference spectrum for SrTiO$_3$ comparable to that used in the heterostructures. All films were grown at Penn State and shipped to Pacific Northwest National Laboratory (PNNL) for XPS analysis. Upon arrival at PNNL, the films were heated in an oxygen plasma to 600 °C and transferred in vacuum to the XPS chamber. Sharp reflection high-energy electron diffraction (RHEED) images of the films were observed at PNNL of comparable quality to those observed from the as-grown films at Penn State, indicating that limited surface degradation of the films occurred during shipping. Figure 7.1(a) shows a θ-2θ x-ray diffraction scan of the 150 Å Sr$_2$TiO$_4$ film indicating that it is phase pure and free of intergrowths. High resolution transmission electron microscopy (TEM) images of the interface between the SrTiO$_3$ and Sr$_2$TiO$_4$ show that it is commensurate and nearly free of defects that could act as scattering sites (Fig. 7.1(b)).$^{16}$

XPS core level and valence band spectra were obtained for all films using monochromatic Al Kα x-rays and a normal emission geometry. The XPS spectrometer was calibrated so the Au 4f$_{7/2}$ peak position and Fermi-edge inflection point were
determined to be 84.00±0.02 eV and 0.00±0.02 eV, respectively for a polycrystalline Au foil. Thus all binding energies are accurate on an absolute scale to within 0.02 - 0.03 eV over the binding energy range 0-100 eV. During measurement, an electron flood gun was used to reduce charging on the oxide surface, so the binding energies in all spectra are not absolute. The spectra obtained for the 150 Å SrTiO₃ homoepitaxial layer and the 150 Å Sr₂TiO₄ epitaxial film are “pure” (i.e. they do not contain components of the underlying films), while the 24 Å, 30 Å, 38 Å, films are sufficiently thin that the spectra are comprised of components of both the Sr₂TiO₄ and the underlying SrTiO₃ films.

The valence band offset between SrTiO₃ and Sr₂TiO₄ was determined by comparing the “pure” SrTiO₃ and Sr₂TiO₄ spectra with the heterostructure spectra. Specifically, the sum of the “pure” SrTiO₃ spectra and the properly scaled and energy shifted “pure” Sr₂TiO₄ spectra should match the spectra obtained from the heterostructures. The fit between these spectra should be optimized when the energy shift correctly accounts for the valence band offset between the compounds and the scaling factors correctly describe the inelastic attenuation of SrTiO₃ photoelectrons by the Sr₂TiO₄ film. Determination of the scaling factors was complicated by the fact that no unique elements were present in either heterostructure layer. As a result, the fit of the summed and heterostructure valence bands was maximized for both valence band offsets and scaling factors. As the attenuation factor was not known a priori, a variety of film thicknesses were investigated to select the heterostructure with an equal contribution from the substrate and film, resulting in maximum sensitivity to the offset of one with respect to the other. Figure 7.2 shows a three dimensional contour plot of the \( \chi^2 \) factors comparing the fit between the summed and 30 Å Sr₂TiO₄ / SrTiO₃ heterostructure valence band spectra as a function of valence band offset and scaling factor. For each scaling factor used, a local minimum in the \( \chi^2 \) values is achieved for a 0.40 eV energy shift. In addition, a global minimum is obtained for equally weighted SrTiO₃ and Sr₂TiO₄ spectra using a 0.40 eV energy offset. The excellent fit
between the valence band spectra for the 30 Å Sr$_2$TiO$_4$ / SrTiO$_3$ heterostructure and the summed spectra using the optimal fitting parameters of 0.40 eV valence band shift and scaling factors of $1(SrTiO_3)$ and $1(Sr_2TiO_4)$ can be seen in Fig. 7.3(a). On the other hand, significant discrepancy in the shape of the curves can be seen when a valence band offset between SrTiO$_3$ and Sr$_2$TiO$_4$ of zero is used, highlighting the sensitivity of this method for the determination of heterostructure valence band alignment (Fig. 7.3(b)). Analysis of the 24 Å and 38 Å films are in close agreement with the 30 Å film, with a valence band offset of 0.3 eV and 0.5 eV, respectively, maximizing the fit. Maximized scaling factors of $1.5(SrTiO_3)$ and $1.0(Sr2TiO_4)$ for the 24 Å film, and $1.0(SrTiO_3)$ and $2.25(Sr_2TiO_4)$ for the 38 Å film are qualitatively consistent with those calculated from a first order thickness dependent absorption model.

Before the conduction band offset could be determined the bandgap of Sr$_2$TiO$_4$ had to be measured. Powders of SrTiO$_3$ and Sr$_2$TiO$_4$ were calcined for 6 hours at 1200 °C, ball milled, and reacted at 1400 °C for 12 hours. Powder x-ray diffraction revealed phase pure SrTiO$_3$ and Sr$_2$TiO$_4$ samples. Figure 7.4 shows the reflectance spectra obtained from the SrTiO$_3$ and Sr$_2$TiO$_4$ powders. Linear fitting of the absorption edge indicates an optical bandgap of 3.17 ± 0.03 eV for SrTiO$_3$ and 3.38 ± 0.03 eV for Sr$_2$TiO$_4$. The value for SrTiO$_3$ is in good agreement with previously measured values$^{12}$ and serves as a check of our measured Sr$_2$TiO$_4$ value. It is important to note, however, that unlike SrTiO$_3$, Sr$_2$TiO$_4$ has a tetragonal crystal structure ($a = b = 3.88$, $c = 12.601$)$^{13}$ and thus may contain an anisotropic band structure. The value obtained using the diffuse reflectance method represents an average of the optical bandgap in all directions.

The band diagram for the SrTiO$_3$ / Sr$_2$TiO$_4$ heterojunction is shown in figure 7.5 with the valence and conduction band offsets calculated from the XPS and reflectance measurements. The materials form a type II junction, with a valence and conduction band offset of $-0.40 \pm 0.1$ eV and $-0.20 \pm 0.1$ eV, respectively. The -0.2 eV conduction
band offset suggests that a heterostructure with donor doped SrTiO$_3$ and un-doped Sr$_2$TiO$_4$ may be appropriate for the creation of a confined carrier system. Activation energies of 0.08 eV for oxygen,$^5$ 0.1–0.12 eV for La,$^{18}$ and 0.10 eV for Nb$^{18}$ have been reported for SrTiO$_3$, indicating that the carrier level may be sufficiently shallow in a doped-SrTiO$_3$ / Sr$_2$TiO$_4$ heterostructure for carrier spillover to occur. This work represents the first step in the investigation of the fundamental materials properties and electronic structure necessary for the possible future realization of a 2DEG in such oxide heterojunctions.

The authors gratefully acknowledge the support of the Department of Energy under grant DE-FG02-97ER45638 for the development of the thin film growth technique and structural characterization. We also acknowledge stimulating discussions with Ying Liu and Harold Hwang. The portion of this work conducted at PNNL was carried out in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research.
FIG 7.1. Structural characterization indicates that high quality Sr$_2$TiO$_4$ films can be grown epitaxially on SrTiO$_3$. (a) $\theta$-$2\theta$ x-ray diffraction scan of the 150 Å Sr$_2$TiO$_4$ film used to obtain a reference spectra for Sr$_2$TiO$_4$ shows sharp peaks and a phase pure film. (b) Cross-sectional TEM image of the interface between Sr$_2$TiO$_4$ and SrTiO$_3$. These images reveal that the interface, indicated with the arrows next to the image, is commensurate and nearly free of defects.
FIG. 7.2. Contour plot of the $\chi^2$ values indicating the fit between the 30 Å Sr$_2$TiO$_4$/SrTiO$_3$ heterostructure spectra and the summed SrTiO$_3$ and Sr$_2$TiO$_4$ spectra as a function of Sr$_2$TiO$_4$ spectra scaling factor (x-axis) and Sr$_2$TiO$_4$ energy offset (y-axis). For the 30 Å heterostructure, a $\chi^2$ minimum at 0.4 eV energy offset and 1.0 scaling factor is observed.
FIG. 7.3. Comparison of the summed SrTiO$_3$ and Sr$_2$TiO$_4$ spectra to that of the 30 Å Sr$_2$TiO$_4$ / SrTiO$_3$ heterostructure, for two different valence band offsets. (a) The Sr$_2$TiO$_4$ spectrum (1) is shifted to higher binding energies by 0.4 eV with respect to the SrTiO$_3$ spectrum (2), simulating a 0.4 eV valence band offset between SrTiO$_3$ and Sr$_2$TiO$_4$. The excellent fit of the summed spectra (3) to the heterostructure spectra (4) indicates that the appropriate scaling factor and valence band offset was used. (b) Sr$_2$TiO$_4$ spectrum (1) is not shifted with respect to the SrTiO$_3$ spectrum (2), simulating a 0.0 eV valence band offset between the SrTiO$_3$ and Sr$_2$TiO$_4$. The poor fit of the summed spectra (3) to the heterostructure spectra (4) as compared to the fit in figure 7.3(a) indicates the sensitivity of this technique for the determination of valence band offset in heterostructures with identical chemical composition.
FIG. 7.4. Powder reflectance spectra of (1) SrTiO$_3$ and (2) Sr$_2$TiO$_4$ powders. The optical bandgap of Sr$_2$TiO$_4$ and SrTiO$_3$ are determined by finding the intersection of the slope of the absorption curve with the x-axis.
FIG. 7.5. Bandstructure of Sr$_2$TiO$_4$/SrTiO$_3$ heterostructure showing a type II junction. Valence and conduction band offsets of $-0.40 \pm 0.1$ eV and $-0.20 \pm 0.1$ eV, respectively, are suggested by our experimental results.
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CHAPTER 8

Epitaxial growth of the first five members of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series

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Epitaxial growth of the first five members of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series

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Abstract

The first five members of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series, $\text{Sr}_2\text{RuO}_4$, $\text{Sr}_3\text{Ru}_2\text{O}_7$, $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, $\text{Sr}_5\text{Ru}_4\text{O}_{13}$, and $\text{Sr}_6\text{Ru}_5\text{O}_{16}$ have been grown by reactive molecular beam epitaxy (MBE). This is the first report of epitaxial thin films of the $\text{Sr}_3\text{Ru}_2\text{O}_7$ and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ phases, and the first time $\text{Sr}_5\text{Ru}_4\text{O}_{13}$ and $\text{Sr}_6\text{Ru}_5\text{O}_{16}$ have been grown in any form. Reflection high-energy electron diffraction (RHEED) intensity oscillations were used for the strict composition control necessary for the synthesis of these phases. X-ray diffraction confirms that these films are epitaxially oriented and nearly free of intergrowths.
Recently, the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series, has received a significant amount of attention as a result of its interesting electronic and magnetic properties. The $n = \infty$ member of this series, SrRuO$_3$, is a ferromagnetic ($T_c = 160$ K) and is widely used as a metallic oxide electrode. The $n = 1$ member, Sr$_2$RuO$_4$, is a paramagnetic metal and is the only known superconducting layered perovskite that does not contain copper. Recent theoretical work has suggested that Sr$_2$RuO$_4$ is an unconventional p-wave superconductor. Experimental work done on single crystal samples has supported these theoretical predictions, but unambiguous determination of the pairing state is difficult and has not been achieved. The growth of superconducting thin films of Sr$_2$RuO$_4$ is essential if phase sensitive measurements, similar to those performed on the high $T_c$ cuprates, are to be used to help clarify the superconducting pairing state of this compound. Although epitaxial thin films of Sr$_2$RuO$_4$ have been grown by pulsed laser deposition (PLD), none of these samples exhibit superconductivity. A recent TEM study has suggested that PLD grown Sr$_2$RuO$_4$ films have a high density of crystallographic defects that may be responsible for the suppression of superconductivity in these samples. We believe that the layer-by-layer growth of Sr$_2$RuO$_4$ by MBE may help to reduce the structural defects in these films and be an important step in the realization of superconducting thin films.

The transition from a ferromagnetic to superconducting paramagnetic compound in the two end members of this series makes the investigation of the transport and magnetic properties of intermediate members of this series interesting. However, despite the success in growing the end member compounds in both single crystal and epitaxial thin film form, the growth of intermediate members of this series has not been as successful. Single crystals of the $n = 2$ and $3$ phases have been reported, although these samples all contain a limited number of intergrowths of other phases. These intergrowths complicate the
unambiguous identification of the magnetic properties of individual phases. For instance, conflicting reports on the magnetic properties of Sr\textsubscript{2}Ru\textsubscript{2}O\textsubscript{7} have been published, with some authors claiming it has a ferromagnetic transition at 100 K\textsuperscript{17} and others observing no magnetic ordering to 4K.\textsuperscript{18} More recent studies indicate that it is, in fact, a paramagnetic metal suggesting that the transition seen in some samples may an artifact of other intergrown phases. Previous attempts to synthesize intermediate (4 < n < ∞) members of this series have resulted in samples with a significant number of intergrowths of other phases.

Recently, we have used molecular beam epitaxy (MBE) to synthesize epitaxial thin films of the first 5 member of the Sr\textsubscript{n+1}Ti\textsubscript{n}O\textsubscript{3n+1} Ruddlesden-Popper homologous series.\textsuperscript{19} Like the Sr\textsubscript{n+1}Ru\textsubscript{n}O\textsubscript{3n+1} Ruddlesden-Popper homologous series, intergrowths had previously prevented the growth of intermediate (4 < n < ∞) members of this series. Because the crystal structure of the Sr\textsubscript{n+1}Ru\textsubscript{n}O\textsubscript{3n+1} compounds are identical to the Sr\textsubscript{n+1}Ti\textsubscript{n}O\textsubscript{3n+1} series, with each member made up of different sequences of SrO and RuO\textsubscript{2} layers (Fig. 8.1), we believe that the layering capability of MBE may also be effective in overcoming the challenging barriers to the synthesis of intermediate members of this series.

The crystal structure of SrRuO\textsubscript{3} consists of alternating RuO\textsubscript{2} and SrO layers, the combination of which will be referred to as a perovskite sheet. The n = 1 (Sr\textsubscript{2}RuO\textsubscript{4}) compound has an additional SrO layer (making a double SrO layer) disrupting each perovskite sheet along the c-axis. Subsequent members of the series have an increasing number of perovskite sheets separated by the double SrO layers. By changing the shuttering sequence of Sr and Ru ions to match the layering sequence of the desired phase, we have grown epitaxial films of these phases.

The growth of the n = 1 - 5 members of this series was achieved using an oxide MBE system. Before growth, the substrates were etched with a buffered HF solution to achieve a TiO\textsubscript{2}-terminated surface.\textsuperscript{20} Monolayer doses (6.6×10\textsuperscript{14} atoms/cm\textsuperscript{2}) of Sr and Ru
were deposited in a sequential manner on well oriented (±0.1°) SrTiO₃ (001) and
(001) LaAlO₃—Sr₂AlTaO₆ (LSAT) substrates. For the double SrO layers in these
structures, a dose corresponding to twice the monolayer dose was delivered. The average
flux of both the Sr and Ru sources was 1.0×10¹⁴ atoms/cm²·s for all growths. During
growth, the substrate temperature was 620 °C as measured by an optical pyrometer. The
substrate was immersed in a continuous flux of molecular oxygen, yielding a background
pressure of 1×10⁻⁶ Torr. The thicknesses of the films were 880 Å, 680 Å, 672 Å,
648 Å, and 666 Å, for the n = 1 - 5 films, respectively.

Reflection high-energy electron diffraction (RHEED) intensity was used to adjust the
stoichiometry of the Sr and Ru molecular beams and ensure that a complete monolayer of
each cation was deposited in each shuttered cycle. A series of growths revealed that the
phase-pure synthesis of these compounds required that both the stoichiometry and absolute
monolayer doses not vary by more than about 5%. The absolute dose required for one
monolayer of Sr was determined by RHEED oscillations during the growth of SrO on
SrTiO₃. During growth, timed Sr shutter wait statements were used to deposit this
predetermined full-monolayer Sr dose. While the Sr flux remains constant to within
1 – 2% throughout a typical 1 hour growth, the Ru flux, delivered from a Thermionics
3 kW rod fed e-gun, demonstrated significant drift throughout the course of a growth.
Decreases in the Ru flux of 10 – 50% during growth were common, even after substantial
time was allowed before growth for the source to stabilize. To overcome this problem, a
method to adjust the Sr to Ru ratio was developed based on the change of the maximum
intensity of the RHEED oscillations during the deposition of the Srₙ₊₁RuₙO₃ₙ₊₁ film. The
shutter time of the Ru source was adjusted to maintain consistent RHEED intensity
oscillations, indicating a stoichiometric mixture of Sr and Ru. During growth this shutter
time was continually increased to ensure stoichiometric, full monolayer doses of Ru were delivered during each shutter cycle.

Films grown outside this narrow composition window (i.e., where the stoichiometry or absolute monolayer doses are off by more than 5%) show clear evidence of intergrowths within the desired phase when examined by x-ray diffraction. A non-periodic stacking sequence in the c-direction (intergrowths) causes certain x-ray peaks to split, broaden, or shift in \( 2\theta \).\textsuperscript{21,22} The monolayer-by-monolayer deposition of films with the correct stoichiometry resulted in single-phase films whose x-ray peaks show narrow widths and the correct \( 2\theta \) positions (Fig. 8.2). The \( c \)-axis lattice constant of these phases as determined by a Nelson-Riley\textsuperscript{23} analysis of the diffraction peak positions is

\[
12.82\pm0.02 \, \text{Å}, \ 20.85\pm0.05 \, \text{Å}, \ 28.8\pm0.2 \, \text{Å}, \ 37.2\pm0.4 \, \text{Å}, \ \text{and} \ 44.7\pm1.0 \, \text{Å}
\]

for the \( n = 1 - 5 \) phases, respectively. This compares to the bulk reported lattice constants of 12.702 Å and 20.552 Å for the \( n = 1 - 2 \) phases, respectively.\textsuperscript{24} X-ray \( \phi \)-scans of the 103, 105, 118, 11\textsuperscript{10}, and 11\textsuperscript{12} peaks of the \( n = 1 - 5 \) films, respectively, indicate epitaxial, \( c \)-axis films with orientation \((001) \text{Sr}_{n+1} \text{Ru}_n \text{O}_{3n+1} \parallel (001) \text{SrTiO}_3 \) (LSAT) and \([100] \text{Sr}_{n+1} \text{Ru}_n \text{O}_{3n+1} \parallel [100] \text{SrTiO}_3 \) (LSAT). The \( \phi \)-scans of the \( n = 1 - 2 \) and \( n = 3 - 5 \) films look identical; one example is shown in Fig. 8.3. The in-plane lattice constants determined from the x-ray measurements are all within experimental error of the bulk lattice parameter.

The growth of epitaxial films of these phases by MBE is an important first step in the realization of superconducting \( \text{Sr}_2\text{RuO}_4 \) films, and in the identification of the magnetic properties of the intermediate members of this series. Currently, transport and magnetic measurements are being made on these films, the results of which will be published elsewhere.
The authors gratefully acknowledge the support of the Department of Energy under grant DE-FG02-97ER45638 for the development of the thin film growth technique and structural characterization. JHH acknowledges a Motorola/SRC graduate fellowship.
FIG. 8.1. Schematic of the crystal structure of a unit cell of the $n = 1$ (Sr$_2$RuO$_4$), $n = 2$ (Sr$_3$Ru$_2$O$_7$), $n = 3$ (Sr$_4$Ru$_3$O$_{10}$), $n = 4$ (Sr$_5$Ru$_4$O$_{13}$), $n = 5$ (Sr$_6$Ru$_5$O$_{16}$), and $n = \infty$ (SrRuO$_3$) members of the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series. Circles represent Sr atoms, while Ru atoms are at the center of the octahedra (coordination polyhedra) with oxygen atoms at each apex.
FIG. 8.2. $\theta$-2$\theta$ x-ray diffraction scans of the $n = 1$ member of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper homologous series grown on a LSAT (001) substrate and the $n = 2$ - 5 members grown on $\text{SrTiO}_3$ (001) substrates. Substrate peaks are labeled with a (*), and the plots are offset for clarity. The narrow peaks at the correct 2$\theta$ positions indicate that each of the films is nearly single phase.
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CHAPTER 9

Dielectric Tensor and Optical Bandgap Measurement of Single Crystals of the Alternative Gate Oxide Candidates $\text{ReScO}_3$

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Dielectric Tensor and Optical Bandgap Measurement of Single Crystals of the Alternative Gate Oxide Candidates ReScO$_3$

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Abstract
Currently, a variety of perovskite materials are being considered as replacement gate dielectrics in silicon MOSFETs. Many of the intrinsic properties of these compounds are unknown, making the selection of materials best suited for this application difficult. We have grown single crystals of GdScO$_3$, DyScO$_3$, SmScO$_3$, and NdScO$_3$ with the Czochralski or floating zone growth techniques and measured their dielectric tensor coefficients and optical bandgaps as a first step in the investigation of their potential as alternative gate dielectrics. Oriented slices of the GdScO$_3$ and DyScO$_3$ crystals were prepared along the three principle axes and the dielectric tensor coefficients were measured using a parallel plate capacitor configuration. These measurements indicate that at room temperature the dielectric constant tensor coefficients for GdScO$_3$ are $\varepsilon_{11} = 22.8$, $\varepsilon_{22} = 19.2$, and $\varepsilon_{33} = 29.5$, and that the dielectric tensor coefficients for DyScO$_3$ are $\varepsilon_{11} = 22.0$, $\varepsilon_{22} = 18.8$ and $\varepsilon_{33} = 35.5$. Measurements on crystals of SmScO$_3$ and NdScO$_3$ revealed dielectric constants of 18 and 23, respectively. Optical bandgaps of 6.5 eV for GdScO$_3$ and $\sim$ 5.5 eV for SmScO$_3$ were measured using transmission measurements and ellipsometry. The magnitude of the bandgap and dielectric constants of these materials, combined with their predicted thermodynamic stability with silicon, make them excellent candidates for alternative gate dielectrics for Si MOSFETs.

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I. INTRODUCTION
Currently, a variety of binary oxides including HfO$_2$, ZrO$_2$, La$_2$O$_3$, Gd$_2$O$_3$, and Y$_2$O$_3$ and ternary silicates including YSi$_x$O$_y$, GdSi$_x$O$_y$, ZrSi$_x$O$_y$, and HfSi$_x$O$_y$ are being investigated as alternative gate dielectrics for Si MOSFETs. These materials are attractive because of their thermodynamic stability with silicon and because their large bandgap (> 4 eV) helps to prevent gate leakage. However, because the dielectric constant of these binary oxides and silicates are all below 23, the scaling of future devices may be limited. By expanding the search to include ternary oxides, materials with higher dielectric constants may be found which still have the advantage of a large bandgap and thermodynamic stability with silicon. Although there is insufficient thermodynamic data available to conclude that any ternary compounds are stable in contact with silicon, a first order approximation based on bond strength considerations suggests that stable ternary compounds will be comprised of stable binary oxides. Sc$_2$O$_3$, and the rare earth (Re) oxides of Sm$_2$O$_3$, La$_2$O$_3$, Dy$_2$O$_3$, Gd$_2$O$_3$, Ho$_2$O$_3$, and Nd$_2$O$_3$, may be thermodynamically stable with silicon, making the perovskites SmScO$_3$, LaScO$_3$, DyScO$_3$, GdScO$_3$, NdScO$_3$, and HoScO$_3$ a promising class of materials to investigate for alternative gate dielectrics. Although the single crystal growth of some ReScO$_3$ has been reported in the past, little data on the dielectric constants or bandgap of these compounds exists. Such data is crucial in the selection of appropriate materials for study as possible alternative gate dielectrics. Thus, we have grown single crystals of GdScO$_3$, DyScO$_3$, SmScO$_3$, and NdScO$_3$ with the Czochralski or floating zone growth techniques and measured their dielectric tensor coefficients and optical bandgaps as a first step in the investigation of their potential as alternative gate dielectrics.
II. EXPERIMENTAL

A. Crystal Growth

DyScO$_3$ and GdScO$_3$ single crystals were grown using the automated Czochralski technique with RF-induction heating. Pre-dried powders of Dy$_2$O$_3$, Gd$_2$O$_3$, and Sc$_2$O$_3$ were mixed in the stoichiometric ratio, pressed, and sintered at about 1400 °C for 15h. Due to the high melting temperature of DyScO$_3$ and GdScO$_3$ (~ 2100 °C), a crucible and afterheater made of iridium were used. Flowing nitrogen or argon was used as the growth atmosphere. Due to the lack of seed crystals, the initial growth experiments were performed with an iridium seed rod. Because both materials tend to grow as large single crystalline grains, suitable seeds could be selected at a very early stage. The DyScO$_3$ crystals were pulled along the [010] orientation and the GdScO$_3$ crystals along the [001] orientation. The pulling rate was 1.5-2 mm h$^{-1}$ and the rotation rate was 10 min$^{-1}$. The crystals were 35-50 mm in length and 18 mm in diameter. The DyScO$_3$ crystals had a light yellow color and the GdScO$_3$ crystals were colorless (Fig. 9.1).

In addition to the Czochralski growth of GdScO$_3$ and DyScO$_3$, the single crystal growth of HoScO$_3$, YScO$_3$, LaScO$_3$, and SmScO$_3$ was also attempted using the floating zone technique. In all cases, pre-dried powders of the Re$_2$O$_3$ and Sc$_2$O$_3$ were ground, pressed into a rod, and sintered at 1250 °C for 6 hours. The floating zone machine was a Giro (model # ???), and heating was performed with two bulbs at the focal point of elliptical mirrors. Unfortunately, the 1 kW rated output power of the quartz-halogen lamps used in this floating zone system coincided with the melting temperature of the compounds, limiting the size of the crystals that could be grown to < 2 mm diameter.
The existing $Re_2O_3$—$Sc_2O_3$ binary phase diagrams show a distinct transition between the $Dy_2O_3$—$Sc_2O_3$ and the $Ho_2O_3$—$Sc_2O_3$ systems. The rare earth elements of La, Nd, Sm, Eu, Gd and Dy all form congruently melting, single phase $ReScO_3$ compounds, while the oxides of Ho, Y, Er, Tm, Yb, Lu, and In form complete solid solutions with $Sc_2O_3$. Although $HoScO_3$ has been synthesized with solid state techniques, all of our results confirm the existing phase diagrams. Analysis of our Y-Sc-O and Ho-Sc-O crystals revealed that they were solid solution mixtures of $Ho_2O_3$—$Sc_2O_3$ and $Y_2O_3$—$Sc_2O_3$, not the desired perovskite structure of $HoScO_3$ and $YScO_3$.

The only compound that did not behave according to its phase diagram was $LaScO_3$. Attempts to grow $LaScO_3$ resulted in crystals that were a mixture of three different phases including $LaScO_3$, $Sc_2O_3$, and a third, unidentified phase. X-ray analysis of the post annealed polycrystalline feed rod showed single phase $LaScO_3$, consistent with the existing phase diagram. The reason for the introduction of second phases during melting is not clear and requires more study.

$SmScO_3$ and $NdScO_3$ crystals were successfully grown with the floating zone technique. A powder pressed polycrystalline seed rod was used to start the growth, and the crystals quickly transitioned (3-5 mm) from polycrystalline to single crystal at a growth rate of 10 mm/hr. The as-grown crystals were approximately 1 mm in diameter × 1 cm in length, and the growth direction did not correspond to a low index plane.

**B. Dielectric Characterization**

Because GdScO$_3$, DyScO$_3$, SmScO$_3$, and NdScO$_3$ are orthorhombic at room temperature, their dielectric tensor contains three independent coefficients that can be
measured along the three principle crystal axis. Oriented slices of GdScO₃ and DyScO₃ samples were cut from the as-grown untwinned single crystals along the [100], [010], and [001] directions and the dielectric tensor coefficients were measured using a parallel plate capacitor configuration. Gold electrodes with an area of 1 cm² were evaporated on both sides of the 0.05 cm thick slabs, and capacitance measurements were made at room temperature with an HP 4284A using a 16034E test fixture at 1 MHz. No edge capacitance corrections were used because of the large ratio of the electrode area to thickness of the samples.

C. Bandgap measurement

A Far UV spectroscopic ellipsometer¹⁵,¹⁶ was used to determine the ellipsometric spectral response of the GdScO₃, and SmScO₃ crystals. The system operates for photon energies up to 9 eV, avoiding the absorption of atmospheric oxide by placing the entire system in a glove box filled with nitrogen. In addition, for GdScO₃ we measured transmission directly in a Perkin Elmer UV/VIS spectrometer, Lambda 40. The analysis procedure accounted for a surface damage layer left by the polishing. We modeled the measured spectra by assuming a two-layer structure, with the surface damaged layer simulated by using the Bruggeman effective medium approximation for a mixture of dielectric and voids while the substrate was the pure dielectric. Following an initial assumption for the thickness and the composition of the surface layer, an initial spectrum was inferred. Iteratively altering the thickness and the composition of the surface layer while seeking a stable and continuous output spectrum eventually converged upon an optimum surface layer structure and a final dielectric spectrum. For GdScO₃ this analysis used both transmission and ellipsometric spectra, whereas we only measured the
ellipsometric response for SmScO$_3$. After obtaining a dielectric spectrum $\varepsilon_1$ and $\varepsilon_2$ we converted them to the complex index of refraction, $n + ik$. The absorption coefficient $\alpha$ was then calculated from the equation $\alpha = 4\pi k/\lambda$, where $k$ is the imaginary component of the complex refractive index, and $\lambda$ is the wavelength in units of cm.

III. RESULTS:

A. Dielectric Tensor

The full dielectric tensor coefficients of the samples are as follows:

GdScO$_3$: $\varepsilon_{11} = 22.8$, $\varepsilon_{22} = 19.2$ and $\varepsilon_{33} = 29.5$

DyScO$_3$: $\varepsilon_{11} = 22.1$, $\varepsilon_{22} = 18.8$ and $\varepsilon_{33} = 35.5$

The dielectric loss, $\tan \delta$, was less than $10^{-4}$ for all samples measured. Figures 9.2(a) and 9.3(a) show three-dimensional representations of the dielectric tensor coefficients for GdScO$_3$ and DyScO$_3$, respectively. Figures 9.2(b), 9.2(c), 9.2(d) and 9.3(b), 9.3(c), 9.3(d) show two-dimensional cross-sections of these tensor coefficients along the major crystallographic planes.

Measurements made on (110) oriented slabs of both these crystals show a dielectric constant of 21.4 for GdScO$_3$ and 20.5 for DyScO$_3$. The dielectric constant in this direction is comprised of components of the $\varepsilon_{11}$ and $\varepsilon_{22}$ tensor values, and serves as a check of these tensor coefficients. Calculation of the dielectric constant in this direction based on the measured $\varepsilon_{11}$ and $\varepsilon_{22}$ values in GdScO$_3$ gives 21.1, in close agreement with the measured value of 21.4. The calculated value for DyScO$_3$ is 20.5, also in close agreement to the measured value of 20.5.

The dielectric constants of cross-sectional pieces of the NdScO$_3$ and SmScO$_3$ crystals are 23 and 18, respectively. Laue investigation revealed that the growth direction
did not coincide with a low index plane, so these values have components of two or more of the primary tensor coefficients. Because of the similarity of the crystal structure of these compounds with GdScO$_3$ and DyScO$_3$, a high degree of anisotropy in the tensor coefficients is expected. This may explain the slightly higher $\kappa$ value of 27 reported in polycrystalline samples of NdScO$_3$. Complete characterization of the full dielectric tensor coefficients of NdScO$_3$ and SmScO$_3$ will be completed when larger crystals are obtained.

**B. Bandgap**

The transmission spectrum of GdScO$_3$ is shown in Fig. 9.4. This spectrum shows considerable sub-bandgap absorption that we interpret in terms of the electronic structure of transition metal insulating elemental and binary oxides. We assign these sharp absorption to the crystal symmetry split features of a transition metal $d$-state. The three features are consistent with the orthorhombic crystal structure, and the additional splitting of each feature is consistent with the fact that the Sc atom is off center in the perovskite structure.

Based on this transmission data, and spectroscopic ellipsometry data from reference 15, we obtained the dielectric function for GdScO$_3$ by the analysis described above (Fig. 9.5). Our final simulation found a 19.5 Å thick top damaged layer with 20.3 % void fraction. The spectral dependence of the absorption coefficient of GdScO$_3$ in the strongly absorbing region was next calculated using these results, indicating a bandgap energy of order 6.5 eV.

For SmScO$_3$, we only obtained ellipsometry data, since the small samples available (diameter ~ 3 mm) did not provide adequate data for the transmission system.
Figure 9.5 also shows the dielectric function of SmScO$_3$ extracted after the simulation. Note that the tail of the $\varepsilon_2$ spectrum does not go to zero at low energies (which we believe to be below the band gap). This may be due in part to scattered light, as the intensity is low in this energy range. It may also reflect the inaccurate response of a rotating polarizer ellipsometer to low absorption coefficient material.\textsuperscript{18} We again extract the spectral dependence of the absorption coefficient in the strongly absorbing region and finally extrapolate a bandgap energy between 5.5 and 6.0 eV for SmScO$_3$.

\textbf{IV. DISCUSSION:}

Two necessary characteristics of a replacement gate dielectric are a high bandgap to reduce gate leakage, and a large dielectric constant which allows films of thicker physical thickness to have the electrical equivalent thickness of $< 10$ Å SiO$_2$. In fact, the international technology roadmap for semiconductors states that an effective gate dielectric must have a bandgap of at least 4-5 eV.\textsuperscript{19} A comparison of the dielectric constants and bandgaps of the ReScO$_3$ with several other thermodynamically stable alternative gate dielectrics shows they are very well suited for this application (Table 9.1)(Fig. 9.6).

Many materials, such as Si$_3$N$_4$ and Al$_2$O$_3$, have large bandgaps but are limited by a small dielectric constants which may restrict the electrical equivalent thickness that can be achieved while maintaining acceptable tunneling currents. Others materials being investigated, such as SrTiO$_3$, have large dielectric constants ($\varepsilon_{33} = 328$ in single crystals),\textsuperscript{40} but suffer from small bandgaps (3.2 eV)\textsuperscript{41} resulting in high gate leakage.\textsuperscript{42} The materials measured in this study, as well as BaZrO$_3$, SrZrO$_3$, and LaAlO$_3$, offer the advantage of large bandgaps and dielectric constants in excess of 23. It is important to
note, however, that most of the dielectric constants used for Fig. 9.6 are taken from single crystals of these samples. It is likely, therefore, that these intrinsic values represent an upper bound to the actual values attainable in an epitaxial or amorphous thin film of these materials.

Because of the highly anisotropic nature of the dielectric tensor coefficients in GdScO$_3$ and DyScO$_3$, the epitaxial implementation of these compounds offers the greatest opportunity to realize the maximum dielectric constant. An analysis of the crystal structure and lattice constants suggests that one of the most likely growth directions of these materials on (100) silicon will be with the orientation relationship of (100) $Re$ScO$_3$ $\parallel$ (100) Si, [001] $Re$ScO$_3$ $\parallel$ [001] Si, and [010] $Re$ScO$_3$ $\parallel$ [010] Si (Fig. 9.7(a)). The areal lattice mismatch for GdScO$_3$ and DyScO$_3$ in this orientation is 6.6% and 4.8%, respectively. Although this lattice mismatch may seem large, it is comparable to that between Si (100) and BaTiO$_3$ (7.4%), whose epitaxial growth on (100) silicon has previously been demonstrated. This growth direction also results in the largest magnitude of the dielectric tensor coefficient of GdScO$_3$ and DyScO$_3$, 29.5, and 35.5, respectively, lying in the same direction as the applied field in the MOSFET. It is also possible that these materials will grow with an orientation relationship of (110) $Re$ScO$_3$ $\parallel$ (001) Si, [001] $Re$ScO$_3$ $\parallel$ [-110] Si, and [-110] $Re$ScO$_3$ $\parallel$ [110] Si with an areal lattice mismatch for GdScO$_3$ and DyScO$_3$ of 6.4% and 5.1%, respectively (Fig. 9.7(b)). This is a less favorable direction electrically, however, because the out of plane dielectric constants of GdScO$_3$ and DyScO$_3$ will be 21.4, and 20.5, respectively.
V. CONCLUSION

This work identifies new materials for study as alternative gate dielectrics. Previous studies have identified several multicomponent oxides that may be thermodynamically stable in contact with silicon, but most do not have known dielectric constants or bandgaps. Here we have grown single crystals of GdScO₃, DyScO₃, SmScO₃ and NdScO₃ and measured their dielectric constant and band gaps. These measurements indicate that these scandates have a band gap > 5 eV, and a dielectric constant between 20 – 30, important prerequisites for their consideration as alternative gate dielectrics.

The growth of these materials on silicon will allow many other important gate oxide requirements, such as low interface state density Dᵢₙ, low leakage, high mobility, and ability to withstand a 1000 °C anneal to be investigated.

Acknowledgements

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FIG. 9.1. Photo of as grown (a) DyScO$_3$ and (b) GdScO$_3$ crystals.
FIG. 9.2. Measurement of the three independent dielectric tensor coefficients for GdScO$_3$ allows the full tensor to be calculated. (a) Three dimensional representation of the dielectric constant of GdScO$_3$ (b) dielectric constant in the $a$-$b$ plane (c) dielectric constant in the $a$-$c$ plane (d) dielectric constant in the $b$-$c$ plane.
FIG. 9.3. Measurement of the three independent dielectric tensor coefficients for DyScO₃ allows the full tensor to be calculated. (a) Three-dimensional representation of the dielectric constant of DyScO₃ (b) dielectric constant in the $a - b$ plane (c) dielectric constant in the $a - c$ plane (d) dielectric constant in the $b - c$ plane
FIG. 9.4. Transmission spectra of GdScO$_3$ single crystals. Significant sub-band absorption features are seen, as well as the fundamental bandgap absorption.
FIG. 9.5. Ellipsometry plots of GdScO$_3$ and SmScO$_3$ crystals.
FIG. 9.6. Plot of dielectric constant, $\kappa$, versus optical bandgap, $E_{g,\text{optical}}$, of several candidates for alternative gate dielectrics in Si MOSFET’s. Materials where the full dielectric tensor is known are denoted with filled circles, and include $\text{SiO}_2$, $\text{La}_2\text{O}_3$, $\text{Sm}_2\text{O}_3$, $\text{Gd}_2\text{O}_3$, $\text{Si}_3\text{N}_4$, $\text{MgO}$, $\text{Sc}_2\text{O}_3$, $\text{CaO}$, $\text{SrO}$, $\text{ZrO}_2$, $\text{BaO}$, $\text{HfO}_2$, $\text{YAlO}_3$, $\text{LaAlO}_3$, $\text{GdScO}_3$, $\text{Al}_2\text{O}_3$, $\text{ZrSiO}_4$, and $\text{Y}_2\text{O}_3$. The variation of $\kappa$ with orientation is denoted by the dashed line between two solid circles, one denoting the orientation where $\kappa$ is minimal and the second where $\kappa$ is maximal. Open circles indicate materials where the complete dielectric constant tensor information is not known, and include $\text{SrZrO}_3$, $\text{SmScO}_3$, and $\text{LaLuO}_3$. The hashmarks indicate the recommendations of Reference 19: a bandgap of at least 4 eV and preferably exceeding 5 eV. (adapted from David Gilmer, Motorola)
FIG. 9.7. The most likely in-plane orientation relationships for the epitaxial growth of GdScO$_3$ on silicon are (a) (001) GdScO$_3$ || (001) Si, [010] GdScO$_3$ || [010] Si, and [100] GdScO$_3$ || [100] Si or (b) (110) GdScO$_3$ || (001) Si, [001] GdScO$_3$ || [-110] Si, and [-110] GdScO$_3$ || [110] Si. Similar orientation relationships would be expected for all of the ReScO$_3$ compounds, although lattice mismatch will vary as lattice constants shift with different Re elements.
TABLE 9.1: Dielectric constant $\kappa$, optical band gap $E_{g,\text{optical}}$ and conduction band offset $\Delta E_c$ (eV) with silicon for several alternative gate dielectric materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\kappa$</th>
<th>$E_{g,\text{optical}}$ (eV)</th>
<th>$\Delta E_c$ (eV)</th>
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</thead>
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<tr>
<td>SiO$_2$</td>
<td>4.5$^{(a)}$, 4.6$^{(c)}$</td>
<td>8.9$^{21}$</td>
<td>3.5$^{22}$</td>
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<tr>
<td>Si$_3$N$_4$</td>
<td>7$^{23}$</td>
<td>5.1$^{24}$</td>
<td>2.4$^{22}$</td>
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<tr>
<td>MgO</td>
<td>9.8$^{20}$</td>
<td>7.6$^{25,26}$</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>12.0$^{20}$</td>
<td>7.7$^{27}$</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>14.5$^{20}$</td>
<td>5.2$^{27}$</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>22.0$^{20}$</td>
<td>5.8$^{28}$</td>
<td>1.4$^{22}$ (calculated)</td>
</tr>
<tr>
<td>BaO</td>
<td>31.1$^{20}$</td>
<td>4.1$^{27}$</td>
<td></td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>22$^{9}$</td>
<td>5.5$^{15}$</td>
<td>1.5$^{22}$ (calculated)</td>
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<tr>
<td>LaAlO$_3$</td>
<td>25.1$^{29}$</td>
<td>5.7$^{15}$</td>
<td></td>
</tr>
<tr>
<td>GdScO$_3$</td>
<td>19.2$^{(a)}$, 22.8$^{(b)}$, 29.5$^{(c)}$</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>11.3$^{20}$</td>
<td>6.1$^{30}$</td>
<td>2.3$^{22}$ (calculated)</td>
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<tr>
<td>Sc$_2$O$_3$</td>
<td>13$^{20}$</td>
<td>6.0$^{31}$</td>
<td></td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>13.6$^{20}$</td>
<td>5.3$^{32}$</td>
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</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>18.4$^{33}$</td>
<td>5$^{32,34}$</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>11.6$^{(a)}$, 9.4$^{(c)}$</td>
<td>8.8$^{34}$</td>
<td>2.8$^{22}$ (calculated)</td>
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<tr>
<td>SrZrO$_3$</td>
<td>30$^{9}$</td>
<td>5.5$^{35,37}$</td>
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<tr>
<td>SmScO$_3$</td>
<td>18</td>
<td>5.5</td>
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<tr>
<td>LaLuO$_3$</td>
<td>22$^{9}$</td>
<td>5.6$^{38}$</td>
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<tr>
<td>ZrSiO$_4$</td>
<td>11.5 - 12.6$^{(a)}$, 11.5 - 12.8$^{(c)}$</td>
<td>6$^{39}$</td>
<td>1.5$^{22}$ (calculated)</td>
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<tr>
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<td>16.8$^{(a)}$, 15.9$^{(b)}$, 16.2$^{(c)}$</td>
<td>7.5$^{30}$</td>
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References


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CHAPTER 10

Epitaxial Growth of SrRuO$_3$ on Silicon by MBE

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Epitaxial Growth of SrRuO$_3$ on Silicon by MBE

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Abstract

An important enabler for a broader range of perovskite-based devices or devices with improved integration density and performance is the ability to have a conducting epitaxial contact to the underlying silicon. We have achieved such a conductive contact by using epitaxial SrRuO$_3$ layers grown on Si (100) by molecular beam epitaxy. Vertical transport measurements show that the SrRuO$_3$ forms a conductive contact with the silicon substrate, although cross section TEM indicates there is a thin, amorphous interfacial Sr-Si-O layer at the substrate / film interface. This metallic, perovskite SrRuO$_3$ film serves as a template for the subsequent growth of an epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_3$ / PbZr$_{0.6}$Ti$_{0.4}$O$_3$ / La$_{0.5}$Sr$_{0.5}$CoO$_3$ stack. This ferroelectric stack exhibits excellent fatigue-free ferroelectric properties up to $10^{10}$ cycles.
The desire to integrate the active properties of perovskites (e.g., ferroelectricity, pyroelectricity, and piezoelectricity) with silicon integrated circuit technology has resulted in the use of a variety of buffer layers to transition from the silicon to the oxide material. The most common transition layers used in ferroelectric devices (e.g. Pt) grows in a polycrystalline or textured manner on silicon and SiO₂. While textured and polycrystalline films are effective for a wide variety of devices, random orientation limits the ability to fully utilize the anisotropic properties of many perovskites, and a high density of grain boundaries limits the scaling of future devices.

The growth of epitaxial perovskites on silicon allows the directionality of the active properties of perovskites to be exploited to the greatest extent, limits grain boundary diffusion, and reduces grain boundary traps. The recent work in the growth of high quality epitaxial SrTiO₃ on silicon for application to alternative gate dielectrics has also proved as an effective template for the deposition of an overlaying ferroelectric layer. Such insulating buffer layers limit the design architecture, however, and fully conductive templates are desired. Recently, we have demonstrated that modification of the transport properties of SrTiO₃ by La-doping is effective in providing a fully conductive pathway to the underlying silicon. However, donor-doped SrTiO₃ is a notoriously unreliable conductor when subject to highly oxidizing conditions at elevated temperatures. Similar difficulties exist with conductive TiN, which has been used as a suitable epitaxial buffer layer for some perovskites, but whose inability to withstand the oxidizing conditions and elevated temperatures necessary for the growth of many ferroelectric oxides is a considerable limitation.
This work focuses on the epitaxial integration of the metallic ferromagnetic perovskite SrRuO$_3$ with silicon as a platform for the subsequent growth of functional perovskites. SrRuO$_3$ has emerged as the electrode of choice for the growth of a variety of ferroelectric, dielectric, and piezoelectric materials on oxide substrates because its lattice constant ($a = b = c = 3.925$) is well matched to many perovskites, and it is able to withstand a wide range of demanding oxidizing and temperature conditions. Attempts to grow SrRuO$_3$ directly on silicon have resulted in a variety of interfacial reaction layers with the ultimate growth of a polycrystalline SrRuO$_3$ film.\textsuperscript{11} Epitaxial SrRuO$_3$ has been grown with a (110) orientation on (100) Si using a thick (800 Å) YSZ buffer layer.\textsuperscript{12,13} While (110) oriented SrRuO$_3$ is well suited for the growth of SrBi$_2$Nb$_2$O$_9$, is not favorable for exploiting the maximum polarizability in a variety of other ferroelectrics such as Pb$_{1-x}$Zr$_x$TiO$_3$, and BaTiO$_3$, where the polarization lies completely in the $c$-axis. The growth of (100) oriented SrRuO$_3$ has been reported with the use of a TiAlN/Pt buffer layer, although electrical contact to the substrate was not measured.\textsuperscript{14} The objective of this work is to grow epitaxial (100) – oriented SrRuO$_3$ on Si and to reduce the thickness of the buffer layer to achieve a conductive stack from the substrate to the ferroelectric.

Deposition of the SrRuO$_3$ was conducted in an oxide MBE chamber. Before growth, the silicon (100) substrate was heated to 900 °C to desorb the native oxide layer. Deposition of a SrSi layer, followed by the room temperature growth of epitaxial, lattice matched (Ba,Sr)O was used as a transition from the Si to the SrRuO$_3$.\textsuperscript{1,15} Ideally, this transition layer could be reduced to a single or double SrO layer, resulting in (Ba,Sr)RuO$_3$, or a layer of (Ba,Sr)$_2$RuO$_4$, in direct contact with the silicon. In practice, we were unable to grow epitaxial SrRuO$_3$ deposited with less than 4 unit cells of (Ba,Sr)O at the interface.
This is most likely due to the difficulty in oxidizing the Ru metal. Unlike Sr, which oxidizes at room temperature in oxygen partial pressures as low as $5.0 \times 10^{-9}$ O$_2$, Ru requires a significant oxygen ambient for the formation of RuO$_2$ to occur. However, the presence of excessive (Ba,Sr)O (i.e. through the deposition of a thicker (Ba,Sr)O layer or through the deposition of less than a full monolayer of Ru in the SrRuO$_3$ step) is believed to act as a catalysis for oxidation of the Ru, similar to what has been observed with other metal cations.\textsuperscript{15,16} This is confirmed by the fact that deposition of Ru metal at 600 °C in a background pressure of $1.0 \times 10^{-6}$ O$_2$ results in a Ru metal film, while sequentially deposited Sr and Ru metal at the same pressure and temperature result in epitaxial SrRuO$_3$, with no Ru metal peaks evident in the x-ray diffraction scan.

Following deposition of the (Ba,Sr)O layer, 3 unit cells of Ru and Sr metals were deposited in a background pressure of $1.0 \times 10^{-7}$ O$_3$. A Thermionics 3 kW rod fed e-gun was used for the deposition of the Ru, while a standard effusion cell was used for the Sr deposition. Reflection high-energy electron diffraction (RHEED) images indicated that this pressure was insufficient to fully oxide the Ru metal, but higher pressures were avoided in an attempt to reduce the oxidation of the underlying silicon substrate.

Once heated to 550 °C, the structure was exposed to additional Sr metal (≈1/2 monolayer) in a $1.0 \times 10^{-7}$ O$_2$ background pressure to complete the oxidation of the Ru metal, resulting in a RHEED pattern indicative of epitaxial SrRuO$_3$. Subsequent growth of the SrRuO$_3$ was conducted by sequential deposition of the Sr and Ru sources in $1.0 \times 10^{-7}$ O$_2$ at a substrate temperature between 500 °C and 600 °C. Figure 10.1 shows the RHEED images after 200 Å of SrRuO$_3$ were deposited. The streaky nature of the RHEED pattern indicates that the film is of high quality, and epitaxially (100)-oriented with the silicon
substrate. Figure 10.2 shows a θ-2θ x-ray diffraction pattern showing only (00l) peaks, indicating that the film is phase pure SrRuO₃ with a (100) orientation. Rocking curve FWHM widths of 2.0 degrees in ω indicate some structural inhomogeneity in the film that can most likely be attributed to the difficulty in oxidizing the Ru metal during the initial step.

Cross-sectional TEM images of the interface between the SrRuO₃ and Si can be seen in figure 10.3. These images reveal a 30 Å – 40 Å Sr – Si – O amorphous interface layer. It is likely that this layer formed during the high temperature deposition of the SrRuO₃ film. The composition of the interface was determined using EELS to have the following weight percent composition: 49% O, 43.3% Si, 5.5% Sr, and 2.2% Ru. This is similar to the composition of the interfacial reaction layer seen in polycrystalline SrRuO₃ films heated to similar temperatures in a variety of oxygen pressures. Growth of epitaxial SrTiO₃ on silicon in a comparable temperature and pressure regime has also been shown to result in a similar interfacial layer. Although it does not seem to effect the quality of the SrRuO₃ film, or impede the electrical contact from the Si to the SrRuO₃, elimination of this layer will be required to form a truly ohmic contact at the SrRuO₃/Si interface. Currently, it is not clear whether the SrRuO₃ can be grown in low enough pressure, or at a low enough temperature to accomplish this goal.

This metallic SrRuO₃ transition layered served as a template for the subsequent deposition of a La₀.₅Sr₀.₅CoO₃ / PbTi₀.₄Zr₀.₆O₃ / La₀.₅Sr₀.₅CoO₃ ferroelectric capacitor heterostructure. Magnetron sputtering was used for the deposition of the La₀.₅Sr₀.₅CoO₃ layers while a low temperature (450 °C) sol-gel method was used for the deposition of
the PbTi$_{0.4}$Zr$_{0.6}$O$_3$. θ-2θ x-ray diffraction analysis revealed that the ferroelectric stack was (100) oriented, single phase and oriented epitaxially with the substrate.

Ferroelectric testing was performed with a RT 6000 test unit. The samples were patterned by photolithography followed by platinum deposition to make 50 µm diameter platinum dots using a lift-off and wet etching method. A 100 nm aluminum film was deposited on the backside of the silicon wafer, and the electrical properties of the capacitors were measured through vertical transport from the back side aluminum electrode to the top platinum electrodes. The 120 nm thick PbZr$_{0.6}$Ti$_{0.4}$O$_3$ films exhibit resistivity values of 1x10$^{10}$ Ω·cm at 5 V that do not change appreciably from 1-12 V. The ferroelectric responses under quasi-static conditions are shown in figure 10.4. The remnant polarization (Pr) and coercive voltage are about 21 µC/cm$^2$ and 1.2 V, respectively, at 5 V.

The switched remnant polarization, ∆P, was measured through pulsed polarization tests as a function of fatigue cycles. Fatigue tests were performed on these structures using bipolar-pulsed cycles of 5 V at 1 MHz (Fig. 10.5). Little measurable fatigue was observed up to 10$^{10}$ cycles, consistent with fatigue resistance seen on conducting perovskite contact electrodes on oxide substrates.

In conclusion, epitaxial (100) oriented SrRuO$_3$ has been grown on Si through the use of a thin (Ba,Sr)O buffer layer. The SrRuO$_3$ forms a conductive contact with the Si substrate, allowing backside contacts to be used to measure a PZT ferroelectric stack. The ferroelectric properties of the PZT are similar to what is achieved on SrRuO$_3$ grown on oxide substrates with minimal fatigue observed.

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FIG. 10.1. RHEED images taken along the (a) [110] azimuth and (b) [100] azimuth, of a 200 Å SrRuO$_3$ film grown on silicon by MBE. The [100] azimuth of the film corresponds to the [110] azimuth of the silicon, and the [110] azimuth of the film corresponds to the [100] azimuth of the substrate indicating a [110] SrRuO$_3$ $\parallel$ [100] Si and [100] SrRuO$_3$ $\parallel$ [110] Si, epitaxial relationship.
FIG. 10.2. θ-2θ x-ray diffraction scan of a 200 Å SrRuO$_3$ film grown on silicon. Substrate peaks are labeled with a (*).
FIG. 10.3. High resolution cross-sectional TEM image of a 200 Å SrRuO$_3$ film grown on silicon. Excess oxygen and elevated temperature during growth caused the (BaSr)O buffer layer to react with the silicon forming a Sr-silicate layer.
FIG. 10.4. Polarization hysteresis loops for La$_{0.5}$Sr$_{0.5}$CoO$_3$ / PbZr$_{0.6}$Ti$_{0.4}$O$_3$ / La$_{0.5}$Sr$_{0.5}$CoO$_3$/SrRuO$_3$ / Si test capacitor made by sol-gel on SrRuO$_3$ / Si at 450 °C.
FIG. 10.5. Fatigue characteristics of a La$_{0.5}$Sr$_{0.5}$CoO$_3$ / PbZr$_{0.6}$Ti$_{0.4}$O$_3$ / La$_{0.5}$Sr$_{0.5}$CoO$_3$/SrRuO$_3$ / Si capacitor at room temperature using 8.6 $\mu$s write pulse width and 130 $\mu$s read pulse width. Little fatigue is seen up to $10^{10}$ cycles.
REFERENCES

10. SrRuO$_3$ is orthorhombic with space group Pbnm and lattice constants $a = 5.53$ Å, $b = 5.57$ Å, and $c = 7.85$ Å at room temperature. The lattice can be considered as a pseudocubic perovskite with $a = 3.925$ Å. Pseudocubic indexing is used throughout this manuscript for SrRuO$_3$.
15. J. Lettieri, J. H. Haeni, and D. G. Schlam, to be published in J. Vac. Sci. and Tech. A.
16. J. Lettieri, J. Rodriguez, D. G. Schlom, unpublished

11. Conclusions and Future Work

The broad range of physical and electrical properties of perovskites promise to make them applicable to a host of commercially viable devices. However, realization of this commercial potential for perovskite microelectronic devices has been a slow process. Two important steps have to first be overcome; the ability to grow high quality oxide thin films, and an understanding of their fundamental properties. The results presented in this thesis represent an incremental step towards this goal. Progress was made in the development of MBE as a viable growth technique for a variety of complex oxide crystal systems and in the understanding of the fundamental properties of the \((\text{Ba},\text{Sr})_{n+1}(\text{Ti},\text{Ru})_{n}\text{O}_{3n+1}\) Ruddlesden-Popper homologous series. A brief summary of the key contributions of this thesis, as well as a discussion of future projects which may stem from this work, are presented below.

11.1. RHEED Intensity Oscillations

Development of RHEED intensity oscillations as a sensitive tool for the control of stoichiometry opened the door to nearly all of the work described in this thesis. The RHEED oscillation technique not only enabled the growth of the composition sensitive \(\text{Sr}_{n+1}\text{Ti}_{n}\text{O}_{3n+1}\) series with relatively stable Sr and Ti sources, it allowed the growth of the \(\text{Sr}_{n+1}\text{Ru}_{n}\text{O}_{3n+1}\) series, with a Ru flux that decreased by 60% in the course of a growth. Composition control continues to be a primary limitation in the growth of multicomponent oxides by molecular beam epitaxy, but this work helped to reduce composition variations thereby increasing the quality of MBE grown thin films and enabling the growth of previously unrealized phases.
The RHEED techniques developed, although used as a quantitative guide to adjust the stoichiometry, are all based on a qualitative understanding of the diffraction intensity oscillations. Recently, progress has been made in developing a more mechanistic understanding of RHEED oscillations as applied to the growth of GaAs. Application of these techniques for a mechanistic understanding of the RHEED oscillations observed during the growth of the \((\text{Ba,Sr})_{n+1}(\text{Ti,Ru})_n\text{O}_{3n+1}\) Ruddlesden-Popper homologous series is a natural progression of the work presented in Chapter 3.

11.2. Atomically Abrupt BaTiO\(_3\) / SrTiO\(_3\) Superlattices

The work presented in chapter 5 represents a significant improvement on the structural properties reported to date in BaTiO\(_3\) / SrTiO\(_3\) superlattices. The interface structure of these superlattices, with nearly atomically abrupt transitions from one layer to the next, is comparable to what is currently achieved in GaAs / AlGaAs superlattice structures. In addition, the possibility of growing digitally graded composition profiles, a technique commonly used in compound semiconductor growth, has been shown to be equally viable in oxide system as well.

In conjunction with our experimental work, significant theoretical work has been done by our coworkers in an attempt to understand, and predict, certain key properties of these superlattices. Testing their predictions, through the growth and electrical characterization of superlattices with varying periodicities, should be the next step in this experimental work. The key roadblock to these experiments is that for reliable electrical measurements to be made, these superlattices must first be grown on conducting bottom electrodes with suitable lattice constants. SrRuO\(_3\) has proven a robust electrode material for the growth of several perovskites by PLD and is the obvious choice as a bottom
electrode for these superlattices. Several attempts during this thesis work to grow these superlattice on SrRuO$_3$ demonstrated that the MBE growth of oxides on SrRuO$_3$ was not trivial. Significant degradation of the SrRuO$_3$ occurred if low (< 1.0 x 10$^{-6}$ Torr) oxygen pressures were used during the deposition of the superlattice. In addition, loss of surface RuO$_2$ at the growth temperature necessary for high quality superlattices (680 °C) complicated composition control during the initial superlattice layers. Recently progress has been made in our lab in the growth of BaTiO$_3$ on SrRuO$_3$ in high (> 4.0 x 10$^{-6}$ Torr) background pressures of ozone, and is a promising first step for the growth of SrTiO$_3$ / BaTiO$_3$ superlattice on SrRuO$_3$. However, the composition control necessary for achieving abrupt superlattice interfaces is difficult at such high pressures. Nonetheless, growth of these superlattice structures on SrRuO$_3$ electrodes, through innovative high pressure composition control techniques, should be the next step in this work.

11.3 Improved Room Temperature Tunability in Strained SrTiO$_3$

The use of DyScO$_3$ and LSAT as substrates for the growth of SrTiO$_3$ proved to be an excellent means to elucidate the effect of strain on the dielectric properties of SrTiO$_3$. Biaxial tensile strain was shown to introduce a near room temperature ferroelectric transition and significant room temperature tunability in the SrTiO$_3$ / DyScO$_3$ films, while no tunability was measured in SrTiO$_3$ / LSAT films. These dielectric measurements indicate that the SrTiO$_3$ / DyScO$_3$ films are well suited for room temperature tunable dielectric devices and our collaborators are currently making device structures with these films.

Several interesting trends in the dielectric properties of the SrTiO$_3$ / DyScO$_3$ films require further study. The dramatic difference in dielectric constant in pre- and post-
annealed samples and in films with different thicknesses suggest that these films are not all coherently strained. X-ray diffraction studies also suggest films with thickness > 200 Å are partially relaxed, but they lack sufficient resolution to determine the critical thickness of these films. The next step in this work is to use plan view TEM to characterize the dislocations density in the SrTiO$_3$ and high resolution cross sectional TEM to directly measure the in-plane lattice constant of the SrTiO$_3$. Once the strain in these samples can be quantitatively determined, this will serve as an excellent system as a test for first principle calculations capable of predicting the shift in Curie temperature as a function of strain.

11.4. \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) Ruddlesden-Popper Homologous Series

The growth of the \( n = 1-5 \) members of the \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) Ruddlesden-Popper homologous series represents a key achievement in the use of sequential deposition to engineer metastable dielectric phases by MBE. Key properties of these phases, such as dielectric constant and band gap, were measured and appear to be tunable as \( n \) is varied from 1 to \( \infty \). The utility of their properties has just begun to be explored, and further applications are sure to arise as more research is conducted.

One issue that remains in question is the agreement between the theoretically predicted dielectric constant of \( \text{Sr}_2\text{TiO}_4 \) and the value measured in this thesis. Theoretical calculations suggest a dielectric constant in the \( c \)-direction (\( \epsilon_{33} \)) of about 1/2 that measured in this work. Contribution of in-plane components of the dielectric constant could cause an artificially high value to be measured in the SEMM measurements, although this should not be a problem in the measurements made in the capacitor structure. It is possible, however, that the presence of intergrowths in these samples
could result in the measurement of artificially high dielectric constant values. However, since no intergrowths were seen in the Sr$_2$TiO$_4$ samples examined by TEM, this is not a likely scenario. Nonetheless, the existence of a more stable Sr source in the MBE chamber, the development of more advanced SEMM measurements, and the possibility of growing Sr$_2$TiO$_4$ on a bottom electrode of SrRuO$_3$ warrant the further investigation of this discrepancy in theoretical and experimental values.

11.5. Bandoffset in Sr$_2$TiO$_4$ / SrTiO$_3$ Heterostructures

The bandgap and band offset measurements described in Chapter 7 are a perfect example of the background work necessary to eventually realize exciting and novel properties, such as a two-dimensional electron gas, in perovskites. Although it is difficult to say whether the conduction band offset present in the SrTiO$_3$ / Sr$_2$TiO$_4$ system will be sufficient for trapping of carriers at the interface to occur, this work is an important step in the accumulation of data on the band structure of oxide materials, knowledge that is essential for band gap engineering of perovskites to be successful. The XPS measurements and data analysis techniques described in this thesis will be an important tool in the collection of this knowledge, as it represents the first successful attempt to determine the band offset in two materials with identical constituent elements. Such compounds are exciting candidates for a variety of heterostructures, as they represent the “ideal” case of chemical compatibility.

In addition to the bandoffset measurements made on the Sr$_2$TiO$_4$ / SrTiO$_3$ heterostructures, significant effort was made during this thesis work to grow and measure the transport properties of La-doped Sr$_2$TiO$_4$ films. The majority of this work was done hoping to find superconductivity in this crystal system, however, recent experiments have
been conducted with a 2DEG structure in mind. This work however, was done without proper understanding of the band structure of these compounds. As a result, La-doped \( \text{Sr}_2\text{TiO}_4 / \text{undoped SrTiO}_3 \) heterostructures were measured. Based on the XPS and powder reflectance data, however, it appears that growth and measurement of the transport properties of La-doped \( \text{SrTiO}_3 / \text{undoped Sr}_2\text{TiO}_4 \) structures may be more appropriate for the formation of a confined carriers region at the interface of these two materials. Growth of La-doped \( \text{SrTiO}_3 / \text{undoped Sr}_2\text{TiO}_4 \) structures, with varying doping levels and setback layer thicknesses should be grown and Hall measurements should be made in an attempt to correlate doping levels and setback layer thickness with carrier concentration and mobility.

11.6. \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \) Ruddesden-Popper Homologous Series

The work done in this thesis to test and install a Ru rod fed E-gun source in the MBE system opened exciting opportunities for the growth of the \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \) Ruddlesden Popper Series. \( \text{SrRuO}_3 \) films were grown and successfully used as bottom and top electrodes for \( \text{BaTiO}_3 \) capacitor structures. The growth of the \( n = 1 \) – \( 5 \) members of this series was a surprising achievement considering the instability of the Ru source. Currently these films are being studied to understand size effects on the magnetic properties in this system.

Perhaps the most exiting future work in this area should concentrate on the growth of superconducting \( \text{Sr}_2\text{RuO}_4 \) thin films. Due to hardware limitations, I was unable to attempt growths of \( \text{Sr}_2\text{RuO}_4 \) in a regime where it is the thermodynamically stable phase. Non-the-less, the \( \text{Sr}_2\text{RuO}_4 \) films grown in this study at \( 620 \, ^\circ\text{C} \), had comparable rocking curve widths to the best films grown by PLD at \( 1000 \, ^\circ\text{C} \), indicating a significant
advantage of layer-by-layer growth. In addition to temperature and pressure optimization, growth of Sr$_2$RuO$_4$ on LaSrGaO$_4$ substrates should be attempted to reduce out of phase boundaries in the film. The substrates used in this thesis work, SrTiO$_3$ and LSAT, have step heights that are not integer multiples of the $c$-axis lattice spacing of Sr$_2$RuO$_4$.

Growth of the Ba$_{n+1}$Ru$_n$O$_{3n+1}$ homologous series is also a natural extension of the growth of the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ homologous series. Initial attempts to grow Ba$_2$RuO$_4$ have shown that it does not grow with comparable quality to Sr$_2$RuO$_4$ at 620 $^\circ$C, and that higher temperatures (e.g. 720 $^\circ$C) are necessary to improve the film quality. As only a few films were grown, however, these results should be treated only as guidelines, and more research should be conducted.

11.7. Growth and Characterization of ReScO$_3$ Single Crystals

The growth and measurement of several ReScO$_3$ single crystals reveal an exciting class of crystals both for application to alternative gate dielectrics and as substrates for the growth of a variety of perovskites. The dielectric constants of these scandate compounds, combined with their large bandgap and predicted thermodynamic stability with Si, suggest that they should be pursued as alternative gate dielectric candidates. The epitaxial growth of these compounds on silicon will require extensive work and will be the focus of future studies. Initial attempts to grow LaScO$_3$ epitaxially on silicon were unsuccessful.

The use of the DyScO$_3$ and GdScO$_3$ crystals for substrates for the growth of perovskites has been very successful. In addition to the work presented in Chapter 4, the DyScO$_3$ and GdScO$_3$ crystals have been used in our lab for the successful growth of
SrRuO$_3$ and BaTiO$_3$. The growth of addition ReScO$_3$ crystals is currently being pursued and should create a full suite of substrates with lattice constants between 3.93 Å and 4.3 Å available for future use.

11.8. Epitaxial SrRuO$_3$ grown on Si

The growth of epitaxial SrRuO$_3$ on Si represents one of the most promising achievements in this thesis in terms of device application. Epitaxial SrRuO$_3$ on Si is of interest for both FRAM and DRAM technology. While the MBE growth of SrRuO$_3$ may not be suitable for production, it is an excellent technique for initial studies and proof of concept experiments. Transferring this technology to a more production line friendly technique such as CVD may be possible in the future. There are several clear steps that must first be achieved, however, before the MBE growth of SrRuO$_3$ is optimized. First, the structural quality of the SrRuO$_3$ should be improved. The films presented in this thesis still have broad rocking curve widths in comparison to the best epitaxial SrTiO$_3$ that can be grown on silicon, indicative of structural disorder in the SrRuO$_3$. I believe this structural disorder is introduced during the recrystallization of the initial SrRuO$_3$ layers. RHEED analysis of the SrRuO$_3$ indicates that it is unable to recrystallize with comparable quality to the SrTiO$_3$ because a significant portion of the Ru metal is not oxidized during deposition. A key advance is this regard would be the delivery of pre-oxidized RuO$_2$ instead of Ru metal. Unfortunately, RuO$_2$ does not evaporate congruently, so traditional evaporation routes are not applicable. It is possible, however, that gas phase introduction of RuO$_2$ may provide a route to introduce pre-oxidized Ru and improve the structure of the SrRuO$_3$. In addition, use of a RuO$_2$ precursor may allow for lower
oxygen pressures to be used during the subsequent high temperature deposition of SrRuO$_3$, reducing the thickness of the interfacial SiO$_2$ region observed in my films.

In conclusion, the growth of epitaxial thin films of the (Ba,Sr)$_{n+1}$(Ti,Ru)$_n$O$_{3n+1}$ Ruddlesden-Popper homologous series described in this thesis has opened several exciting opportunities for the study of fundamental magnetic, superconducting, and dielectric phenomena and for the eventual realization of microelectronic devices.
Appendix A

Transport Properties of (Sr_{1-x}La_{x})_2TiO_4 Films

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Abstract

Synthesis of the Sr_{n+1}TiO_{3n+1} Ruddlesden-Popper homologous series offers a promising avenue to explore the effect of dimensionality on superconductivity. SrTiO_3, the n = \infty member of this series, has a three-dimensional network of perovskite octahedral and is superconducting when doped with oxygen vacancies or Nb, Ta, or La. Sr_2TiO_4, the n = 1 member, has a two-dimensional layered structure, like all high temperature superconductors. We have studied the effect of La-doping on the electrical transport of Sr_2TiO_4. Metallic conductivity or superconductivity was not achieved in any of the films grown directly on LSAT substrates. However, a thin SrTiO_3 buffer layer between the LSAT substrate and doped Sr_2TiO_4 resulted in heterostructures with metallic conductivity to low temperatures.
A.I. Introduction

One question of current interest is what effect dimensionality has on superconductivity. All high temperature perovskite superconductors \( T_c \) greater than 77 K have layered (two-dimensional) perovskite structures, with no known three-dimensional counterparts. SrTiO\(_3\), on the other hand, was one of the first oxide superconductors discovered and contains a three-dimensional network of perovskite octahedra. In addition, a derivative structure of SrTiO\(_3\), Sr\(_2\)TiO\(_4\), has a layered structure with two-dimensional perovskite sheets. Sr\(_2\)TiO\(_4\) is isostructural with two other well known superconductors with the K\(_2\)NiF\(_4\) structure, Sr\(_2\)RuO\(_4\) and (La,Sr)\(_2\)CuO\(_4\). Achieving superconductivity in the Sr\(_2\)TiO\(_4\) system would be a unique opportunity to study the effect of dimensionality on superconductivity.

Although superconductivity has been predicted to occur in doped-Sr\(_2\)TiO\(_4\) based on crystal chemistry considerations,\(^1\) several experimental studies have been unable to achieve metallic conduction in Sr\(_2\)TiO\(_4\) bulk samples doped with La, Ta, and Nb.\(^2,3\) Single crystals of Sr\(_2\)TiO\(_4\) can not be grown because of a reconstructive phase transition at 1550 °C. We have grown epitaxial thin films of La-doped Sr\(_2\)TiO\(_4\) films using molecular beam epitaxy in an attempt to study the transport properties of this system with the ultimate goal of achieving superconducting La-doped Sr\(_2\)TiO\(_4\) films.

A.II. Experimental

An MBE system (EPI 930)\(^4\) was used for the growth of all \((\text{Sr}_{1-x}\text{La}_x)\)\(_2\)TiO\(_4\) films.\(^5\) Molecular beams of strontium, lanthanum, and titanium were generated using a conventional “low-temperature” effusion cell\(^4\) for strontium, a “high-temperature” effusion cell for lanthanum, and a Ti-Ball\(^\text{TM}\),\(^6\) heated by a precision power supply, for titanium.\(^7\) All films were grown on LaAlO\(_3\)—Sr\(_2\)AlTaO\(_6\) (LSAT) (001) substrates. In addition to an excellent lattice match with Sr\(_2\)TiO\(_4\), LSAT does not become reduced when heated to
growth temperatures in reducing conditions, ensuring that the measured transport properties are not affected by a conductive substrate. All films were grown by sequential deposition of the Sr and Ti cations. Because the lanthanum dopant substitutes onto the Sr-site in the lattice, the strontium and lanthanum were codeposited.

A homoepitaxial SrTiO$_3$ buffer layer about 20-60 Å thick was grown on some of the LSAT substrates prior to the deposition of the (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ film. Growth of this SrTiO$_3$ buffer layer allowed the shutter timing needed to provide stoichiometric monolayer doses of SrO and TiO$_2$ to be adjusted with an accuracy of 1% using reflection high-energy electron diffraction (RHEED) intensity oscillations.

RHEED intensity oscillations were also used to adjust the lanthanum doping levels in all film. To grow a La-doped film, the correct titanium dose was first determined using the methods described above for the growth of pure SrTiO$_3$. The strontium dose was then decreased by the desired doping level and both the dopant and strontium were deposited simultaneously. If excess dopant is deposited, the RHEED intensity pattern will increase. If insufficient dopant is added, the pattern will decrease. In this manner, the dopant’s effusion cell temperature (or codeposition time) is adjusted until a sufficient flux is achieved to compensate for the strontium deficiency, and a stoichiometric RHEED pattern is again reached.

The Sr fluxes were measured with a quartz crystal microbalance before growth and timed wait statements were used for all elements during growth. The average flux of the strontium and titanium sources was $1.0 \times 10^{14}$ atoms/cm$^2$·s for all growths. All films were grown with a substrate temperature between 650 - 750°C and background oxygen partial pressure of $1.0 \times 10^{-7}$ Torr.

DC transport properties of the (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ films were studied using the standard 4-wire method. Electrical contacts consisting of 50 Å of Cr overlaid by 500 Å Au were evaporated onto the films and to these contacts copper wires were attached with silver
epoxy. The films are mounted on a dip probe inserted into liquid He storage dewars, and the temperature dependence of the resistance in these films were measured from 300 K to 4.2 K. Additional measurements were made on some samples in a dilution refrigerator down to 100 mK.

A.III. Results / Discussion

A.III.1. Structural Characterization:

Previous studies have demonstrated that the phase-pure growth of Sr$_2$TiO$_4$ films requires that the stoichiometry of the constituent elements not vary by more than 1%. Figure A.1 shows an x-ray diffraction pattern of a (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ film with $x = 0.2$ (also referred to as 20% doping in this manuscript). The narrow peaks in the correct 2\(\theta\) position are indicative of a phase pure Sr$_2$TiO$_4$ film, indicating that the structure was able to incorporate this high La doping level. In addition, the excellent structural properties of this film offer strong support for the fact that the La-dopant is sitting on the Sr site. A Sr$_2$TiO$_4$ film grown with 20% Sr deficiency typically does not exhibit any peaks in 2\(\theta\) corresponding to the Sr$_2$TiO$_4$ structure. The narrow peaks in Fig. A.1 indicate that the excess La is compensating for the reduced Sr flux. The excellent structural quality of this film could not be reproduced in films with doping levels $x > 0.25$. It is not known if this represents the upper bound of the thin film solid solution limit of substitutional La doping or whether the composition of these films was off stoichiometry.

A.III.2. Transport Properties:

Figure A.2(a) shows the resistivity as a function of temperature for a 700 Å (Sr$_{0.9}$La$_{0.1}$)$_2$TiO$_4$ film grown directly on LSAT. Although the La doping did result in conductivity in this sample, the resistivity increases with decreasing temperatures, indicative of lightly-doped semiconductor behavior. Several samples grown under different oxygen partial pressures, different doping levels (up to $x = 0.2$), and at different
temperatures were measured but all exhibited an increase in resistivity with decreasing temperatures.

Figure A.2(b) shows a film grown under identical conditions to the one shown in Fig. A.2(a) with the exception that a 60 Å SrTiO$_3$ buffer layer was grown between the LSAT substrate and the (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ film. The reason for this drastic difference in transport properties between the single layer and bilayer films is unknown. It is possible that the transport is dominated by the thin SrTiO$_3$ layer at the interface which may have become conductive via La diffusion from the overlayer La-doped Sr$_2$TiO$_4$ film, or from oxygen vacancies. Another possibility is that the SrTiO$_3$ film acts as a catalysis for reduction of the overlying Sr$_2$TiO$_4$ film helping to prevent compensation of the La dopant with the incorporation of excess oxygen. Finally, although the XPS measurements presented in chapter 7 of this thesis suggest that the band structure of this heterojunction would require doping of the SrTiO$_3$ layer for the formation of a accumulation layer at the interface to occur, it is possible that the conductivity is a result of a confined carrier system at the interface of the (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ and SrTiO$_3$.

A sharp resistance drop was found at low temperatures in several SrTiO$_3$ / (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ bilayer films, as shown in Fig. A.3. Such a drop was found in two films around 6 K. However, only one with 13.6% La doping was measured to temperatures below 4 K. The sharpness of the resistance drop might seem to indicate the occurrence of superconductivity even though the sample resistance does not drop to zero. However, this possibility was ruled out based on the results of transverse magnetoresistance (MR) measurements. As shown in Fig. A.4, the MR measured at low temperatures were negative at high fields, inconsistent with the occurrence of superconductivity that would lead to a positive MR. Similar behavior, including a sharp resistance drop and negative MR, was also found in a 10% La-doped film. The cause of this resistance drop is currently unknown, however, other researchers have observed similar phenomena in films with non-homogeneous oxygen concentrations caused by local
areas of poor thermal contact between the substrate holder and substrate resulting in local
temperature variations within the film during growth. The fact that the resistance drop
was not reproducible in several films of nearly identical composition grown under the same
growth conditions suggests that it is either not an intrinsic property of the bilayer structure
or extremely sensitive to an uncontrollable variable.

A.IV. Conclusion

Epitaxial thin films of La-doped Sr₂TiO₄ were successfully grown by MBE with
doping levels between 1 and 20%. None of the films grown directly on the LSAT
substrate exhibited metallic conductivity or superconductivity. Metallic conductivity and, in
some cases, sharp resistance drops were observed for films grown on a thin SrTiO₃ buffer
layer. Additional studies are needed to determine if this metallic conductivity is a intrinsic
property of the (Sr₁₋ₓLaₓ)₂TiO₄ film, a result of unintentional doping of the SrTiO₃ layer, or
caused by a confined carrier system at the interface of the SrTiO₃ and (Sr₁₋ₓLaₓ)₂TiO₄ layers.
FIG A.1. θ-2θ x-ray diffraction scan of a \((\text{Sr}_{0.8}\text{La}_{0.2})_2\text{TiO}_4\) epitaxial film. The sharp peaks indicate that the film is phase pure, with the La dopent substituting on the Sr site.
FIG. A.2. Transport properties of two nominally identical \((\text{Sr}_{0.9}\text{La}_{0.1})_2\text{TiO}_4\) films. (a) the \((\text{Sr}_{0.9}\text{La}_{0.1})_2\text{TiO}_4\) film is grown directly on the LSAT substrate and (b) a 60 Å SrTiO$_3$ buffer layer was grown between the LSAT substrate and the \((\text{Sr}_{0.9}\text{La}_{0.1})_2\text{TiO}_4\) film.
FIG. A.3. Transport properties of two bilayer (Sr$_{1-x}$La$_x$)$_2$TiO$_4$ / SrTiO$_3$ films showing metallic conductivity and a sharp resistance drop around 6 K. The cause of this resistance drop is unknown, and is not reproducible.
FIG. A.4. Low temperature magneto-resistance of the same film shown in FIG. A.3.
REFERENCES

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Jeffrey Haeni was born in 1975 in New Haven, Connecticut. Jeff grew up on a small farm in Deep River, CT. Between working on the farm and managing his lawn mowing business, Jeff was able to attend Valley Regional High School, graduating in 1993. Upon graduation, he enrolled at Colgate University in Hamilton, NY where he majored in physics. During the summer of his junior year, Jeff took part in the Cornell Nanofabrication Facility REU program where he became interested in thin film deposition and materials science under the guidance of Professor James Engstrom. In 1997 Jeff graduated from Colgate and entered graduate school at The Pennsylvania State University. At Penn State, he worked with Darrell Schlom in the Intercollegiate Program in Materials, focusing on the growth and characterization of perovskite thin films. During his second year of graduate school, Jeff conducted research at Lehrstuhl für Experimentalphysik VI in Augsburg, Germany under the guidance of Jochen Mannhart. Jeff’s graduate work was supported by a Motorola/SRC graduate fellowship. Jeff’s hobbies include hunting, dancing, hiking, singing, and bingo.