STRAIN-INDUCED PHENOMENON IN COMPLEX OXIDE THIN FILMS

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by

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Abstract

Complex oxide materials wield an immense spectrum of functional properties such as ferroelectricity, ferromagnetism, magnetoelectricity, optoelectricity, optomechanical, magnetoresistance, superconductivity, etc. The rich coupling between charge, spin, strain, and orbital degrees of freedom makes this material class extremely desirable and relevant for next generation electronic devices and technologies which are trending towards nanoscale dimensions. Development of complex oxide thin film materials is essential for realizing their integration into nanoscale electronic devices, where theoretically predicted multifunctional capabilities of oxides could add tremendous value. Employing thin film growth strategies such as epitaxial strain and heterostructure interface engineering can greatly enhance and even unlock novel material properties in complex oxides, which will be the main focus of this work. However, physically incorporating oxide materials into devices remains a challenge. While advancements in molecular beam epitaxy (MBE) of thin film oxide materials has led to the ability to grow oxide materials with atomic layer precision, there are still major limitations such as controlling stoichiometric compositions during growth as well as creating abrupt interfaces in multi-component layered oxide structures. The work done in this thesis addresses ways to overcome these limitations in order to harness intrinsic material phenomena.

The development of adsorption-controlled stoichiometric growth windows of CaTiO$_3$ and SrTiO$_3$ thin film materials grown by hybrid MBE where Ti is supplied using metal-organic titantium tetraisopropoxide material is thoroughly outlined. These growth windows enable superior epitaxial strain-induced ferroelectric and dielectric properties to be accessed as demonstrated by chemical, structural, electrical, and optical characterization techniques. For tensile strained CaTiO$_3$ and compressive strained SrTiO$_3$ films, the critical effects of nonstoichiometry on ferroelectric properties are investigated, where enhanced ferroelectric
responses are only found for stoichiometric films grown inside of the growth windows, whereas outside of the optimal growth window conditions, ferroelectric properties are greatly deteriorated and eventually disappear for highly nonstoichiometric film compositions. Utilizing these stoichiometric growth windows, high temperature polar phase transitions are discovered for compressively strained CaTiO$_3$ films with transition temperatures in excess of 700 K, rendering this material as a strong candidate for high temperature electronic applications.

Beyond the synthesis of single phase materials using hybrid MBE, a methodology is presented for constructing layered (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattice structures, where precise control over the unit cell layering thickness ($n$) is demonstrated using in-situ reflection high energy electron diffraction. The effects of interface roughness and layering periodicity ($n$) on the strain-induced ferroelectric properties for a series of $n$=1-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattice films are investigated. It is found that the stabilization of a ferroelectric phase is independent of $n$, but is however strongly dominated by the degree of interface roughness which is quantified by measuring the highest $n^{th}$ order X-ray diffraction peak splitting of each superlattice film. A counter-intuitive realization is made whereby a critical amount of interface roughness is required in order to enable the formation of the predicted strain-stabilized ferroelectric phase, whereas sharp interfaces actually suppress this ferroelectric phase from manifesting. It is shown how high-quality complex oxide superlattices can be constructed using hybrid MBE technique, allowing the ability to control layered materials at the atomic scale.

Furthermore, a detailed growth methodology is provided for constructing a layered $n$=4 SrO(SrTiO$_3$)$_n$ Ruddlesden-Popper (RP) phase by hybrid MBE, where the ability to deposit single monolayers of SrO and TiO$_2$ is utilized to build the RP film structure over a time period of 5 hours. This is the first time that a thin film RP phase has been grown using hybrid MBE, where an a stable control over the fluxes is demonstrated during relatively long time periods of growth,
which advantageously facilitates the synthesis of high-quality RP materials with excellent structural and chemical homogeneity.

Additionally, this work demonstrates some major advancements in optical second harmonic generation (SHG) characterization techniques of ferroelectric thin film materials. The SHG characterization techniques developed here proved to be the ‘bread-and-butter’ for most of the work performed in this thesis, providing a powerful tool for identifying the existence of strain-induced ferroelectric phases, including their temperature dependence and polar symmetry.

The work presented in this dissertation will hopefully provide a preliminary road map for future hybrid MBE growers, scientists and researchers, to develop and investigate epitaxial strain and heterostructure layering induced phenomena in other complex oxide systems.
# Table of Contents

List of Figures ........................................................................................................................................ix

List of Tables ........................................................................................................................................xxvii

Acknowledgements ..............................................................................................................................xxviii

Chapter 1 Introduction ..........................................................................................................................1

1.1 Structure-property relationships in complex oxides .................................................................1
1.2 Strain-induced ferroelectricity in complex oxides .................................................................14
1.3 Layering-induced ferroelectricity in complex oxides ............................................................23
1.4 Effects of nonstoichiometry on properties of complex oxides ................................................34
1.5 Hybrid molecular beam epitaxy of complex oxides ..............................................................41
1.6 Thesis organization ..................................................................................................................49
1.7 References ............................................................................................................................51

Chapter 2 Experimental techniques ..................................................................................................56

2.1 Hybrid molecular beam epitaxy ...............................................................................................56
2.2 Reflection high-energy electron diffraction ............................................................................61
2.3 High-resolution X-ray diffraction ..........................................................................................67
2.4 Scanning force microscopy techniques ...................................................................................72
2.5 Photolithography techniques ..................................................................................................77
2.6 Dielectric measurements .........................................................................................................80
2.7 Second harmonic generation experiments .............................................................................85
2.8 References ............................................................................................................................92

Chapter 3 Unleashing strain-induced ferroelectricity in complex oxide thin films via precise stoichiometry control ..........................................................................................................................93

3.1 Abstract ......................................................................................................................................93
3.2 Introduction .............................................................................................................................94
3.3 Thin film growth and structural characterization ......................................................................96
3.4 Optical second harmonic generation characterization .............................................................101
3.5 Electrical characterization of strained CaTiO₃ films .................................................................104
3.6 Conclusions ............................................................................................................................107
3.7 Figures .....................................................................................................................................108
3.8 References ............................................................................................................................125
Chapter 4 Strain-engineering polar properties in CaTiO$_3$ ........................................ 128

4.1 Abstract ..................................................................................................................... 128
4.2 Constructing the strained CaTiO$_3$ series ............................................................. 129
4.3 Structural analysis of strained CaTiO$_3$ series ..................................................... 131
4.4 Probing polar phases of strained CaTiO$_3$ film series using SHG ...................... 133
4.5 PFM switching of CaTiO$_3$/CaVO$_3$/(001)LSAO film ........................................ 139
4.6 Conclusions ............................................................................................................. 141
4.7 Figures ................................................................................................................... 142
4.8 References ............................................................................................................. 158

Chapter 5 Stoichiometry as key to ferroelectricity in compressively strained SrTiO$_3$ .... 160

5.1 Abstract ..................................................................................................................... 160
5.2 Introduction .............................................................................................................. 161
5.3 Thin film growth and structural characterization ................................................. 163
5.4 Optical second harmonic generation characterization ......................................... 164
5.5 Conclusions ............................................................................................................. 167
5.6 Figures ................................................................................................................... 169
5.7 References ............................................................................................................. 177

Chapter 6 Overlapping growth windows to build (SrTiO$_3$)$_n$/CaTiO$_3$$_n$ superlattices .... 179

6.1 Abstract ..................................................................................................................... 179
6.2 Emergent phenomenon in oxide superlattices ...................................................... 180
6.3 Overlapping stoichiometric growth windows of SrTiO$_3$ and CaTiO$_3$ .............. 182
6.4 Growth of superlattice films using RHEED oscillations ..................................... 186
6.5 STEM imaging of superlattice interfaces ............................................................. 187
6.6 X-ray diffraction characterization of superlattice structural quality .................... 188
6.7 SHG characterization of strained SrTiO$_3$ and CaTiO$_3$ films ......................... 190
6.8 Discussion ............................................................................................................... 193
6.9 Figures ................................................................................................................... 196
6.10 References ........................................................................................................... 212

Chapter 7 Creating Ruddlesden-Popper phases by hybrid molecular beam epitaxy ...... 215

7.1 Abstract ..................................................................................................................... 215
7.2 Introduction .............................................................................................................. 216
7.3 Calibrating atomic layer deposition times using RHEED feedback .................... 218
7.4 Atomic layer-by-layer deposition of $n=4$ Sr$_3$Ti$_4$O$_{12}$ RP film ..................... 221
7.5 XRD and HRTEM analysis of RP film structure quality ....................................... 221
7.6 Conclusions ............................................................................................................ 222
7.7 Figures .................................................................................................................... 224
7.8 References ............................................................................................................. 232
Chapter 8 Nonlinear optical properties of strained BiFeO$_3$ thin films ...........................................236

8.1 Large nonlinear optical coefficients in pseudo-tetragonal BiFeO$_3$ films ..................236
  8.1.1 Abstract ..................................................................................................................236
  8.1.2 Strain-induced tetragonal phase of BiFeO$_3$ .......................................................237
  8.1.3 Transmission second harmonic generation polarimetry analysis .......................239
  8.1.4 Determination of nonlinear optical $d_{ij}$ coefficients through reflection second
       harmonic generation analysis using standard reference .............................................243
  8.1.5 Conclusions ........................................................................................................245
  8.1.6 Figures .................................................................................................................246
8.2 Orthorhombic BiFeO$_3$ ..........................................................................................254
  8.2.1 Strain-phase diagram of BiFeO$_3$ .........................................................................254
  8.2.2 Tensile strained BiFeO$_3$ films on (110)NdScO$_3$ and (110)PrScO$_3$ substrates .255
  8.2.3 Determination of orthorhombic phase by PFM and SHG analysis ....................256
  8.2.4 Conclusions ........................................................................................................258
  8.2.5 Figures .................................................................................................................259
  8.2.6 References ..........................................................................................................265

Chapter 9 Summary, Future Work and Conclusions.........................................................267

9.1 References ................................................................................................................272

Appendices .......................................................................................................................273

Appendix A. Derivation of transmitted and reflected SHG intensity for isotropic absorbing
film/substrate interface .......................................................................................................273
Appendix B. Derivation of reflected SHG intensity for a birefringent non-absorbing single
interface ............................................................................................................................276
List of Figures

Figure 1-1. A unit cell of the ABO₃ perovskite structure, with the A-site shown in green, the B-site shown as blue, and the O atoms shown as red. Note that the size of the atoms are not to scale. A periodic table of elements is shown below and is color coded with the ABO₃ unit cell to show which elements can go on other the A and/or B-sites. Image was adapted from Ref.[1].

Figure 1-2. The ABO₃ structure (unit cell shown in the middle) can be insulating or conducting and hosts a broad spectrum of material properties ranging from ferroelectricity, ferromagnetism, and superconductivity by changing the cations on the A and B-sites. Image adapted from Ref.[2].

Figure 1-3: The atomic orbitals for the A, O, and B atoms in the ABO₃ perovskite structure. The s, p, d, and f electronic orbitals (from top to bottom) are shown on the right. The A-site atom (top and bottom) can have either a spherical s-orbital shape, or a 6-lobe f-orbital shape. The pₓ, pᵧ, and pₑ orbitals of the O atoms have a 2-lobe shape, and the B-site atom has 4-lobed dₓᵧ, dₓz, dᵧz, dₑ₂, and dₑ₂₋ᵧ₂ orbitals. The n = 4, 5, and 6 shells are shown for the s-orbital on top.

Figure 1-4. (a) Unit cell of cubic SrTiO₃ perovskite which has a TiO₆ tilt symmetry of a½d½d0. (b) Cross section of the SrO plane showing the cubic arrangement of the Sr s-orbital and oxygen p-orbitals. (c) Unit cell of orthorhombic CaTiO₃ perovskite which has a TiO₆ tilt symmetry of a′a′ c′. (d) Cross section of the CaO plane showing the non-cubic arrangement of the Ca s-orbital and oxygen p-orbitals, with shifting of the Ca and oxygen atoms away from the cubic symmetry, indicated by the dashed black square.

Figure 1-5. (a) TiO₆ octahedral unit. (b) Cross section of the TiO₂ plane indicated by the dashed blue rectangle in (a), showing the atomic orbitals of the Ti and O atoms. (c) A zoom in section of (b) showing the overlapping between the p-orbitals of the O atoms (red) and the d-orbitals of the B atom (blue and orange). (d) Energy splitting of the d orbitals into the eₓ and t₂g where the difference in energy is Δₑ.

Figure 1-6. (a) Unit cell structure of tetragonal BaTiO₃ crystal which as an a₀d₀d₀ tilt structure. (b) Zoom-in of the distorted TiO₆ octahedra, showing the displacement of the Ti⁺⁺⁺ atom and the O²⁻ atoms, resulting in a net dipole moment and ferroelectric polarization to occur in this material.

Figure 1-7. (a) The distribution of octahedral rotation tilt patterns among known ABO₃ perovskites materials. Image adapted from Ref.[25]. (b) Lowest ferroelectric mode frequencies for ABO₃ perovskites in the naturally occurring orthorhombic Pnma (a′ a′ c′) and cubic Pm-3m (a₀d₀d₀) space groups, shown as red squares and black circles, respectively, as a function of the tolerance factor. Image adapted from Ref.[15].

Figure 1-8: A diagram showing how electric field (E), magnetic field (H) and stress (s) are coupled to polarization (P), magnetization (M), and strain (s) parameters which can lead to ferroelectric, ferroelastic, and ferromagnetic ordering, respectively, in a material. Cross coupling between different ferroic order parameters can lead to multiferroic properties such as magnetoelectricity, piezomagnetism, and piezoelectricity.
Figure 1-9. (a) The in-plane pseudo-cubic lattice parameters of several commercially available bulk single-crystal perovskite materials ranging from aluminates (Lu, Y, Nd, La)AlO$_3$, gallates (Nd,La)GaO$_3$, and scandates (Dy, Tb, Gd, Eu, Sm, Nd, Pr)ScO$_3$, as well as layered aluminate perovskite materials with cubic in-plane lattice parameters such as (LaAlO$_3$)$_{0.35}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT) and (NdAlO$_3$)$_{0.4}$(Sr$_2$AlTaO$_6$)$_{0.3}$ (NSAT). (b) Images of single crystalline boules of several perovskite materials taken from www.surfacenet.de. Figure was adapted from Ref.[37], Ref.[38], and Ref.[39]. ..............................................................18

Figure 1-10. The interface between a substrate (shown as the shaded blue region) and a perovskite film under (a) compressive, and (b) tensile strains, with arrows showing direction of the strain on the perovskite unit cell structure, where the red atoms are oxygen, and the gray shaded boxes are the BO$_6$ octahedral cages. The A-site atoms are not shown for visual quality. Compressive (tensile) strain results in an elongated (shortened) out-of-plane (OOP) distortion of the BO$_6$ cages, resulting in OOP (in-plane) polarizations. The BO$_6$ octahedral rotations for (c) compressive strain and (d) tensile will have enhanced out-of-plane ($\gamma$) and enhanced in-plane ($\alpha$ and $\beta$) rotations, respectively. Image adapted from Ref.[27]. .................................................19

Figure 1-11. Theoretically calculated strain-phase-temperature diagrams for (a) BaTiO$_3$ (Ref.[21]), (b) PbTiO$_3$ (Ref.[22]), (c) SrTiO$_3$ (Ref.[23]), and (d) CaTiO$_3$ (Ref.[24]) perovskite materials. The upper-limit of the predicted ferroelectric-to-paraelectric phase transition is indicated by the shaded area in each graph. Experimentally determined transition temperatures for thin films are shown as filled squares in the graphs, with labels indicating the substrate used to grow the films on. Transitions temperatures found for films studied in this thesis are shown as yellow stars in (c) and (d). The predicted ferroelectric polarization ($P$) direction is shown by the arrows which will be out-of-plane for compressive strain, and in-plane for tensile strain. .....20

Figure 1-12. (a) Temperature dependent dielectric constant $K$ (1 kHz) and (b) P-E loops ($T=10$ K) for CaTiO$_3$ (CTO) films grown on LSAT (green) and NdGaO$_3$ (NGO) (purple) substrates, with $T_C$ values indicated by black arrows. STEM HAADF and ABF images for (c) CTO/LSAT and (d) CTO/NGO films, where the LSAT and NGO regions are highlighted in green and purple respectively, and the CTO film is highlighted in blue. The TiO$_6$ octahedral rotations across the substrate/film interface are shown. (e) Magnitude of the BO$_6$ rotation ($\beta$) across the substrate/film interface for CTO/LSAT (green squares) and CTO/NGO (purple circles), where the dashed red line indicates the bulk rotation value of CTO. Image adapted from Ref. [24]. ....21

Figure 1-13. Atomic force microscopy (AFM) image taken at room temperature for a 50 nm CaTiO$_3$ film grown on LSAT substrate which induces a tensile strain of +1.2%, where the critical relaxation thickness has been exceeded as indicated by the observation of cracks in the film surfaces. The scale bar in the image is 1 $\mu$m. .................................................................22

Figure 1-14. (a) Crystal structures of n=1, 2, and 3 (A’BO$_3$)$_n$ perovskite superlattices. The individual (A,A’)$^n$O and BO$_2$ layers are shown for the n=3 superlattice structure. The BO$_6$ octahedra are highlighted in blue, and the A and A’ atoms are shown as blue and purple spheres, respectively. (b) Crystal structures of n=1, 2, and 3 AO(ABO$_3$)$_n$ Ruddlesden-Popper (RP) series, where the red spheres are the A-site atoms, with the individual AO and BO$_2$ layers shown for the n=3 RP structure on the right showing the double AO rocksalt layers in the stacking sequence of an RP........................................................................................................27
Figure 1-15. (a) Scanning transmission electron microscopy (STEM) image of atomically abrupt interfaces in a (BaTiO$_3$)$_3$/(SrTiO$_3$)$_2$/(CaTiO$_3$)$_2$ superlattice thin film crystal structure, shown schematically on the right with the (Ba, Sr, Ca) atoms represented by (green, blue, red) spheres, and the TiO$_6$ octahedral shown in light blue. Image adapted from Ref. [40]. (b) Polarization-hysteresis (P-E) loops taken at 100 Hz for ceramic bulk BaTiO$_3$ (black), and a (SrTiO$_3$)$_2$/(CaTiO$_3$)$_2$/(BaTiO$_3$)$_4$ superlattice (blue) from Ref. [40] and for (CaTiO$_3$)$_2$/(BaTiO$_3$)$_2$ (red) and (CaTiO$_3$)$_2$/(SrTiO$_3$)$_1$ (green) superlattices from Ref. [41].

Figure 1-16. Mechanisms for hybrid improper ferroelectric polarization in (A,A’)B$_2$O$_6$ superlattices in (a) layered and (b) rocksalt stacking sequences shown by the two-dimensional AO and A’O sheets in the layered geometry and the intercalation of A and A’ in each layer for the rocksalt geometry. Cross sections of the superlattice structures are shown in the middle with octahedral rotations and the displacements of the A and A’ atoms in the layers, indicated by orange and green arrows. One the right is the alternating polarization directions of the A-site cation displacements, with the orange and green blocks representing the A and A’ cation displacements, respectively. Image adapted from Ref. [45] and Ref. [46].

Figure 1-17. (a) Linear temperature dependence of polarization for an (PbTiO$_3$)$_2$/(SrTiO$_3$)$_3$ superlattice grown on (100)SrTiO$_3$ substrate, with the linear fit shown as the red line and the fitting parameters indicated in the panel and the transition at $T \sim 500$ K. (b) Temperature dependence of the c/a tetragonality ratio. (c) Temperature dependence of the dielectric constant, extrapolating the expected transition at $T \sim 500$ K. Image adapted from Ref. [50].

Figure 1-18. (a) Antipolar displacements of A-site cations (shown as red arrows) in the CaMnO$_3$ perovskite structure which has a Pnma space group structure and $a’a’c’$ tilt symmetry. The layer-resolved polarization is shown on the right, where the alternating A-site displacements in neighboring AO layers cancel each other out, resulting in a non-polar structure. (b) A-site displacements in the n=2 Ca$_3$Mn$_3$O$_9$ RP crystal structure, where unequal A-site cation displacements in the perovskite (purple) and rocksalt (red) layers results in a net polarization and hybrid improper ferroelectricity to emerge in this layered perovskite structure. Image adapted from Ref.[51].

Figure 1-19. (a) Optical circular differential interference contrast image of a cleaved (001) plane of a Ca$_{3.46}$Sr$_{0.54}$Ti$_2$O$_7$ RP single crystal at room temperature. The orthorhombic twins walls are observed with changing contrasts with the a-axis (|| [100]) orientation indicated for several domain areas. (b) Polarization-hysteresis (P-E) loops of Ca$_{3.8}$Sr$_x$Ti$_2$O$_7$ (x=0, 0.54, 0.85) single crystals at room temperature with the electric field applied along the [100] direction at a frequency of 260 Hz. Image adapted from Ref.[52].

Figure 1-20. (a) Bright-field scanning transmission electron microscopy (STEM) images of a 50 nm thick n=6 Sr$_7$Ti$_8$O$_{10}$ RP film grown on (110)DyScO$_3$ substrate. The DyScO$_3$ substrate region is shown on the bottom, and the white scale bar is 10 nm. (b) Square of the in-plane polar soft mode frequency versus n in Sr$_{n+1}$Ti$_3$O$_{3n+1}$ RP structure under no strain (gray circles) and under +1.10 tensile strain (blue squares) with theory fits shown as red lines. The negative squared frequencies indicate a polar instability. (c) Experimentally measured ferroelectric transitions ($T_c$) shown as filled blue squares and remanent polarizations ($P_r$), shown as open blue squares, for n=3, 4, 5, 6 Sr$_{n+1}$Ti$_3$O$_{3n+1}$ RP films grown on (110)DyScO$_3$ substrates. The black lines are shown as a visual aid to show increasing $T_c$ and $P_r$ with increasing n. Image adapted from Ref. [54] and Ref. [53].
Figure 1-21. Temperature-phase equilibrium diagrams for (a) SrO-TiO$_2$, and (b) CaO-TiO$_2$ with the phase and composition lines indicated in each diagram. Images adapted from Ref.[57]. Ref.[58].

Figure 1-22. (a) An extra SrO bilayer in a SrTiO$_3$ film, resulting in an expansion of the unit cell of the film. (b) A Sr vacancy site (Ti-rich film) shown as the dashed circle in the middle of the image where the neighboring TiO$_6$ octahedra (highlighted in green) will structurally distort, resulting in an expansion of the unit cell. Image adapted from Ref. [60].

Figure 1-23. (a) Out-of-plane c-axis lattice parameter for Sr$_{1+x}$TiO$_3$ films grown by MBE (blue circles), PLD (red squares), and sputtering (green triangles). For $x$=1.0, the films showed the same c-axis parameter as bulk SrTiO$_3$, indicated by the dashed black line. (b) STEM images of Sr$_{0.8}$TiO$_3$, SrTiO$_3$, and Sr$_{1.0}$TiO$_3$ films showing Ti-rich, stoichiometric, and Ca-rich type defects, from left-to-right, respectively. The interface between the SrTiO$_3$ substrate and film is indicated by the black arrow on the left, which is for all image panels. The white scale bars are 2 nm. Figure adapted from Ref.[59].

Figure 1-24. (a) Out-of-plane c-axis lattice parameter for three different SrTiO$_3$ films grown on (110)DyScO$_3$ substrates by MBE[61]: a Ti-rich (green) Sr$_{0.95}$TiO$_3$, a stoichiometric (red) Sr$_{1.00}$TiO$_3$, and Sr-rich (orange) Sr$_{1.05}$TiO$_3$ films, with the bulk SrTiO$_3$ c-axis indicated by the dashed black line. (b) The temperature dependence of the in-plane dielectric constant, $K_{11}$, for the stoichiometric (top, red), Ti-rich (middle, green), and Sr-rich (bottom, orange) films in (a), where the ferroelectric transition temperature is indicated by the dashed lines extending to the bottom axis. Image adapted from Ref. [61].

Figure 1-25: The calculated temperature and flux dependent equilibrium curves with the upper boundary (dashed lines) of the growth windows determined by the reaction of AO(s) ↔ AO(g), and the lower boundary (solid lines) determined by the reaction between AO(g) + TiO$_2$(s) ↔ ATiO$_3$, where A = (Ca, Sr, Ba, and Pb). Typical growth rates ~ (1-100) nm/min, and growth temperature ~600-1000°C are highlighted by the red boxed region.

Figure 1-26: A molecule of titanium tetraisopropoxide (TTIP) with chemical formula Ti-(O-CH(CH$_3$)$_3$)$_4$. Ti, O, C, and H atoms are labeled and indicated by dashed arrows. The Ti atom is in a tetrahedral arrangement with the 4 O atoms, resulting in Ti-O bond angles of ~109.5°.

Figure 1-27: The vapor pressure of titanium tetraisopropoxide (TTIP) shown as the dashed black curve at the bottom with the TTIP molecule shown on the bottom right. The vapor pressures of the organic byproducts after decomposition of the TTIP molecule are also shown, including water, isopropanol, acetone, and propene.

Figure 1-28. The out-of-plane c-axis lattice parameter measured by X-ray diffraction for several series of SrTiO$_3$ films grown on (001)SrTiO$_3$ substrates at growth temperatures of $T$ = (700, 725, 800)°C from bottom to top, where each data point represents the c-axis value for an individual film grown at different TTIP/Sr beam equivalent pressures (BEP). The c-axis value for bulk SrTiO$_3$ is indicated in each panel by the dashed black line, where films grown that had equal c-axis parameters define the growth window range (highlighted in gray), where to the left and right of this range the films are Sr-rich or Ti-rich, resulting in increased lattice parameter values from bulk. Image adapted from Ref. [70].
Figure 2-1: Hybrid molecular beam epitaxy chamber equipped with a regulated gas inlet system to supply titanium tetraisopropoxide (TTIP) from a heated bubbler source, as well as Sr and Ca effusion cells, and a regulated O₂ gas inlet system. The gas flow of TTIP and O₂ are regulated using PID controlled leak valves positioned downstream to a capacitance manometer (CM) gauge. The Sr and Ca fluxes are calibrated using a quartz crystal microbalance (QCM) and the TTIP flux is calibrated using an ion-gauge, which can both be inserted in the chamber at the growth position. An electron gun is for reflection high energy electron diffraction (RHEED) which is monitored on a photoluminescent screen attached to the chamber. The atomic species are shown on the bottom left.

Figure 2-2: (a) Flux calibrations for Sr (blue dots) and Ca (red dots) effusion cells inside of an MBE chamber. The cells were heated up and the flux was measured at several different temperatures by a quartz crystal microbalance. The flux versus temperature data was fit to an Arrhenius equation which is shown as the black lines. (b) The TTIP pressure measured by the capacitance manometer located outside of the MBE chamber versus the measured ion gauge (IG) pressure (black dots) at the growth position inside of the MBE chamber. The linear relationship is shown by the linear fit (black line).

Figure 2-3: The normalized flux versus time for the TTIP gas (black line) which was measured by an ion gauge, as well as Sr (blue) and Ca (red) fluxes which were measured by a quartz crystal microbalance. The fluxes do not drift more than ~ ±1% over a time period of 30 minutes, as indicated by the shaded gray area.

Figure 2-4: An Ewald construction showing the comparison between the reciprocal space and real space of the RHEED process. The Ewald sphere is shown which contains the incident electron beam produced by the electron gun, \( k_0 \) (green), and the diffracted wavevectors, \( k_1 \) (red) and \( k_2 \) (blue) which all have equal magnitudes. The intersection of the Ewald sphere with the reciprocal lattice planes of the sample produce diffractions spots which are detected on a photo luminescent (PL) screen where the top half of the 0th and 1st Laue zones (L₀ and L₁, respectively) are observed. The shadow edge above which only the reflected wavevectors are observable is shown. The sample orientation is shown below, with the common directions measured are along the <100> and <110> azimuths.

Figure 2-5: A comparison between the real space of a film surface crystal structure (left column), the reciprocal space (middle column), and the observed RHEED pattern (right column), for the cases of (a) flat and single crystalline surface, which result in sharp reciprocal rods and intensity RHEED spots, (b) flat surface with small domains which results in thicker reciprocal rods and RHEED streaks, (c) multilevel stepped surface which gives modulated intensities of the rods and RHEED streaks, and (d) 3D islands which give reciprocal and RHEED spots. Image adapted from Ref. [2].

Figure 2-6: The intensity of a RHEED spot during layer-by-layer growth, where the beginning (a), middle (c) and end (e) of a layer completion result in the max., min., and again max. in the RHEED intensity oscillation profile shown on the right for each of the layer times. Image adapted from Ref. [3].

Figure 2-7: Bragg’s Law showing the incident X-ray beam (red arrow) on the left at an angle of incidence, \( \omega \), with respect to the plane of a periodic array of atoms (blue dots) with lattice spacing.
of \( d \), as shown on the right. The reflected beams will have maximum constructive interference when the difference in their path length is equal to \( 2d\sin\theta \).

Figure 2-8: Geometry of 4-circle high-resolution X-ray diffractometer. The incident X-ray beam is at an angle \( \omega \) with respect to the sample plane, where the reflected X-rays are detected at an angle \( \theta \) and in the plane of incidence. The sample can be translated along the x, y and z directions, as well as rocked about the y and z directions at angles of \( \chi \) and \( \phi \) as shown by the dashed circle arrows.

Figure 2-9: A projection of the three-dimensional reciprocal lattice space (HKL) on the HH0-00L plane, showing the diffraction spots for (a) the film (pink) and substrate (blue) sample where the film is (a) fully strained as shown below the reciprocal space map, resulting in a tetragonal distortion of the film unit cell which has the same HH0 position of the substrate, and (b) a fully relaxed film, where the in-plane lattice parameter of the film is different than the substrate, resulting in different HH0 positions than that of the substrate. Image adapted from Ref. [8].

Figure 2-10: Schematic of tapping-mode atomic force microscopy (AFM) setup. A laser beam is reflected off a cantilever with a tip on the end which is in contact with the sample, and the laser beam is steered onto a 4-quadrant detector which is monitored by the Nanoscope controller. The cantilever is oscillated using an AC driven piezoelectric actuator and the amplitude of the deflection is kept constant using a feedback loop between the detector, piezoelectric actuator (piezo) and raster stage. The data is analyzed in real time to display the sample surface height as well as other properties such as adhesion.

Figure 2-11: Piezoresponse force microscopy (PFM) experimental setup. A conducting tip is in contact with a polar film sample which can be biased with respect to the tip. An AC voltage is applied to the tip, which will deflect or extend depending on the polarization vector (\( P \)) orientation of the film area being probed. This causes the reflected laser beam to move up in down on the 4-quadrant photodetector which is then measured using a lock-in amplifier which is part of the Nanoscope controller. The phase and amplitude of the tip deflection with respect to the AC field are extracted and observed on a display screen in real time.

Figure 2-12: The complete process for photolithography deposition of metal electrodes. (a) Rinse cleaning using acetone, isopropanol, and water. (b) Depositing the lift-of-resist layer, (c) depositing the photoresist layer, (d) ultra-violet exposure using a mask, (e) developing or removing the exposed photoresist areas, (f) oxygen plasma etch cleaning the surface before (g) sputtering of the metal electrode material, and finally (h) removing the remaining photoresist layers using remover PG.

Figure 2-13: Diagram of a planar capacitor consisting of a thin film (dielectric constant \( \varepsilon_{\text{film}} \)) on a substrate (dielectric constant \( \varepsilon_{\text{sub}} \)) with two interdigitated electrode fingers on top of the film. The relevant parameters for describing this structure are the finger gap, \( s \), the distance between the ends of the fingers, \( l \), and the length of the fingers, \( w \). The thickness of the film and substrate, \( t_{\text{film}} \) and \( t_{\text{sub}} \), respectively, are shown on the right.

Figure 2-14: (a) A photo image of several CaTiO\(_3\)/(001) LSAT substrate samples each showing an array of photolithographically deposited interdigitated electrode patterns (100 nm Au // 30 nm Cr) with alternating pads having different finger gaps of (b) 6 \( \mu \)m and (c) 10 \( \mu \)m. The finger length = 1 mm and the finger width = 10 \( \mu \)m. The number of fingers in (b) is 51, and in (c) 41.
Figure 2-15: Nonlinear optical second harmonic generation process, which can be thought of as (a) the conversion of two photons at frequency \( \omega \) (wavelength \( \lambda \)) which are converted into one photon of light at frequency \( 2\omega \) (wavelength \( \lambda/2 \)) by a nonlinear material where the second order optical susceptibility, \( \chi^{(2)} \neq 0 \). This process can also be thought of using an energy level diagram shown in (b) where two photons of energy \( h\omega \) excite an electron from the ground state (solid line) to a virtual state (dashed line), which then emits a single photon with energy \( h2\omega \)..............89

Figure 2-16: Table top setup for transmission SHG of a sample \((x, y, z)\) which can be rotated by \( \theta \) about a particular axis. The fundamental (80 fs pulse, 1 kHz repetition rate, wavelength \( \lambda=80\text{nm} \)) is aligned using mirrors M\(_1\) and M\(_2\) to be collinear with the sample normal \((z \text{ at } \theta=0^\circ)\). A beam splitter (BS1) allows only \( p \)-polarized light to propagate \((s\)-polarized light is dumped\), and a half-wave plate \((\lambda/2)\) is used to rotate the fundamental light field by an angle \( \phi \), where a long pass filter (LPF) stops parasitic wavelengths \((\lambda>700\text{nm})\) from propagating to the sample. The L\(_1\) lens focuses the fundamental onto the sample, where the generated \( \lambda=400 \) is collimated by L\(_2\) lens (attached to L\(_1\) by a translation stage). A short-pass filter (SPF) gets rid of red light, and BS\(_2\) filters out \( s \)-polarized blue light. The \( p \)-polarized blue light is steered using mirrors M\(_3\) and M\(_4\), and focused via L\(_3\) and filtered \((\lambda=400\pm10\text{nm})\) using a notch filter (NF) before entering the photo-multiplier tube (PMT) which is contained inside of a ‘black box’ indicated by the shaded gray area..........................90

Figure 2-17: (a) Schematic of experimental SHG tilt scan setup where the focus of the incident light \((\omega)\) can be varied with respect to the crystal physics axes of a sample \((z_1, z_2, z_3)\) which can be rotated about the axis by an angle of incidence \( \theta \). (b) Example of a focus series tilt scan on SrTiO\(_3\)//(001)LSAT film sample where \( \theta \) was rocked from \(-45^\circ\) to \(45^\circ\) in \(15^\circ\) increments, the focus was scanned from \(-4\) to \(4\) mm through the center of the film, and the SHG intensity was measured as a function of focus. (c) Contour map of the projected SHG intensity as a function of focus and \( \theta \), showing the corrected tilt path by the white dashed line. (d) Change in the focal point at which the maximum SHG intensity is measured for \( \theta=-45^\circ\) and \(45^\circ\). (e) The corrected (green circles) and uncorrected (dashed red line) tilt scans. .................................................................91

Figure 3-1: X-ray diffraction 20-\(\omega\) scans around the 002\(_p\) CaTiO\(_3\) film peaks (indicated by arrows) at varying p\(_{TTIP}\) pressures shown on the right axis. The Ca-rich (bottom) and Ti-rich (top) films are labeled and colored green and red, respectively. The stoichiometric growth window range are indicated on the right side and are shown as blue curves in the XRD scans which yield the largest 20 film peak values over the range of p\(_{TTIP}\) values highlighted. The 002 LSAT substrate peak is shown with an asterisk (*).................................108

Figure 3-2: X-ray reciprocal space map around the 303\(_p\) peak for a CaTiO\(_3\) film in the middle of the growth window \((p_{TTIP} = 31.5\times10^8 \text{ Torr})\). The intensity map is plotted in reciprocal lattice units \((\text{r.l.u.})\) of the LSAT substrate peak located at \(H=L=3.00\). The 303\(_p\) CaTiO\(_3\) peak has the same in-plane position along \(H\) indicating that the film is coherently strained to the (001)LSAT substrate. .................................................................109

Figure 3-3: Atomic force microscopy (AFM) images for the entire CaTiO\(_3\) film series showing the change in surface morphology throughout the stoichiometric growth window indicated by the blue outline, as well as Ca-rich (left) and Ti-rich (right) films. The AFM z-height scale bar is in nm and shown on the right side of each image. The p\(_{TTIP}\) \((\times10^8 \text{ Torr})\) values are shown on the middle axis for each image..................110
Figure 3-4: Reflection high energy electron diffraction (RHEED) intensity oscillations of the 01 reflection spot recorded along the <110> azimuth from the diffraction patterns shown on the right, where the region of interest being shown is indicated by the dashed white rectangles. The Ca-rich (bottom) and Ti-rich (top) films are labeled with respect to the stoichiometric films (middle), and the $p_{\text{TTIP}}$ values given above each curve on the right side of the panel. Ca-rich films showed c(4x4) reconstructions, indicated by the vertical white dashed arrows, stoichiometric films showed c(2x2) reconstructions, and Ti-rich films showed no reconstructions in the RHEED images. ................................................................. 111

Figure 3-5: Post-growth RHEED images taken inside of the MBE chamber at $T=200$ °C for each film in the series along the <100> and <110> azimuth as indicated for the images on the left. The most Ca-rich films (highlighted in the green boxed area) showed c(4x4) reconstructions, whereas stoichiometric films showed c(2x2) reconstructions, as indicated by the dashed white arrows. Ti-rich films did not show any reconstructions, with streaky diffraction spots indicating rough surfaces for these films. ................................................. 112

Figure 3-6: Energy-dispersive X-ray spectroscopy (EDS) spectra for the CaTiO$_3$ stoichiometric film series. The top panel shows EDS spectra for a bulk CTO reference sample with the Ca K$_\alpha$, Ca K$_\beta$, and the Ti K$_\alpha$ peaks labeled on the top panel for bulk CTO, with the dashed vertical lines running through each panel below showing the expected Cad Ti peaks. The peak on the far right of the spectra is from the La L$_\beta$ of the LSAT substrate. The calculated Ti:Ca ratios from the Ca K$_\alpha$ and the Ti K$_\alpha$ peaks are labeled in each panel. Ca-rich films are shown at the bottom (green), Ti-rich films are shown at the top (red), separated by films grown inside the growth window (blue). The error bar for these measurements is ±0.05. ......................................................... 113

Figure 3-7: (a) Out-of-plane c-axis lattice parameter extracted from on-axis XRD measurements. (b) The growth rate determined from RHEED intensity oscillations (filled circles) and XRD thickness fringes (open circles). (c) Ti:Ca atomic percent ratios measured by EDS. The growth window range is highlighted in blue on top, with the Ca-rich and Ti-rich regions labeled. The horizontal shaded orange area with a dashed line in each panel indicates the range of values observed within the growth window including the error bars of the measurement. .......... 114

Figure 3-8: Plane-view cross-section high-resolution transmission electron microscopy (HRTEM) images for (a) Ti-rich, (b) stoichiometric, and (c) Ca-rich CaTiO$_3$ films. The corresponding Ti:Ca ratios are shown on the top right of each image, and the darker LSAT substrate region is labeled in (c) along with the scale bar shown which applies to all images. 115

Figure 3-9: HAADF STEM images for (a) Ca-rich, (b)-(d) stoichiometric growth window, and (e) Ti-rich CaTiO$_3$ films. Below each image are zoomed-in regions indicated by the dashed white rectangles in the top panels. The CaO rocksalt layers in the Ca-rich film are indicated in the bottom panel of (a) by vertical arrows, and a TiO$_4$ defect cluster is shown in the bottom panel of (c) by the dashed white circle. The corresponding Ti:Ca atomic percent ratios are labeled below each image. The contrast and intensity of each STEM image was adjusted to emphasize the CaTiO$_3$ features. The scale bar in the bottom panel of (e) applies to all images. The LSAT substrate region at the bottom of the film is shown in the top panel of (a). .................. 116

Figure 3-10: The atomic percent ratios of Ti:Ca determined from EDS measurements are plotted as a function of $p_{\text{TTIP}}$. The total change in Ti:Ca is $\Delta\text{Ti:Ca} = 0.032$, and the total change in the TTIP flux throughout the window is $\Delta p_{\text{TTIP}} = \sim 10\times10^8$ Torr. Knowing that the fluctuation in the
TTIP flux is $\delta_{TTIP} = 0.6 \times 10^8$ Torr, the error in the Ti:Ca ratio is $\delta_{Ti:Ca} = 0.002$ inside the growth window, highlighted in red. If the error bars are considered, then $\Delta_{Ti:Ca} = 0.132$ and $\delta_{Ti:Ca} = 0.008$, highlighted in blue. Note that only the lowest and highest error bars are shown for visual clarity.

Figure 3-11: (a) Experimental SHG geometry showing the linear polarized fundamental field ($E_0$) at frequency $\omega$ rotated by an angle $\phi$ and incident to the film normal by an angle $\theta$. The generated second harmonic ($E_{2\omega}$) is detected parallel to the plane of incidence. The pseudo-cubic axes of the film are labeled. (b) SHG intensity as a function of $\theta$ taken at $T=77$ K using a fixed input polarization of $\phi = 0^\circ$. Insets show polar plots taken at fixed angles of incidence $\theta$ and continuously scanning $\phi$ 360°. The red line is the calculated SHG intensity using a monoclinic point group model ($m$).

Figure 3-12: Temperature dependent SHG scans ($\theta=0^\circ$, $\phi=0^\circ$) of the stoichiometric series with $p_{TTIP}$ values labeled on the top right axis. The SHG transition temperatures, $T_B$, of CaTiO$_3$ are indicated by vertical arrows, the black curve is the SHG intensity of the (001)LSAT substrate. The transition temperature is taken as the intersection of the SHG signal from the substrate and the film.

Figure 3-13: The polarization ($P$) versus electric ($E$)-field ($P$-$E$ loop) applied along [100]$_p$ direction at cryogenic temperature, $T=77$ K, and at a frequency of 1 kHz, for the entire stoichiometric CaTiO$_3$ series with the TTIP flux values labeled on the right axis. The growth window range is highlighted by the blue shaded area on the right. The P-E loops have larger areas for stoichiometric films. Ca-rich (bottom) and Ti-rich (top) films showed linear dielectric behavior with no switching at $T=77$K.

Figure 3-14: The temperature ($T=77$-$300$ K) and frequency (1 kHz – 1 MHz) dependence of (a) the in-plane dielectric constant, $K_{11}$, and (b) dielectric loss, tan($\delta$). The $T_C$ is determined from the peak in $K_{11}(T)$ and indicated by the dashed black line in both (a) and (b). The temperature range of the ferroelectric phase is highlighted by the shaded areas under each curve. The $p_{TTIP}$ values are labeled on the right axis of (b) and also apply to (a), with the stoichiometric growth window region highlighted in blue.

Figure 3-15: Inverse dielectric constant, $10^4/K_{11}$, for each film grown at $p_{TTIP}$ values shown on the right axis. Curie-Weiss fits are shown as the dotted black lines, with the extracted Curie constants shown on the far right axis.

Figure 3-16: (a) The ferroelectric transition temperature ($T$) as a function of $p_{TTIP}$ measured from dielectric (filled diamond) and SHG (open circle) experiments. The Ca-rich, growth window, and Ti-rich regions are labeled on top. (b) Saturation polarization, $P_s$, (c) maximum dielectric constant, $K_{11}\max$ and (d) maximum dielectric loss tan($\delta$)$_{\max}$ as a function of $p_{TTIP}$. The average values inside of the growth window are highlighted by the horizontal orange bars with dotted black lines.

Figure 3-17: (a) $T_C$ vs. Ti:Ca and (b) $T_C$ vs growth rate for the CaTiO$_3$ series. The Ca-rich, and Ti-rich sample are labeled, and the growth window area is highlighted in blue. There is no obvious trend of $T_C$ versus either Ti:Ca or growth rate within the stoichiometric growth window range.
Figure 4-1: (a) RHEED oscillations recorded from the 01 streak along the <110> azimuth during the first 10 minutes of growth for CaTiO$_3$ films grown on several substrates. The corresponding in-plane strain is shown on the right axis. The substrate crystals are indicated in each sub-panel. (b) The time-dependent change of the in-plane lattice parameter of strained CaTiO$_3$ films...

Figure 4-2: RHEED intensity oscillations (left-axis) and change of the in-plane lattice parameter, $\Delta a$ (right-axis) for (a) tensile strained CTO/LSAT and (b) compressive strained CTO/LSAO, resulting in in-phase and out-of-phase oscillations, respectively. The dashed red lines show alignment of the maxima in the RHEED oscillations with the oscillations in $\Delta a$.........

Figure 4-3: Post-growth RHEED images for the strained CaTiO$_3$ films taken at $T_{\text{substrate}} \sim 200$ °C. The top and bottom rows show RHEED images captured along the <110> and <100> azimuths, respectively, with the in-plane strain of the CaTiO$_3$ films shown on the bottom axis, and the substrate material indicated on the top axis. ..............................................

Figure 4-4: XRD 20–ω scans of the 002 CaTiO$_3$ peaks (indicated by black arrows) around the pseudocubic 002 substrates which are labeled in the graph. The in-plane strain for each film is shown on the right-axis. The expected 20 position for bulk CaTiO$_3$ is shown as the dashed black line. .................................................................

Figure 4-5: AFM images taken for (a) compressively and (b) tensile strained CaTiO$_3$ films. The substrate materials and strain are shown above each image, with the vertical height displacement scale bar shown on the right of each image. The scale bars in each image are 300 nm. ......

Figure 4-6: AFM images for (a) compressive strained 15 nm CaTiO$_3$/LaSrAlO$_4$ and (b) tensile strained 15 nm CaTiO$_3$/DyScO$_3$. The large cracks shown in the AFM image indicate signs of in-plane structural relaxation due to the large strained induced by these substrate materials on CaTiO$_3$ films. The scale bar in each image is 3 μm..........................

Figure 4-7: (a) Synchrotron-source XRD 20–ω scan about the 004 LSAO substrate peak showing the 001 CaTiO$_3$ peak giving an out-of-plane c-axis lattice parameter of $c=3.874$ Å for the 15 nm film. (b) RSM scan about the 106 LSAO substrate peak, showing that the 102 CaTiO$_3$ film peak has an equal in-plane lattice parameter to the substrate, but is just on the brink of relaxation. (c) Rocking curves of the 001 CaTiO$_3$ film (blue, left-axis) and 002 LSAO substrate (black, right-axis), which have FWHM values of 36 and 30 arcsec, respectively. (d) EDS spectra taken from three spots on the same CaTiO$_3$/LSAO sample, which revealed Ti:Ca ratios of 0.99, 1.00, and 1.01. The Ca Kα, Ca Kβ, and Ti Kα peaks are shown on top for bulk CaTiO$_3$ sample, with the La La substrate peak shown on the right for each film measurement........

Figure 4-8: Room temperature STEM HAADF image of ~ 15 nm thick CaTiO$_3$ film grown on (001)LaSrAlO$_4$ substrate. A zoom in section from the white outlined area shows the Ca (blue) and Ti (green) atoms. The tetragonal unit cell is shown by the black lines, and the red lines indicate the mid-point between the top and bottom of the unit cells. Image courtesy of Jason Lapano at PSU..........................

Figure 4-9: SHG characterization of CaTiO$_3$ strain series with (a) tilt scans and (b) polar plots taken at $T=77$ K. The tilt scans were generated by rocking the films samples at several values of 0 and measuring the in-plane SHG intensity for a fixed input polarization of $\phi=0^\circ$. The polar
plots were generated by fixing $\theta$ and rotating $\phi$ by 360° and measuring the in-plane SHG intensity. The substrate materials are indicated in each subpanel of (a) and (b). The polarization direction for each film is shown as arrow insets in (a). ......................................................150

Figure 4-10. Temperature dependent SHG signal for the strained CaTiO$_3$ series, with the SHG signal from the substrate materials shown as black lines which indicates the noise-floor for the optical measurements. The temperature scans were taken at fixed geometries of $\theta=45^\circ$ and $\phi=0^\circ$. The transition temperatures are indicated by arrows. ......................................................151

Figure 4-11: Room temperature SHG polarimetry for CaTiO$_3$ films grown on (a) LAO, (b) LSAO, and (c) YAO substrates from top to bottom, respectively. Tilt scans were taken at $\phi=0^\circ$ and polar plots shown as top insets were taken at $\theta = (-45, 0, 45)^\circ$. SHG data shown as filled circles and theory fits are shown as red lines. Theory fits were calculated assuming either monoclinic ($m$) or tetragonal ($4mm$) point group symmetries with polarization directions shown schematically on the right with the film axes shown as black arrows, polarization shown as gray arrows, and the mirror planes shown in red. ......................................................152

Figure 4-12. High-temperature SHG intensity measurements ($\phi=0^\circ$, $\theta=45^\circ$), for CaTiO$_3$ films on LAO, LSAO, and YAO substrates from top to bottom, respectively. The SHG signal from the bare substrate is shown as black curves. Transitions are indicated by the stars and the shaded regions......................................................153

Figure 4-13. Strain-phase-temperature diagram for CaTiO$_3$ with SHG transition temperatures shown as filled stars. The open stars are transitions observed below the final transition where the SHG signal equals the signal from the bare substrate. The light gray region represent the phase-field theoretical predictions where the strain-induced ferroelectric-to-paraelectric values occur. The $T_c$ values for bulk BaTiO$_3$ and PbTiO$_3$ are shown for comparison. ......................................................154

Figure 4-14: XRD 20-2$\theta$ scans about the 004 LSAO substrate peak showing the 002 film peaks for a 5 nm CaVO$_3$/(001)LSAO (black), 14 nm CaTiO$_3$/(001)LSAT (red), and a 14 nm CaTiO$_3$/5nm CaVO$_3$/(001)LSAT film sample. ......................................................155

Figure 4-15: PFM scans of a 15nm CaTiO$_3$/5nm CaVO$_3$/(001)LSAO sample showing the out-of-plane (a) phase, and (b) amplitude, for an area which was poled at +3V in the inner region (10x10 $\mu$m) with a smaller area poled at -3V in the center (5x5 $\mu$m). (c) A line profile taken from the dashed blue line in (a) showing the phase 180 ° phase shift between oppositely poled regions, where the amplitude of the PFM response is nearly equal in each region, and decreased sharply at the domain walls. PFM scans of (e) phase, and (f) amplitude, of the film taken 30 minutes after the first scan. ......................................................156

Figure 4-16: PFM switching measurement of the (a) phase and (b) amplitude of the out-of-plane PFM response for the CTO/CVO/LSAO film, where switching occurs at 1.5V tip bias. The tip bias was not calibrated. The dashed red lines in (a) highlight the 180° switching of up and down domains in the film. ......................................................157

Figure 5-1: (a) Out-of-plane lattice parameter (c-axis) as a function of TTIP flux ($p_{TTIP}$) for a stoichiometric series of ~20-nm-thick SrTiO$_3$ films on (001)LSAT. The stoichiometric growth window region is highlighted in blue, located between Ca-rich (green-left) and Ti-rich (red-right)
growth conditions. (b) Growth rates given in unit cell height per minute as determined by RHEED oscillation periods (filled circles) and XRD thickness fringes (open circles). ........169

Figure 5-2: (a) XRD 20-ω scans about the 002 SrTiO₃ film peaks (indicated by black arrow), and (b) RHEED intensity oscillations of each film in the stoichiometric series. Corresponding p_RHED values are shown on the right axis above each curve in (a) and (b).........................170

Figure 5-3: Post-growth RHEED images taken at T ~ 200 °C taken along the <110> (top row) and <100> (bottom row) azimuths. The Sr-rich (green-left), stoichiometric growth window (blue-middle), and Ti-rich (red-right) films are labeled on top. .............................................171

Figure 5-4: Temperature dependent SHG intensity for the stoichiometric (blue), Sr-rich (green), and Ti-rich (red) SrTiO₃ films, and the LSAT substrate for comparison (black). The ferroelectric to paraelectric transition is indicated by the dashed blue lines at T ~ 180 K. The top inset shows the experimental SHG geometry, where the fundamental (wavelength λ₀ = 800 nm) electric field (E₀) can be rotated about the 002 SrTiO₃ film where E₀ could be rotated about the z₁ crystal physics axes, with z₁ lying in the y-z plane. The second harmonic light (wavelength λ₂ = 400 nm) is detected in the x-z plane. ..................172

Figure 5-5: (a) Low temperature (T = 77 K) focus series tilt scan of a stoichiometric SrTiO₃/(001)LSAT film where θ was rocked from -45° to 45° in 15° increments, and the focus was scanned through the sample from -4 to 4 mm and the SHG intensity was measured as a function of focus. (b) Contour map of the projected SHG intensity as a function of focus distance and ω, showing the corrected tilt path by the white dashed line. (c) The corrected (green circles) and uncorrected (dashed red line) tilt scans generated form the focus series shown in (a). ....173

Figure 5-6: (a) Tilt scans taken at T = 77K with ϕ=0° and the angle of incidence θ scanned from -45° to +45° in 15° increments for the stoichiometric (middle), Sr-rich (bottom), and Ti-rich (top) films grown at beam equivalent TTIP pressures p_TTIP (x10⁸ Torr) shown on the top right of each sub-panel. (b) Polar plots taken at T = 77K with θ fixed at -45°, 0°, and +45° and ϕ scanned 360°. The p_TTIP values (x10⁸ Torr) are shown above each curve in (a) and on the top right of each panel in (b) and (c)..................................................................174

Figure 5-7: Temperature dependent SHG intensity for a stoichiometric (blue) SrTiO₃ film and the LSAT substrate (black). The ferroelectric (FE) transition is at ~ 180 K, the discontinuity in the SHG intensity at T ~ 385 K marks the antiferrodistoritve (AFD) structural transition. ........175

Figure 5-8: SHG polarimetry data taken at T = 77 K (open circles) and T = 298 K (open squares) showing tilt scans (ϕ = 0°). The top insets show polar plots taken at θ = -45°, 0° and +45°. Theoretical fits to a tetragonal 4mm point group symmetry model are shown as red lines on top of the data.................................................176

Figure 6-1: Unit cells of (a) SrTiO₃ and (b) CaTiO₃, which are under compressive (-0.95 %) and tensile (+1.26 %) strain when grown on (001)LSAT. Arrows indicate the strain direction. (c) The anti-directional strains for SrTiO₃ and CaTiO₃ layers in the superlattice grown on LSAT substrate. .................196
Figure 6-2: Reflection high energy electron diffraction (RHEED) recorded from the 01
diffraction streak along the <110> azimuth for SrTiO₃//(001)LSAT films grown at Sr fluxes of (a)
Φₘ=2.5×10¹³ atoms/cm²s⁻¹ and (b) Φₘ=3.0×10¹³ atoms/ cm²s⁻¹, as well as CaTiO₃//(001)LSAT
films grown at Ca fluxes of (c) Φₐ=2.5×10¹³ cm²s⁻¹ and (d) Φₐ=2.0×10¹³ cm²s⁻¹. Only the first
12 minutes of growth are shown to better emphasize the RHEED oscillations. The corresponding
TTIP flux (pₜt                 ) values are shown on the right axis of each graph. The growth window regions
are indicated by the shaded area on the right axis of each panel, with the Ti-rich and A-site rich
films labeled in the graphs. ................................................................. 197

Figure 6-3: X-ray diffraction 2θ scans about the 002p film peak of SrTiO₃//(001)LSAT films
grown at Sr fluxes of (a) Φₘ=2.5×10¹³ atoms/cm²s⁻¹ and (b) Φₘ=3.0×10¹³ atoms/ cm²s⁻¹, as well as
CaTiO₃//(001)LSAT films grown at Ca fluxes of (c) Φₐ=2.5×10¹³ cm²s⁻¹ and (d) Φₐ=2.0×10¹³ cm²s⁻¹. The corresponding TTIP flux (pₜt                 ) values are shown on the right axis of
each graph. The film peaks are indicated by arrows, and the LSAT substrate peak is indicated by
an asterisk (*). The growth window regions are indicated by the shaded area on the right axis of
each panel, with the Ti-rich and A-site rich films labeled in the graphs. ................................. 198

Figure 6-4: (a) The out-of-plane c-axis lattice parameter extracted from XRD measurements,
and (b) growth rate extracted from RHEED, as a function of TTIP flux (pₜt                 ) for each
SrTiO₃//(001)LSAT film series (left-axis) grown at Sr fluxes of Φₘ=2.5×10¹³ atoms/cm²s⁻¹
(purple up triangles) and Φₘ=3.0×10¹³ atoms/ cm²s⁻¹ (green down triangles), as well as
CaTiO₃//(001)LSAT films (right-axis) grown at Ca fluxes of (c) Φₐ=2.5×10¹³ cm²s⁻¹ (blue
squares) and (d) Φₐ=2.0×10¹³ cm²s⁻¹(red circles). The growth window regions are indicated by
the shaded areas, with the overlapping growth window region highlighted in gray................. 199

Figure 6-5: Schematic of the growth scheme for an n=2 superlattice, showing the deposition
sequence where Sr and TTIP sources are both opened to build the SrTiO₃ layer, which are then
closed and a pause period is allowed, and then Ca and TTIP sources are both opened to build the
CaTiO₃ layer. This sequence is then repeated to build the superlattice crystal structure shown
below. The shuddering times of the sources are determined by RHEED intensity oscillations
where the maxima in the oscillations correspond to the completion of individual unit cell
layers. .................................................................................................................. 200

Figure 6-6: (a) Time dependent RHEED intensity oscillations over > 2 hours of growth time for
the n=1-10 (SrTiO₃₀/(CaTiO₃)n) superlattices from bottom to top, respectively. The deposition
of the individual SrTiO₃ and CaTiO₃ layers for the n=10 superlattice are indicated on the top curve
by green and blue shaded areas, respectively. Zoom-in sections of the time dependent RHEED
oscillations shown at (a) the beginning of growth, and (b) the end of growth, which show
qualitatively very similar features................................................................. 201

Figure 6-7: STEM ADF images for the (a) n=2 and (b) n=5 (SrTiO₃₀/(CaTiO₃)n) superlattices,
where the brightest dots correspond to Sr atoms. The initial SrTiO₃ buffer layer is labeled in each
image, above the LSAT substrate region. The SrTiO₃ and CaTiO₃ layers are labeled in (b) on the
right. The scale bar in (a) and (b) is 10 nm. Zoom in HAADF STEM images for (c) n=2, (d)
n=3, (e) n=4, and (f) n=5 superlattices; the vertical scale bar in each panel is 2 nm. Intensity
profiles of the dashed red lines are plotted to the right of each panel, showing the pixel intensity
of the Sr and Ca atomic columns................................................................. 202
Figure 6-8: STEM ADF images for (a) n = 3 and (b) n = 4 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices. The SrTiO$_3$ and CaTiO$_3$ layers are shown on the right side of each image, where the brightest dots correspond to the Sr atoms. The white scale bar in each image is 5 nm. Images courtesy of Jason Lapano and Greg Stone at PSU.

Figure 6-9. (a) EDS mapping of (a) Ti, (b) Ca, and (c) Sr atoms in n = 3 superlattice. (e) Overlapping EDS maps of Ti, Ca, and Sr atoms. The purple arrows on the right indicate the Sr and Ca intermixing (purple dots) which occur in the first unit cell layer of each SrTiO$_3$ and CaTiO$_3$ slab. Image courtesy of Jason Lapano.

Figure 6-10: Reciprocal space maps around the 103 LSAT substrate peak for (a) n=3 and (b) n=8 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices. The 10L superlattice film peaks are indicated with the L index underlines. The RSM plots are in reciprocal lattice units (r.l.u.) of the LSAT substrate.

Figure 6-11: X-ray diffraction 2θ-ω scans of the 00L peaks in reciprocal lattice units (r.l.u.) of the LSAT substrate for the n = 1-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices. The 00(n), 00(2n), 00(3n) and 00(4n) peak positions are labeled in top, with dashed red lines and asterisks corresponding to the 001 and 002 LSAT substrate peaks. The n$^\text{th}$ order satellite diffraction peaks are highlighted in blue.

Figure 6-12. (a) Zoom-in of the 00(2n) peaks, showing the thickness fringes. (b) Zoom-in of the peak splitting for the 00(3n) peaks, with the error in n determined from the degree of peak splitting which is indicated by the red arrows. (c) The interface roughness parameter, $\Delta n$, and (b) the c-axis lattice parameter for the n=1-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices, as determined from the degree of splitting of the 00(3n) peaks and superlattice satellite peak positions with linear fit to the c-axis values in shown as the black line. The linear fit parameters are shown with a coefficient of determination of $R^2=1$.

Figure 6-13: (a) Schematic of the SHG experimental setup, where the linear polarized electric field of the fundamental laser beam ($E_0$) can be rotated by an angle $\phi$, and is focused onto the film/substrate sample, and the second harmonic field ($E_{20}$) is measured in the plane of incidence. The film/sample axes are shown, where the sample can be rotated about the [010] axis by $\theta$. (b) Temperature dependent SHG intensity for a stoichiometric SrTiO$_3$ (green) and CaTiO$_3$ (blue) film, with the LSAT substrate signal show as the black line, indicating the noise level for the measurements performed with the sample orientation fixed at $\theta=45^\circ$ and $\phi=0^\circ$. The transitions for the SrTiO$_3$ and CaTiO$_3$ film are indicated by the green and blue arrows, respectively.

Figure 6-14: Low temperature (T=77K) SHG intensity as a function of $\theta$ ($\phi=0^\circ$) for the (c) SrTiO$_3$ (green squares) and (d) CaTiO$_3$ (blue circles) films, with polar plots shown as the top insets taken at $\theta=-45^\circ$, $0^\circ$, and $+45^\circ$ where $\phi$ was rotated $360^\circ$. Theoretical fits for a tetragonal 4mm and monoclinic m point group symmetry are shown as red lines to the SHG data in (c) and (d), respectively. The polarization direction for (e) the SrTiO$_3$ film is assumed to be out-of-plane along the [001] and (f) the CaTiO$_3$ film is in the mirror (m) plane and has both an in-plane and out-of-plane polarization component.

Figure 6-15: Temperature dependence of the SHG intensity ($\theta=45^\circ$, $\phi=0^\circ$) for n=1-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices, with the same incident laser power density of $\sim$3.0 W/cm$^2$. Transitions for n=3, 7-10 are indicated by arrows for the heating (right) and cooling (left) scans, with the SHG intensity for the LSAT substrate shown in each panel as the black line. No
transitions are observed for the \( n = 1, 2, 4, 5, \) and 6 superlattices over the measured temperature range (black curves). (b) Low temperature \( (T = 77K) \) SHG tilt scans (bottom), and polar plots (top), for \( n = 3, 7-10 \) superlattices...

Figure 6-16: (a) Transition temperature determined from SHG experiments and the SHG intensity \( (I_{2\omega}) \) measured at \( T = 77 K \) \( (\theta = 45^\circ, \phi = 0^\circ) \) on the left and right axes respectively, for the \( n = 1-10 \) superlattices. (b) \( \Delta n \) parameter for the \( n = 1-10 \) superlattices. The top axis shows the half c-axis unit cell thickness as a function of \( n \). The highlighted region around \( n = 3 \) indicates that the polar transition is caused by A-site intermixing, whereas the highlighted region around \( n = 6-7 \) indicates the critical thickness for ferroelectricity to emerge in the superlattices.

Figure 7-1: Schematic of a hybrid MBE chamber used for sequential shuttered growth of layered \( \text{SrTiO}_3 \) films with \( \text{Sr} \) supplied from a standard effusion cell and TTIP from a gas injector in the presence of molecular oxygen \( \text{O}_2 \). The TTIP and \( \text{O}_2 \) gas inlet pressures are PID controlled using a motorized leak valve (LV) and capacitance manometer gauge (CM).

Figure 7-2: (a) Deposition sequence of alternating \( \text{SrO} \) and \( \text{TiO}_2 \) MLs to build (b) the \( \text{SrTiO}_3 \) perovskite structure. (c) RHEED oscillation profile for precisely one monolayer of \( \text{SrO} \) and \( \text{TiO}_2 \) doses.

Figure 7-3: (a) \( \text{Sr} \) and TTIP shutter time parameter space map for depositing \( \text{SrTiO}_3 \) with 1:1 \( \text{Sr}:\text{Ti} \) cation stoichiometry (red dotted line) and single ML dosage which is located at point 7 (red square). The Ti-rich region (top left corner) and Sr-rich region (bottom right corner) are shaded in blue and green, respectively. (b) RHEED intensity oscillations for Ti-rich (top) and Sr-rich (bottom) with shutter times corresponding to points 1, 2 and 3, 4 in panel (a).

Figure 7-4: RHEED intensity oscillation beating for stoichiometric shutter times and doses systematically adjusted from \( (0.90, 0.95, 1.00, 1.05, 1.10) \) MLs corresponding to points (5, 6, 7, 8 and 9) in Figure 7-4(a). The beating periods are indicated by blue arrows, which increase as the 1.0/1.0 \( \text{SrO}/\text{TiO}_2 \) ML dosage timing is approached.

Figure 7-5: X-ray diffraction 20-\( \omega \) scan of the 002 \( \text{SrTiO}_3 \) reflection for a 30-nm-thick \( \text{SrTiO}_3 \) film grown on (100)\( \text{SrTiO}_3 \) using sequential shuttering of \( \text{Sr} \) and TTIP. The good overlap of film and substrate peak, i.e. the absence of a film peak on the substrate peak shoulder towards smaller scattering angles indicates that cation stoichiometric \( \text{SrTiO}_3 \) films can be grown by hybrid MBE in a layer-by-layer fashion.

Figure 7-6: (a) RHEED intensity oscillation profile for entire growth of \( n = 4 \) \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) RP film on (100)\( \text{SrTiO}_3 \) substrate. The RP stack was built by depositing 50 repeat units of the \( \text{Sr} \) and TTIP shuttering sequence shown in (b) with the corresponding RP crystal structure show above containing the extra \( \text{SrO} \) rocksalt layer in the middle. The gray regions indicates a pause period where nothing was deposited, enabling a smooth interface for the additional \( \text{SrO} \) rocksalt layer to be deposited. The initial RHEED in (a) shows the 10 unit cell thick \( \text{SrTiO}_3 \) buffer layer deposited to ensure a well terminated seed layer for RP film growth. (c) RHEED oscillation profiles of a single RP unit cell at the end of growth (top right inset) has consistent RHEED features compared to the beginning of growth.
Figure 7-7: X-ray diffraction 2θ-ω scan of the 00L peaks of the n=4 Sr₂Ti₄O₁₁ RP film. The out-of-plane c-axis lattice parameter of the n=4 RP film structure was determined to be $c = (35.7±0.2)$ Å.

Figure 7-8: HRTEM image of the entire RP film with the SrTiO₃ buffer layer region labeled on bottom and epoxy on top. The unit cell crystal structure of the RP film is shown on the right, corresponding to the black outlined rectangle area in the image.

Figure 8-1: Temperature-strain-phase diagram of BiFeO₃. Compressive strain drives the symmetry of BiFeO₃ from the rhombohedral (R3c) to tetragonal (P4mm) structure which occurs at -4.3% compressive strain at room temperature. The polarization ($P_3$) switched from the <111> $P_3$ direction in the R3c phase to <001> in the P4mm phase. Tensile strain drives BiFeO₃ from R3c to an orthorhombic Pnma symmetry. The pseudo-rhombohedral (R) BFO film studied in this work was grown on (111)SrTiO₃ substrate and the pseudo-tetragonal (T) BFO film was grown on (110)YAlO₃ substrate, where the resulting misfit strains are indicated by arrows in the graph. The R-BFO and T-BFO unit cells are shown with their lattice parameter values labeled.

Figure 8-2: X-ray diffraction data for T-BFO and R-BFO. 2θ-ω scans of (a) the 00L reflections of T-BFO yield an out-of-plane lattice parameter of $c = 4.670 ± 0.002$ Å, and (c) the 111 $P_3$ and 222 $P_3$ reflections for R-BFO yield a pseudo-cubic lattice parameter of $a_p = 3.958 ± 0.002$ Å. Rocking curves for (b) the 001 reflection of the T-BFO film (blue line) and the 110 reflection of the YAO substrate (black line) yield a FWHM of 0.024° and 0.027°, respectively, and (d) the 111 $P_3$ reflection of the R-BFO film (red line) and 111 reflection of the STO substrate (black line) yield a FWHM of 0.37° and 0.024°, respectively. The broadened FWHM of the R-BFO film is likely due to thermal cycling. The STO and YAO substrate reflections are marked by an asterisk (*). Films were grown by Alex Melville at Cornell.

Figure 8-3: Refractive index (n) and absorption coefficient (k) over the spectral range from 200 nm to 1690 nm for R-BFO and T-BFO shown as the dashed red and solid blue lines, respectively. The onset of absorption for the R and T-BFO films occurs at approximately 577 nm and 588 nm, respectively.

Figure 8-4: (a) Transmission SHG polarimetry geometry showing the linearly polarized fundamental field, $E_{xx}$, rotated by an angle $\phi$ and incident to the film normal by an angle $\theta$ in the x-z plane, and the p-polarized ($\parallel$) SHG field, $E_{200}$ which is detected by a photomultiplier tube (PMT). The (x,y,z) laboratory axes are shown, where the crystal physics axes of the films ($z_1$, $z_2$, $z_3$) are related for the R and T-BFO films as $R_1$ ($z_1 = y$, $z_2 = -x$, $z_3 = z$), $R_2$ ($z_1 = -y$, $z_2 = x$, $z_3 = z$), and $T_1$ ($z_1 = x$, $z_2 = y$, $z_3 = z$) configurations. (b) Reflection SHG polarimetry geometry showing the reference crystal which has the backside interface wedged and roughened to stop reflections.

Figure 8-5: SHG polarimetry data of the R-BFO film showing (a) tilt scans of the transmitted $p$-polarized SHG intensity for a fundamental wavelength of $\lambda = 800$ nm as a function of the angle of incidence $\theta$ for a fixed input polarization of $\phi = 0^\circ$ in the $R_1$ (blue circles) and $R_2$ (red squares) configurations. Polar plots taken at $\lambda = 800$ nm are shown to the right for (b) $R_1$ and (c) $R_2$ configurations, taken at $\theta = 45^\circ$ (red circles) and $\theta = -45^\circ$ (green triangles), where $\phi$ was scanned 360°. Tilt scans and polar plots were also collected for a fundamental wavelength of $\lambda = 1550$ nm,
shown in (d), (e) and (f), respectively, with the same configurations as (a), (b) and (c) but at a different wavelength. Theoretical fits according to a $3m$ point group symmetry model are shown as black lines.

Figure 8-6: SHG polarimetry data of the T-BFO film showing (a) tilt scan of the transmitted $p$-polarized SHG intensity for a fundamental wavelength of $\lambda=800\,\text{nm}$ as a function of the angle of incidence $\theta$ for a fixed input polarization of $\phi=0^\circ$ in the $T_1$ (blue circles). Polar plots taken at $\lambda=800\,\text{nm}$ are shown to the right for (b) $T_1$ configuration, taken at $\theta=45^\circ$ (red circles) and $\theta=30^\circ$ (green triangles), where $\phi$ was scanned $360^\circ$. Tilt scans and polar plots were also collected for a fundamental wavelength of $\lambda=1550\,\text{nm}$, shown in (c) and (d), respectively, with the same configurations as (a) and (b). Theoretical fits according to a $4mm$ point group symmetry are shown as black lines.

Figure 8-7: A comparison of the magnitude of $d_3$ nonlinear optical coefficients for several of the best nonlinear optical perovskite materials including LiTaO$_3$, BaTiO$_3$, KNbO$_3$, and LiNbO$_3$, which are all at fundamental wavelengths of 1064 nm, as well as the largest $d_3$ coefficients measured for R-BFO and T-BFO at a fundamental wavelength of 800 nm.

Figure 8-8: Calculated strain-temperature phase diagrams of BiFeO$_3$ thin films from phase-field simulations for (a) short-circuit or closed-circuit boundary conditions, and (b) under open-circuit boundary conditions. The rhombohedral (R) and orthorhombic (O) phases, which have $3m$ and $mm2$ point group symmetries, respectively, are labeled, as well as the high temperature cubic phase. The $\{110\}$ PrScO$_3$ substrate strain and $\{110\}$NdScO$_3$ substrate strains are shown in (a) and (b), respectively. An orthorhombic unit cell of BiFeO$_3$ is shown as an inset in (b), with the $a_1$, $a_2$, and $a_3$ lattice parameters, with the polarization direction in the $\{110\}$ direction. The dashed line shows the intersection of the expected polar phase for the substrates in (a) and (b).

Figure 8-9: A TEM micrograph of a BiFeO$_3$ thin film on NdScO$_3$ substrate for (a) high angle annular dark field STEM image with the substrate/film interface shown. (b) Planar-view image showing the striped domain pattern of the film. The crystal physics axes are shown in both (a) and (b). (c) Out-of-plane and (d) in-plane PFM images obtained under a 5 V ac bias of the BiFeO$_3$ film, with the polarizations, $P_1$ and $P_2$ of each domain configuration labeled in (d) with the film axes also shown. Image adapted from Ref. [30].

Figure 8-10: The refractive index, $n$ (left axis), and absorption coefficient, $k$ (right axis), for a 15 nm BiFeO$_3$ film grown on $\{110\}$NdScO$_3$ substrate. The linear optical properties of the film were determined through spectroscopic ellipsometry analysis.

Figure 8-11: Second harmonic generation polarimetry analysis at a fundamental wavelength of 800 nm and at room temperature for the 15 nm BiFeO$_3$ film on $\{110\}$NdScO$_3$ substrate. The SHG tilt scan shows the SHG intensity as a function of the angle of incidence, $\theta$ where the input polarization of the fundamental field was fixed to $\phi=0^\circ$ with data shown as the blue circles and the theoretical fit according to a multi-domain $mm2$ orthorhombic point group symmetry model shown as red lines. Polar plots are shown above at fixed angles of incidence of $\theta=-45^\circ$, $0^\circ$, and $+45^\circ$, where $\phi$ was rotated by $360^\circ$.

Figure 8-12: PFM analysis of the 30 nm BiFeO$_3$ film grown on $\{110\}$PrScO$_3$ by molecular beam epitaxy. The top panels show the in-plane PFM phase (left) and amplitude (right) response, and the bottom panels show the out-of-plane PFM phase (left) and amplitude (right) response. The
Figure 8-13: Second harmonic generation polarimetry analysis at a fundamental wavelength of 800 nm and at room temperature for the 30 nm BiFeO$_3$ film on (110)PrScO$_3$ substrate grown by molecular beam epitaxy. The SHG tilt scan shows the SHG intensity as a function of the angle of incidence, $\theta$ where the input polarization of the fundamental field was fixed to $\phi=0^\circ$ with data shown as the green circles and the theoretical fit according to a multi-domain $mm2$ orthorhombic point group symmetry model shown as blue lines, and the theoretical fit for a multi-domain monoclinic $m$ point group symmetry model shown as red. Polar plots are shown above at fixed angles of incidence of $\theta=-45^\circ$, $0^\circ$, and $+45^\circ$, where $\phi$ was rotated by $360^\circ$. 
List of Tables

Table 8-1: Nonlinear optical $K_{ij}$ ratios ($d_{ij}/d_{15}$) and $d_{ij}$ (pm/V) coefficient values from experimental work presented here (Expt.) and theoretical values (Theory) reported by Ju et al. for R-BFO[17] and T-BFO[18] at fundamental wavelengths of 800 nm and 1550 nm. ...............253
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Chapter 1

Introduction

1.1 Structure-property relationships in complex oxides

For materials scientists, a crystal lattice is the ‘canvas’ and atoms are the ‘medium’ with which to paint a masterpiece. One of the most versatile material ‘canvases’ is the ABO$_3$ perovskite crystal structure, shown in the top of Figure 1-1, where the available ‘medium’ consists of over 30 elements that can go on the A-site, nearly half of the periodic table which can be inserted onto the B-site, and halogen anions such as oxygen (O) which are bonded to both the A and B-site cations.[1] By simply changing the A and B-site chemistries in the perovskite structure, a rich tapestry of different materials can be explored ranging from insulators to conductors, as shown in Figure 1-2,[2] giving rise to a broad spectrum of functional material properties and applications that can be accessed such as ferroelectricity, ferromagnetism, piezoelectricity, superconductivity, giant magnetoresistance, magnetoelectricity, metal-to-insulator transitions, tunable dielectrics, actuators, sensors, optical second harmonic generators, etc.

Within the ABO$_3$ perovskite, the A-site cation, which is typically an alkali, alkaline, or lanthanide metal, sits in the center of the unit cell and is ideally in a 12-fold coordination with the 12 oxygen (O) atoms sitting at the face edges. The B-site cation, typically a transition metal, sits on the corners of the unit cell and is in 6-fold coordination with the neighboring oxygen atoms,
creating BO$_6$ octahedral cages.[3] The different electron orbitals of each atom in the ABO$_3$ compound are shown in Figure 1-3. A-site atoms that are alkali or alkaline metals have s-orbitals which have a spherical shape, and for rare-earth A-site atoms the individual f-orbital shells have 6-lobed shapes, where together they make a nearly spherical shape. The oxygen atoms have 2-lobed p-orbitals ($p_x$, $p_y$, $p_z$) and the transition metal B-site d-orbitals ($d_{x^2-y^2}$, $d_{xz}$, $d_{yz}$, $d_{xy}$) have 4-lobed shapes, as shown in Figure 1-3. Depending on the size of the A and B-site atoms, the structure will distort in order to coordinate their orbitals with the oxygen p-orbitals, thus minimizing the electronic energy of the structure.

To accommodate an optimal electronic coordination of the orbitals in the perovskite structure, two main types of distortions can occur. The first type of distortion is through rotations of BO$_6$ octahedra, which can rotate about the three different B-O-B axes in the perovskite unit cell. The magnitude of the octahedral rotations is governed by how well the A, B and O ions are packed together, and is described by the Goldschmidt tolerance factor, $t = (r_A + r_O)/\sqrt{2(r_B + r_O)}$, where $r_A$, $r_B$, and $r_O$ are the ionic radii of the A, B, and O atoms.[4] For an ‘ideally’ cubic packing arrangement of the ions, tolerance factors range between $0.96 < t < 1.0$, and no tilting of the BO$_6$ octahedra is predicted to occur.[5] For example, the cubic (Pm-3m space group symmetry) SrTiO$_3$ perovskite structure, which has ionic radii of $r_{Sr} = 1.44$ Å, $r_{Ti} = 0.605$ Å, and $r_O = 1.40$ Å,[6] has a tolerance factor of $t = 1.00$, resulting in no TiO$_6$ tilting and a tilt symmetry of $a^0a^0a^0$.[7] shown in Figure 1-4(a), where in Glazer notation[8] the superscript 0 means that there are no rotations of the TiO$_6$ along that direction. This allows equal distant bonds between the Sr and O atoms, and a cubic arrangement of the Sr and O orbitals, as shown in Figure 1-4(b).

For tolerance factors ranging between $0.7 < t < 0.96$, the A-site cation is too small for the cubic arrangement of the BO$_6$ octahedra, and they will rotate in order to optimize the A-site coordination from 12-fold coordination to a lower-coordination number (i.e. 8-fold coordination) with the oxygen atoms.[6, 9] For example, the orthorhombic (Pnma space group symmetry)
CaTiO$_3$ perovskite structure, which has a relatively small A-site cation ($r_{Ca} = 1.12$ Å)[10], yields a tolerance factor of $t = 0.89$, resulting in the TiO$_6$ octahedra to rotate in an $a'a'c^+$ tilt symmetry,[11] where the superscript – (+) denotes out-of-phase (in-phase) rotations, as shown in Figure 1-4(c). Figure 1-4(d) shows the orbitals of the Ca and O atoms in a CaO-plane cross section of the CaTiO$_3$ structure, where the Ca atom shifts with respect to the O positions in order to optimize their orbital energy, and thus breaking the cubic symmetry of the TiO$_6$ octahedral arrangements.

Another type of distortion that can occur in the perovskite structure are Jahn-Teller distortions,[12] which can involve displacements of the B-site cation with respect to oxygen ions. If we consider the shape of the BO$_6$ octahedral cage, shown in Figure 1-5(a), orbital overlapping must occur between some of the $d$-orbitals and $p$-orbitals of the B-site and oxygen atom, respectfully. Figure 1-5(b) shows a cross section of the BO$_6$ cage, showing the orbitals lying in a BO$_2$-plane. The $e_g$ orbitals point towards the oxygen atoms, and these particular $d$-orbitals will overlap with oxygen $p$-orbitals, which is more clearly seen in Figure 1-5(c) showing a zoomed-in cross section of the BO$_2$ orbital plane. The $t_{2g}$ orbitals, shown as the orange shaded orbitals in Figure 1-5(c), point away from the oxygen atoms and will not overlap with the oxygen $p$-orbitals. This creates the potential for energy splitting of the $e_g$ and $t_{2g}$ electron orbital occupancies, as shown in Figure 1-5(d). However, in general, the BO$_6$ octahedra prefer to have a cubic symmetry with equal B-O bond lengths, and for $d_0$ cations such as Ti$^{4+}$, Jahn-Tellar distortions do not occur since there are no electrons to fill the $d$ orbitals.

For perovskite materials that have large A-site cations, or tolerance factors that are slightly greater than 1, distortions of the BO$_6$ octahedra are generally preferred over rotations in order to minimize the free energy of the structure.[12] For example, the BaTiO$_3$ perovskite structure which has a relatively larger A-site cation ($r_{Ba} = 1.60$ Å), has tolerance factor of $t = 1.06$,[13] and octahedral rotations are absent in the structure with an $a^0d^0a^0$ tilt symmetry.[14] as
shown in Figure 1-6(a). At ambient temperatures, a distortion of the TiO$_6$ octahedra occurs in the BaTiO$_3$ structure, as shown in Figure 1-6(b), where the positively charged titanium cation and negatively charged oxygen anion move in opposite directions, creating a net dipole moment and a built-in polarization, or ferroelectricity.

However, of the vast number of possible ABO$_3$ perovskite structures that can be constructed, the majority of them adopt the non-polar centrosymmetric orthorhombic $Pnma$ space group symmetry with a BO$_6$ octahedral tilt symmetry of $a'a'c'$.[15-18] as shown in Figure 1-7. Polar properties such as ferroelectricity are rare among perovskites, often only found in perovskite materials with very small A-site cations such as Li in LiNbO$_3$ resulting in a rhombhedral structure, or large A-site cations such as Ba in BaTiO$_3$ which is tetragonal, or for perovskites containing lone-pair 6$s$ electrons such as Pb in PbTiO$_3$ which is tetragonal.[15] One of the most prolific materials scientist of his time, Dr. Robert E. Newnham, pondered as to the peculiarity of perovskites to adopt non-polar structures, and asked, “…why is it that centrosymmetric crystals are three times more common that noncentrosymmetric crystals? It is unclear why most crystals possess a center of symmetry. What physical principle favors inversion symmetry? Is it that atoms and molecules reside in potential wells where the interatomic forces are balanced? Inversion symmetry leads to equal forces in opposing directions favoring stability.”[18]

To answer this question, Bennedek and Fennie [15] used density functional theory to investigate why ferroelectricity is suppressed in the majority of ABO$_3$ perovskites which adopt the non-polar orthorhombic $a'a'c'$ tilt pattern with $Pbnm$ space group symmetry. They discovered that the main reason why ferroelectricity is suppressed is due to the anti-polar displacements of the A-site cations, which is caused by the octahedral rotations, and that while the octahedral rotations do play a role for suppressing ferroelectricity, it is not the main reason as was commonly thought. They demonstrate this by calculating the frequency of the lowest energy
ferroelectric mode for several different \textit{Pnma} (\textit{a} \textit{a} \textit{c})*perovskite materials with different tolerance factors, as shown in Figure 1-7(b). In the naturally occurring \textit{Pnma} structure, the ferroelectric mode frequencies for all of the materials are all stable (\(\omega \gg 0\)) and independent of the tolerance factor. However, if the octahedral rotations and A-site distortions are ‘turned off’ by forcing them into the cubic \textit{Pm-3m} structure, a ferroelectric instability will occur (\(\omega < 0\)) and this instability increases with decreasing tolerance factor (i.e. smaller A-site cations). This has profound implications in that the vast majority of possible ABO\(_3\) perovskite structures can be turned into polar materials by tuning their distortion modes which are inherent to this structure.

Although naturally occurring ferroelectric perovskite materials (at ambient temperatures) such as BaTiO\(_3\) “appear to be an exception rather than the rule and is not representative of the majority of perovskite and perovskite-like ferroelectrics” as Benedek and Fennie state,[15] there are several strategies that can be implemented for designing and creating ferroelectric perovskite materials by utilizing the strong coupling that can occur between the different degrees of freedom in the ABO\(_3\) structure, such as lattice (strain), charge (polarization), and spin (magnetization), as shown schematically in Figure 1-8.[2, 19] The strong coupling between strain and polarization (or ferroelectricity) has led to intense research efforts in past years in epitaxial strain-engineering of ferroelectric properties in thin film perovskite materials.[20] By growing thin film perovskites on lattice mismatched substrates, huge strains can be imparted that dramatically distort the perovskite unit cell, which can drastically enhance ferroelectric polarizations and transition temperatures in BaTiO\(_3\),[21] and PbTiO\(_3\),[22] as well as induce ferroelectricity in otherwise non-polar perovskite materials such as SrTiO\(_3\),[23] and CaTiO\(_3\),[24] which is discussed in greater detail in the next section.
Figure 1-1. A unit cell of the ABO$_3$ perovskite structure, with the A-site shown in green, the B-site shown as blue, and the O atoms shown as red. Note that the size of the atoms are not to scale. A periodic table of elements is shown below and is color coded with the ABO$_3$ unit cell to show which elements can go on other the A and/or B-sites. Image was adapted from Ref.[1].
Figure 1-2. The ABO$_3$ structure (unit cell shown in the middle) can be insulating or conducting and hosts a broad spectrum of material properties ranging from ferroelectricity, ferromagnetism, and superconductivity by changing the cations on the A and B-sites. Image adapted from Ref.[2].
Figure 1-3: The atomic orbitals for the A, O, and B atoms in the ABO₃ perovskite structure. The s, p, d, and f electronic orbitals (from top to bottom) are shown on the right. The A-site atom (top and bottom) can have either a spherical s-orbital shape, or a 6-lobe f-orbital shape. The pₓ, pᵧ, and pₗ orbitals of the O atoms have a 2-lobe shape, and the B-site atom has 4-lobed dₓᵧ, dₓz, d₂z, dᵧz, and dₓ²₋ᵧ² orbitals. The n = 4, 5, and 6 shells are shown for the s-orbital on top.
Figure 1.4. (a) Unit cell of cubic SrTiO$_3$ perovskite which has a TiO$_6$ tilt symmetry of $a^0 a^0 a^0$. (b) Cross section of the SrO plane showing the cubic arrangement of the Sr $s$-orbital and oxygen $p$-orbitals. (c) Unit cell of orthorhombic CaTiO$_3$ perovskite which has a TiO$_6$ tilt symmetry of $a^+ a^+ c^+$. (d) Cross section of the CaO plane showing the non-cubic arrangement of the Ca $s$-orbital and oxygen $p$-orbitals, with shifting of the Ca and oxygen atoms away from the cubic symmetry, indicated by the dashed black square.
Figure 1-5. (a) TiO$_6$ octahedral unit. (b) Cross section of the TiO$_2$ plane indicated by the dashed blue rectangle in (a), showing the atomic orbitals of the Ti and O atoms. (c) A zoom in section of (b) showing the overlapping between the $p$-orbitals of the O atoms (red) and the $d$-orbitals of the B atom (blue and orange). (d) Energy splitting of the $d$ orbitals into the $e_g$ and $t_{2g}$ where the difference in energy is $\Delta_e$. 
Figure 1-6. (a) Unit cell structure of tetragonal BaTiO$_3$ crystal which as an $a^0a^0a^0$ tilt structure. 
(b) Zoom-in of the distorted TiO$_6$ octahedra, showing the displacement of the Ti$^{4+}$ atom and the O$^{2-}$ atoms, resulting in a net dipole moment and ferroelectric polarization to occur in this material.
Figure 1-7. (a) The distribution of octahedral rotation tilt patterns among known ABO$_3$ perovskites materials. Image adapted from Ref.[25]. (b) Lowest ferroelectric mode frequencies for ABO$_3$ perovskites in the naturally occurring orthorhombic Pnma ($a' a' a'$) and cubic Pm-3m ($a^0 a^0 a^0$) space groups, shown as red squares and black circles, respectively, as a function of the tolerance factor. Image adapted from Ref.[15].
Figure 1-8: A diagram showing how electric field ($E$), magnetic field ($H$) and stress ($\sigma$) are coupled to polarization ($P$), magnetization ($M$), and strain ($\varepsilon$) parameters which can lead to ferroelectric, ferroelastic, and ferromagnetic ordering, respectively, in a material. Cross coupling between different ferroic order parameters can lead to multiferroic properties such as magnetoelectricity, piezomagnetism, and piezoelectricity.
1.2 Strain-induced ferroelectricity in complex oxides

The effects of strain on the material properties of perovskite materials has been well studied. One way to impose strain is through isovalent cation substitution, usually on the A-site of a perovskite material, inducing a ‘chemical pressure’ in a material. For example, doping Ca into the incipient ferroelectric SrTiO$_3$ perovskite material, i.e. Sr$_{1-x}$Ca$_x$TiO$_3$, relaxor ferroelectricity can be stabilized for Ca concentrations ranging between 0.0018 < x < 0.016, with ferroelectric transition temperatures of $T_c$~30 K.[26] Chemical substitution, or doping, is the primary strategy for tailoring the properties of perovskite materials.

Another route for applying strain in perovskite materials is through epitaxial strain, which is done by synthesizing perovskites as thin films on substrate crystals which have similar structural, chemical, and thermal properties but with different in-plane lattice parameters than the targeted film material. A variety of high quality single crystal perovskite substrate materials are commercially available, as shown in Figure 1-9(a) and (b), which have a broad range of in-plane lattice parameters that can be used to induce epitaxial strains in perovskite thin films such as SrTiO$_3$, CaTiO$_3$, and BaTiO$_3$. In this way, huge strains can be imparted in a film which is well beyond the point at which the bulk material would crack or deform. For compressive strains, the crystal structure is squished in-the-plane and thus increases the out-of-plane lattice parameter, resulting in a polarization along the out-of-plane direction, shown schematically in Figure 1-10(a). For tensile strains, the perovskite structure is stretched in the plane, resulting in an in-plane distortion and in-plane polarization to occur, as shown in Figure 1-10(b).[27] Strain can also affect the octahedral rotations in a perovskite material, where compressive strain has been found to enhance out-of-plane rotations ($\gamma$) and tensile strain tends to enhance in-plane rotations ($\alpha$ and $\beta$) as shown in Figure 1-10(c) and (d), respectively.
Theoretical calculations predict that with increasing strain, the ferroelectric polarization and ferroelectric transition temperatures of bulk ferroelectric materials such as BaTiO$_3$ and PbTiO$_3$ will increase, as shown in Figure 1-11(a) and (b), respectively. This was experimentally demonstrated for BaTiO$_3$ films grown on DyScO$_3$ and GdScO$_3$ substrates, which induce in-plane compressive strains of -1.7 % and -1.0 %, respectively,\cite{21} which can enhance the ferroelectric transition temperature of BaTiO$_3$ ($T_C$~130 °C in bulk) to $T_C$~ 540 °C and $T_C$~ 400 °C, respectively, shown as the filled squares in Figure 1-11(a). Increased remanent polarizations are also observed of $P_r$ ~ 70 μC/cm$^2$ and $P$ ~ 50 μC/cm$^2$ for BaTiO$_3$ films on DyScO$_3$ and GdScO$_3$ substrates, respectively, whereas the bulk polarization of BaTiO$_3$ is $P$ ~ 26 μC/cm$^2$. Similarly, strained PbTiO$_3$ on a SrTiO$_3$ substrate (-1.0% compressive strain) increases the ferroelectric transition temperatures to $T_C$ ~ 700 °C, whereas in bulk PbTiO$_3$ this transition will occur at $T_C$ ~ 492 °C.\cite{22}

Theoretical calculations also predict that strain can induce ferroelectricity in incipient ferroelectric perovskite materials such as SrTiO$_3$ and CaTiO$_3$,\cite{23, 24, 28} as shown in Figure 1-11(c) and (d), respectively. For tensile strained SrTiO$_3$ films grown on (110)DyScO$_3$ and (110)GdScO$_3$ substrates, a ferroelectric transition temperature of $T_C$ ~ 290 K, and $T_C$ ~ 360 K has been experimentally confirmed,\cite{23, 29} and for compressively strained SrTiO$_3$ films grown on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT) substrates, transition temperatures of $T_C$~150 K have recently been reported,\cite{30, 31} shown in Figure 1-11(c), and these transition values are very close to the theoretically predicted temperatures for SrTiO$_3$.

For CaTiO$_3$ perovskite material, the effects of strain on ferroelectric properties are a bit more complex since CaTiO$_3$ has octahedral rotations and this must be taken into account when minimizing the free energy of the system as a function of strain. Shown in Figure 1-11(d) are recent theoretical calculations for the strain-phase-temperature diagram of CaTiO$_3$, with
experimentally reported transition temperatures of CaTiO$_3$ films grown by pulsed laser deposition on LSAT (+1.2 % tensile strain) and NdGaO$_3$ (+1.1% tensile strain) substrates shown as filled squares, which have transitions at $T_C \approx 140$ K and $T_C \approx 70$ K, respectively. which were determined as the peak in the temperature dependent dielectric constant as shown in Figure 1-12(a).[24] Although the strain state for each of these films is approximately the same, the transition temperatures and ferroelectric polarizations [Figure 1-12(b)] are much different, and this is believed to be due to the different octahedral tilt symmetries of the LSAT and NdGaO$_3$ substrates. LSAT does not have any octahedral rotations ($a^0b^0c^0$) and NdGaO$_3$ has a tilt symmetry of $a'a'c'$.

For CaTiO$_3$/LSAT, octahedral rotations are suppressed at the substrate/film interface, as shown in Figure 1-12(c) from scanning transmission electron microscopy (STEM) high-angular annular dark field (HAADF) and annual bright field (ADF) image analysis, and for CaTiO$_3$/NGO, octahedral rotations are matched across the substrate/film interface, as shown in Figure 1-12(d). This matching of the octahedral rotations across the different substrate/film interfaces is better demonstrated in Figure 1-12(e) which plots the magnitude of the in-plane octahedral rotations ($\beta$) as a function of the atomic columns across the interface for each film, revealing that the rotations are equal to the bulk value of CaTiO$_3$ shown as the dashed red line for the CaTiO$_3$/NdGaO$_3$ film, and that the rotations across the CaTiO$_3$/LSAT film, the rotations change from 0° in the bulk of the LSAT substrate, to the bulk value of CaTiO$_3$ after approximately 4-5 unit cell layers in the CaTiO$_3$ film, and that these rotations gradually change across the interface. Clearly, the effects of substrate tilt symmetries can play a major role on strain-induced ferroelectric properties in perovskites such as CaTiO$_3$ which have octahedral rotations.

While epitaxial strain has proven to be a powerful tool for unlocking emergent ferroic phenomenon in non-polar perovskite materials such as SrTiO$_3$ and CaTiO$_3$, there are serious limitations to the strain-engineering strategy. Due to the large in-plane strains imposed by the substrate crystals, strain-relaxation in films can occur where the in-plane lattice parameter of the
film will transition from a fully-strained state (equal to the substrate) to a fully-relaxed state (equal to the bulk film) and this relaxation is typically accompanied by the formation of threading dislocations and cracks in the film material. This obscures intrinsic strain-induced phenomenon to be measured as the strain state is inhomogeneous throughout a relaxed film material. The thickness at which a film lattice will relax to the bulk lattice value can be estimated to some degree by the Matthews-Blakeslee equilibrium limit which predicts the thickness at which slip dislocations become more energetically favorable to occur with respect to the strain energy imposed by the substrate,[32, 33] but this approximation often underestimates the actual relaxation thickness that are experimentally observed for thin film materials,[34] as this simple equilibrium condition does not take into account Peierls-Nabarro stresses,[35, 36] the energy barriers for nucleation of dislocation sites, and the interaction between neighboring dislocations in a film material. This discrepancy between theory and experiment for critical strain relaxation thicknesses was shown by Biegalski et. al.[34], where the actual critical thicknesses for strained SrTiO$_3$ ($\nu$=0.23) films grown on DyScO$_3$ substrates ($\varepsilon$ = 1.14%) was observed to be $t_c \sim 35$ nm, although the predicted critical thickness is predicted to occur at $t_c = 6$ nm. Similarly, in this work, for CaTiO$_3$ thin films epitaxial strained on LSAT substrates (+1.2% tensile strain), film thickness of $\sim 50$ nm resulted in large cracks in the film surfaces as determined by atomic force microscopy measurements, as shown in Figure 1-13.

Another drawback for strain-engineering functional properties is the discontinuity of available strain states that can be induced, due to the limited availability of commercially produced perovskite substrate materials. Alternative routes for accessing emergent phenomenon in perovskite and perovskite related materials, beyond strain, are therefore highly desirable. Other schemes such as perovskite layering, where heterostructures composed of 2 or more perovskite or perovskite-related phases, which can lead to emergent ferroic phenomenon, is discussed in the next section.
Figure 1-9. (a) The in-plane pseudo-cubic lattice parameters of several commercially available bulk single-crystal perovskite materials ranging from aluminates (Lu, Y, Nd, La)AlO$_3$, gallates (Nd,La)GaO$_3$, and scandates (Dy, Tb, Gd, Eu, Sm, Nd, Pr)ScO$_3$, as well as layered aluminate perovskite materials with cubic in-plane lattice parameters such as (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT) and (NdAlO$_3$)$_{0.4}$(Sr$_2$AlTaO$_6$)$_{0.3}$ (NSAT). (b) Images of single crystalline boules of several perovskite materials taken from www.surfacenet.de. Figure was adapted from Ref.[37], Ref.[38], and Ref.[39].
Figure 1-10. The interface between a substrate (shown as the shaded blue region) and a perovskite film under (a) compressive, and (b) tensile strains, with arrows showing direction of the strain on the perovskite unit cell structure, where the red atoms are oxygen, and the gray shaded boxes are the BO$_6$ octahedral cages. The A-site atoms are not shown for visual quality. Compressive (tensile) strain results in an elongated (shortened) out-of-plane (OOP) distortion of the BO$_6$ cages, resulting in OOP (in-plane) polarizations. The BO$_6$ octahedral rotations for (c) compressive strain and (d) tensile will have enhanced out-of-plane ($\gamma$) and enhanced in-plane ($\alpha$ and $\beta$) rotations, respectively. Image adapted from Ref.[27].
Figure 1-11. Theoretically calculated strain-phase-temperature diagrams for (a) BaTiO$_3$ (Ref.[21]), (b) PbTiO$_3$ (Ref.[22]), (c) SrTiO$_3$ (Ref.[23]), and (d) CaTiO$_3$ (Ref.[24]) perovskite materials. The upper-limit of the predicted ferroelectric-to-paraelectric phase transition is indicated by the shaded area in each graph. Experimentally determined transition temperatures for thin films are shown as filled squares in the graphs, with labels indicating the substrate used to grow the films on. Transitions temperatures found for films studied in this thesis are shown as yellow stars in (c) and (d). The predicted ferroelectric polarization ($P$) direction is shown by the arrows which will be out-of-plane for compressive strain, and in-plane for tensile strain.
Figure 1-12. (a) Temperature dependent dielectric constant $K$ (1 kHz) and (b) P-E loops ($T=10$ K) for CaTiO$_3$ (CTO) films grown on LSAT (green) and NdGaO$_3$ (NGO) (purple) substrates, with $T_c$ values indicated by black arrows. STEM HAADF and ABF images for (c) CTO/LSAT and (d) CTO/NGO films, where the LSAT and NGO regions are highlighted in green and purple respectively, and the CTO film is highlighted in blue. The TiO$_6$ octahedral rotations across the substrate/film interface are shown. (e) Magnitude of the BO$_6$ rotation ($\beta$) across the substrate/film interface for CTO/LSAT (green squares) and CTO/NGO (purple circles), where the dashed red line indicates the bulk rotation value of CTO. Image adapted from Ref. [24].
Figure 1-13. Atomic force microscopy (AFM) image taken at room temperature for a 50 nm CaTiO$_3$ film grown on LSAT substrate which induces a tensile strain of +1.2%, where the critical relaxation thickness has been exceeded as indicated by the observation of cracks in the film surfaces. The scale bar in the image is 1 μm.
1.3 Layering-induced ferroelectricity in complex oxides

Artificially layered oxide materials, such as (ABO$_3$)$_n$/(A’BO$_3$)$_n$ superlattices, shown in Figure 1-14(a), and AO(ABO$_3$)$_n$ Ruddlesden-Popper phases, shown in Figure 1-14(b), are of scientific and technological interest as these types of exotic layered materials can exhibit material properties that are beyond the functionalities of their bulk counterparts. For example, perovskite superlattice thin film structures which are built of alternating layers of ferroelectric BaTiO$_3$, paraelectric SrTiO$_3$, and paraelectric CaTiO$_3$, as shown in Figure 1-15(a), can exhibit enhanced polarizations beyond that of bulk BaTiO$_3$ for certain layering schemes of a tri-color superlattice, shown in Figure 1-15(b).[40] The tri-color (SrTiO$_3$)$_2$/(CaTiO$_3$)$_2$/(BaTiO$_3$)$_4$ superlattice show a larger polarization ($P_r=16.5$ µC/cm$^2$) than bulk BaTiO$_3$ ($P_r=27$ µC/cm$^2$),[40] whereas bi-color superlattices composed of BaTiO$_3$ layers with additional CaTiO$_3$ or SrTiO$_3$ can be used to tune the polarization, and superlattices composed of paraelectric SrTiO$_3$ and CaTiO$_3$, i.e. (SrTiO$_3$)$_1$/(CaTiO$_3$)$_1$, do not exhibit any ferroelectric behavior at room temperature, as demonstrated by the linear polarization response versus applied electric field in Figure 1-15(b).[41]

Although there are actually few examples in literature of dramatically enhanced ferroelectric material properties in perovskite superlattices,[42-44] theoretical investigations have recently predicted that an improper ferroelectric polarization can be induced in superlattices built from alternating layers of non-polar perovskite materials which have orthorhombic $Pnma$ space group symmetries and an octahedral tilt symmetry of $a^a e^e$.[45-48] For improper ferroelectrics, the polarization order parameter in the free energy is linearly coupled to the unequal octahedral rotation order parameters ($R_1$ and $R_2$) of the two different perovskite materials, where $P \propto R_1 R_2 \propto (T_0-T)$ is the improper ferroelectric transition temperature ($T_0$), and the dielectric permittivity, $\varepsilon \propto \alpha_p$, is constant with no critical temperature dependence.[49] This layering-induced improper
Ferroelectric polarization is indirectly caused by the change in the magnitude of the octahedral rotations across the interfaces of alternating perovskite layers, which results in a dissimilar magnitude of the A-site and A’-site cation displacements, resulting in a net in-plane polarization for the overall superlattice material, as shown in Figure 1-16(a). Other layering schemes such as ‘rock-salt’ layering, where mixed (A, A’)O layers are sandwiched between BO\textsubscript{2} layers, and have rock-salt ordering between alternating (A, A’)O sheets, as illustrated in Figure 1-16(b). The ‘rock-salt’ A-site cation ordering arrangement also leads to a net polarization which is caused by the asymmetric A-site and A’-site cation displacements in the alternating layers of the superlattice structure, although the expected polarization would be smaller for ‘rock-salt’ layering than for the ‘layering’ scheme.

Theory predicts that superlattice structures composed of (SrZrO\textsubscript{3})/(CaZrO\textsubscript{3}), (SrHfO\textsubscript{3})/(CaHfO\textsubscript{3}), and (LaGaO\textsubscript{3})/(NdGaO\textsubscript{3}), which all have non-polar bulk perovskite materials that are orthorhombic (Pnma) with large a’ a c\textsuperscript{+} octahedral tilts, result in relatively large expected net polarizations of $P = (3.61, 3.09, 5.22)$ $\mu$C/cm$^2$ for ‘layering’ geometry, and $P = (2.8, 2.3, 1.8)$ $\mu$C/cm$^2$ for ‘rock-salt’ geometry, respectively.[45] However, no experimental examples for a rotation induced improper ferroelectric phase has been reported for these superlattice systems.

One of the few examples of improper ferroelectricity in a perovskite superlattice material is for a (PbTiO\textsubscript{3})\textsubscript{2}/(SrTiO\textsubscript{3})\textsubscript{3} films grown on (100)SrTiO\textsubscript{3} substrates.[50] The intrinsic improper ferroelectric behavior was demonstrated for the (PbTiO\textsubscript{3})\textsubscript{2}/(SrTiO\textsubscript{3})\textsubscript{3} superlattice film by showing a linear response of the measured polarization with temperature, a nonlinear response of the c/a tetragonality ratio, as well as a near constant value of the dielectric permittivity up until the improper ferroelectric transition of $T_0 = 500$ K, as shown in Figure 1-17.[50] However, no other reports an unambiguously clear improper ferroelectric phase in perovskite superlattices has been reported.
Improper ferroelectricity is also predicted to occur for layered RP structures if the $n=\infty$ bulk ABO$_3$ perovskite material has a non-polar orthorhombic $Pnma$ space group symmetry with an $a'a'c^+$ tilt system. Such is the case for CaMnO$_3$, shown in Figure 1-18(a), which in bulk has $Pnma$ $a'a'c^+$ symmetry, but when layered in the $n=2$ Ca$_3$Mn$_2$O$_7$ RP structure, shown in Figure 1-18(b),[51] the net polarization of the asymmetric anti-polar A-O cation displacements between the perovskite and rock-salt layers gives rise to a net improper ferroelectric polarization. This type of improper ferroelectric polarization has been experimentally demonstrated for single crystals of (Ca$_{3-x}$Sr$_x$)Ti$_2$O$_7$, shown in Figure 1-19(a), where for increasing values of $x=(0, 0.54, 0.85)$, the bulk RP films showed decreasing remanent polarizations.[52] In this work, it was claimed that the decreased polarization with increased doping levels of Sr for Ca atoms on the A-site was due to the fact that the rotations decreased with increasing Sr concentrations, which for SrTiO$_3$ perovskite structure, the material would tend to form a cubic crystal structure with no octahedral rotations.[52] Therefore, the octahedral rotations in an RP structure are linked to the emergence of hybrid improper ferroelectricity for this type of layered material, where robust octahedral rotations are abundant in the majority of available perovskite RP chemistries, leading to a multitude of possible RP materials that could exhibit exciting layer-induced phenomenon.

Another important factor inducing ferroelectric phenomenon in layered RP perovskite structures is the strain involved with epitaxial synthesis of artificially grown layered films. For instance, strain can induce ferroelectricity in tensile strained Sr$_{n+1}$Ti$_n$O$_{3n+1}$ RP films, where the ferroelectric polarization as well as ferroelectric transition temperatures increase with strain as well as the layering thickness, $n$, as shown in Figure 1-20(a), and this was experimentally demonstrated for a series of 50 nm thick $n=6$ Sr$_7$Ti$_6$O$_{19}$ RP film grown by molecular beam epitaxy on a (110)DyScO$_3$ substrate, the polarization is $P_r=8 \mu$C/cm$^2$ (at $T=10$ K) and $T_c=220$ K.[53] as shown in Figure 1-20. The remarkable fact about producing such a high quality Sr$_7$Ti$_6$O$_{19}$ RP film, albeit the relatively low polarization and low ferroelectric transition below room
temperature, is that the electrical losses in gigahertz frequencies (GHz) are lower than in current (Ba,Sr)TiO$_3$ based capacitor materials with a relatively same amount of change in the permittivity with applied field. The large dielectric tunability and ultra-low losses in strained RP structures provides new routes for achieving materials with lower-power consumption within the typical commercial frequency range of > 1 GHz, i.e. telecommunication frequencies such as smartphones, where Ca$_{n+1}$Ti$_n$O$_{3n+1}$ RP materials provide an ideal next leap for future exploration of layered- and strain-enabled functional phenomenon in RP structures, where this CaTiO$_3$ based RP structure already shows a tendency towards a ferroelectric phase at room temperature. So, what are the difficulties that emerge for experimentalists in trying to grow these layered perovskite materials?[53]

Though theory can also pave the way for experimental exploration of emergent properties in complex oxide materials, the theoretical models typically assume that the simulated material response is for a perfect material, i.e. no inclusions of defects. But no material can ultimately be perfect. Due to the laws of thermodynamics and entropy, any material that is experimentally probed at finite temperatures will contain at least some amount of ‘defects’, which can manifest in various forms ranging from interstitial atoms or vacancies on the A-site, B-site, or oxygen sites in a perovskite unit cell. These types of charged defects can either greatly enhance or hinder material properties in perovskites, depending on the applications, and is discussed in the next section.
Figure 1-14. (a) Crystal structures of n=1, 2, and 3 (ABO$_3)_n/(A'B'O_3)_n$ perovskite superlattices. The individual (A,A')O and BO$_2$ layers are shown for the n=3 superlattice structure. The BO$_6$ octahedra are highlighted in blue, and the A and A' atoms are shown as blue and purple spheres, respectively. (b) Crystal structures of n=1, 2, and 3 AO(ABO$_3)_n$ Ruddlesden-Popper (RP) series, where the red spheres are the A-site atoms, with the individual AO and BO$_2$ layers shown for the n=3 RP structure on the right showing the double AO rocksalt layers in the stacking sequence of an RP.
Figure 1-15. (a) Scanning transmission electron microscopy (STEM) image of atomically abrupt interfaces in a (BaTiO$_3$)$_2$/(SrTiO$_3$)$_2$/(CaTiO$_3$)$_2$ superlattice thin film crystal structure, shown schematically on the right with the (Ba, Sr, Ca) atoms represented by (green, blue, red) spheres, and the TiO$_6$ octahedral shown in light blue. Image adapted from Ref. [40]. (b) Polarization-hysteresis (P-E) loops taken at 100 Hz for ceramic bulk BaTiO$_3$ (black), and a (SrTiO$_3$)$_2$/(CaTiO$_3$)$_2$/(BaTiO$_3$)$_4$ superlattice (blue) from Ref. [40] and for (CaTiO$_3$)$_2$/(BaTiO$_3$)$_2$ (red) and (CaTiO$_3$)$_1$/(SrTiO$_3$)$_1$ (green) superlattices from Ref. [41].
Figure 1-16. Mechanisms for hybrid improper ferroelectric polarization in \((A,A')B_2O_6\) superlattices in (a) layered and (b) rocksalt stacking sequences shown by the two-dimensional AO and A’O sheets in the layered geometry and the intercalation of A and A’ in each layer for the rocksalt geometry. Cross sections of the superlattice structures are shown in the middle with octahedral rotations and the displacements of the A and A’ atoms in the layers, indicated by orange and green arrows. One the right is the alternating polarization directions of the A-site cation displacements, with the orange and green blocks representing the A and A’ cation displacements, respectively. Image adapted from Ref. [45] and Ref. [46].
Figure 1-17. (a) Linear temperature dependence of polarization for an (PbTiO$_3$)$_2$/(SrTiO$_3$)$_3$ superlattice grown on (100)SrTiO$_3$ substrate, with the linear fit shown as the red line and the fitting parameters indicated in the panel and the transition at $T \sim 500$ K. (b) Temperature dependence of the c/a tetragonality ratio. (c) Temperature dependence of the dielectric constant, extrapolating the expected transition at $T \sim 500$ K. Image adapted from Ref. [50].
Figure 1-18. (a) Antipolar displacements of A-site cations (shown as red arrows) in the CaMnO$_3$ perovskite structure which has a $Pnma$ space group structure and $\alpha \alpha' \epsilon^*$ tilt symmetry. The layer-resolved polarization is shown on the right, where the alternating A-site displacements in neighboring AO layers cancel each other out, resulting in a non-polar structure.  (b) A-site displacements in the n=2 Ca$_3$Mn$_2$O$_7$ RP crystal structure, where unequal A-site cation displacements in the perovskite (purple) and rocksalt (red) layers results in a net polarization and hybrid improper ferroelectricity to emerge in this layered perovskite structure. Image adapted from Ref.[51].
Figure 1-19. (a) Optical circular differential interference contrast image of a cleaved (001) plane of a Ca_{2.46}Sr_{0.54}Ti_{2}O_{7} RP single crystal at room temperature. The orthorhombic twins walls are observed with changing contrasts with the a-axis (|| [100]) orientation indicated for several domain areas. (b) Polarization-hysteresis (P-E) loops of Ca_{3-x}Sr_{x}Ti_{2}O_{7} (x=0, 0.54, 0.85) single crystals at room temperature with the electric field applied along the [100] direction at a frequency of 260 Hz. Image adapted from Ref.[52].
Figure 1-20. (a) Bright-field scanning transmission electron microscopy (STEM) images of a 50 nm thick n=6 Sr$_7$Ti$_6$O$_{19}$ RP film grown on (110)DyScO$_3$ substrate. The DyScO$_3$ substrate region is shown on the bottom, and the white scale bar is 10 nm. (b) Square of the in-plane polar soft mode frequency versus n in Sr$_{n+1}$Ti$_n$O$_{3n+1}$ RP structure under no strain (gray circles) and under +1.10% tensile strain (blue squares) with theory fits shown as red lines. The negative squared frequencies indicate a polar instability. (c) Experimentally measured ferroelectric transitions ($T_C$) shown as filled blue squares and remanent polarizations ($P_r$) shown as open blue squares, for n=3, 4, 5, 6 Sr$_{n+1}$Ti$_n$O$_{3n+1}$ RP films grown on (110)DyScO$_3$ substrates. The black lines are shown as a visual aid to show increasing $T_C$ and $P_r$ with increasing n. Image adapted from Ref. [54] and Ref. [53].
1.4 Effects of nonstoichiometry on properties of complex oxides

The study of how nonstoichiometric defects affect the ferroelectric properties of ABO₃ perovskites is well documented in literature.[55] As no material can be ‘perfect’, defects play a critical role and need to be considered when reporting intrinsic material responses, as charged defects which are manifest in nonstoichiometric compositions of ABO₃ perovskites can greatly obscure optimal material properties. Typically, bulk perovskite materials are obtained through solid state reactions or wet-chemical routes such as sol-gel and Pechini preparation methods which are very popular due to their low cost and high yields of material.[56] Although high quality stoichiometric single crystal bulk materials can be obtained, controlling the composition in a thin film material at typical growth temperatures (< 1000 °C) can be challenging. According to the temperature-phase equilibrium diagrams of SrTiO₃ and CaTiO₃ perovskite materials, shown in Figure 1-21, stoichiometric compositions of SrO (CaO) and TiO₂ will result in single phase materials.[57, 58] For nonstoichiometric compositions that are just off of the stoichiometric line, the formation of either Sr(Ca)-rich or Ti-rich phases will precipitate in a material. Therefore, controlling the composition of ABO₃ perovskites during growth requires the supplied fluxes of the A, B and O atoms to be well maintained throughout an entire growth in order to achieve nominally stoichiometric films.

For ultra-high vacuum thin film growth techniques such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), the effects of nonstoichiometry on structural and ferroic properties of perovskite materials has been well studied.[59] One of the easiest ways to determine if as-grown thin films are stoichiometric is by measuring the out-of-plane lattice parameter of thin films by X-ray diffraction techniques, where defects will result in an expansion of the out-of-plane lattice parameter of a film, and thus shifting in the positions of the expected X-ray reflection planes.[60] This expansion is caused by the inclusion of either extra AO rock
salt layers for AO-rich films, and can also be caused by coulomb repulsions between charged vacancy sites for B-rich films as shown in Figure 1-22. For example, for homoepitaxy growth of Sr$_{1+x}$TiO$_3$ films on SrTiO$_3$ substrates, stoichiometric films (x=0) films will have the same out-of-plane lattice parameter as the bulk SrTiO$_3$ substrate, as shown in Figure 1-23, for films grown by both MBE [59] (blue circles) and PLD [60] (red squares). However, Sr-rich and Ti-rich films are clearly observed by the increasing lattice parameter as x varies from 0 for several films, and the change in the c-axis with change in the Sr composition (x) is more pronounced for PLD grown films as compared to MBE films. The inclusion of these types of defects is directly observed in the STEM images shown in Figure 1-23(b) for Ti-rich, stoichiometric, and Sr-rich films, which show blurred regions of excess TiO$_x$ phases in Ti-rich films, and vertically aligned SrO layers in Sr-rich films.

The effects of Sr-rich and Ti-rich defects on strain-enabled ferroelectric properties has been demonstrated for SrTiO$_3$ films grown on (110)DyScO$_3$ substrates.[61] A series of strained SrTiO$_3$ films were grown with intentionally induced nonstoichiometric compositions, as shown in Figure 1-24(a) in order to observe the change on the temperature dependence of the dielectric constant, as shown in Figure 1-24(a). A transition of $T_C \sim 285$ K was observed for the stoichiometric film (Sr$_{1.00}$TiO$_3$) which had a large dielectric constant ($K_{11} \sim 6000$), whereas decreased transitions (and dielectric constants) of $T_C \sim 220$ K ($K_{11} \sim 2000$) and $T_C \sim 280$ K ($K_{11} \sim 0.3$) were found for Sr-rich (Sr$_{0.95}$TiO$_3$) and Ti-rich (Sr$_{1.05}$TiO$_3$) films, respectively.[61] Therefore, deviations of around $\sim 5\%$ stoichiometry can result in degraded ferroelectric and dielectric properties in strained perovskite films.

In order to yield stoichiometric perovskite thin film samples, the supplied fluxes of cations during growth must be well controlled. For MBE growth, supplying low-vapor pressure cations such as Ti requires very high temperatures in order to evaporate the metals, and even with the use of Ti-Balls, which are more volatile at higher temperatures as compared to elemental Ti
metal heated in a crucible, fluxes inside of an MBE chamber can drift as much as \( \sim 2.5\% \) per hour.[62] This magnitude of flux drift could ultimately lead to the incorporation of unintentional defects throughout a thin film thickness, and thus can lead to degraded targeted properties. In the next section, the use of hybrid MBE, where Ti is supplied using a metal-organic molecule instead of a metal charge of Ti, is discussed, where the presence of adsorption controlled growth windows enables an easier way to control stoichiometry during thin film deposition.
Figure 1-21. Temperature-phase equilibrium diagrams for (a) SrO-TiO$_2$, and (b) CaO-TiO$_2$ with the phase and composition lines indicated in each diagram. Images adapted from Ref.[57], Ref.[58].
Figure 1-22. (a) An extra SrO bilayer in a SrTiO$_3$ film, resulting in an expansion of the unit cell of the film. (b) A Sr vacancy site (Ti-rich film) shown as the dashed circle in the middle of the image where the neighboring TiO$_6$ octahedra (highlighted in green) will structurally distort, resulting in an expansion of the unit cell. Image adapted from Ref. [60].
Figure 1-23. (a) Out-of-plane c-axis lattice parameter for $\text{Sr}_{1+x}\text{TiO}_3$ films grown by MBE (blue circles), PLD (red squares), and sputtering (green triangles). For $x=1.0$, the films showed the same c-axis parameter as bulk $\text{SrTiO}_3$, indicated by the dashed black line. (b) STEM images of $\text{Sr}_{0.8}\text{TiO}_3$, $\text{SrTiO}_3$, and $\text{Sr}_{1.1}\text{TiO}_3$ films showing Ti-rich, stoichiometric, and Ca-rich type defects, from left-to-right, respectively. The interface between the $\text{SrTiO}_3$ substrate and film is indicated by the black arrow on the left, which is for all image panels. The white scale bars are 2 nm. Figure adapted from Ref.[59].
Figure 1.24. (a) Out-of-plane c-axis lattice parameter for three different SrTiO$_3$ films grown on (110)DyScO$_3$ substrates by MBE[61]; a Ti-rich (green) Sr$_{0.95}$TiO$_3$, a stoichiometric (red) Sr$_{1.00}$TiO$_3$, and Sr-rich (orange) Sr$_{1.05}$TiO$_3$ films, with the bulk SrTiO$_3$ c-axis indicated by the dashed black line. (b) The temperature dependence of the in-plane dielectric constant, $K_{11}$, for the stoichiometric (top, red), Ti-rich (middle, green), and Sr-rich (bottom, orange) films in (a), where the ferroelectric transition temperature is indicated by the dashed lines extending to the bottom axis. Image adapted from Ref. [61].
1.5 Hybrid molecular beam epitaxy of complex oxides

For conventional MBE growth of thin film materials, the advantages of an adsorption controlled self-regulating stoichiometric growth window has been well demonstrated in semiconductor materials such as GaAs, which can yield electron mobility values in excess of \(~36,000,000 \text{ cm}^2/\text{V},[63]\) suggesting. The excellent quality that can be achieved for GaAs films grown by MBE is due to the fact that it can easily be synthesized under ‘growth window’ conditions, meaning that the Ga-to-As ratio will self-regulate to be 1-to-1 over a broad range of supplied Ga and As fluxes. The growth window of GaAs is caused by the high volatility of As, which is typically delivered using AsH\(_3\) hydride gas,[64] where excess As at a film surface during growth will desorb rather than being incorporated into the film since the free energy of formation for the stoichiometric phase pure GaAs compound is lower than the energy of formation of parasitic nonstoichiometric defects. Figure 1-25 shows the calculated growth window boundaries for GaAs (gray shaded region), where the lower bound is defined by the equilibrium conditions between the supplied Ga(s) and As\(_2\)(g)As forming GaAs(s), and the upper bound is defined as the equilibrium where As(s) will become As\(_4\)(g). These lower and upper boundaries define the temperature and pressure dependent growth windows, which span nearly 6 order of magnitude of supplied As\(_2\)(g) gas pressures at relatively low growth temperatures of 600 °C, enabling easily accessible growth window conditions for MBE thin film growth of GaAs.

These types of growth windows have also been demonstrated for perovskite materials such as PbTiO\(_3\),[64] BiFeO\(_3\),[65] and BiMnO\(_3\),[66] and are enabled by the highly volatile Pb- and Bi-based components of these perovskite materials. The calculated equilibrium growth conditions for PbTiO\(_3\) are shown in Figure 1-25 (orange shaded region), where the lower limit of the growth window is determined by the equilibrium vapor pressure of PbO(g) over a TiO\(_2\) rich PbTiO\(_3\) surface. For a PbO gas pressure above this lower limit, PbO will condense on the TiO\(_2\) covered
surface of the film. The upper limit of the growth window is defined by the equilibrium vapor pressure of gaseous PbO(s) and pure condensed PbO, where below this boundary, PbO will not precipitate out of the gas phase at the film surface and will desorb into the vacuum chamber. The range of PbO gas pressures between the lower and upper growth window boundaries spans nearly three orders of magnitude at a growth temperature of ~600 °C, [64] as shown in Figure 1-25.

However, for perovskite materials that have less volatile AO species such as CaO, SrO, and BaO, the calculated growth window boundaries exist at elevated temperatures and very low AO(g) gas pressures, which is clearly seen for the growth windows of CaTiO$_3$ (blue), SrTiO$_3$ (red), and BaTiO$_3$ (green) plotted in Figure 1-25. For conventional growth rates ranging anywhere between ~1 nm per minute up to 100 nm per minute, the supplied gaseous AO(g) pressures would typically range between $P_{AO(g)} = 10^{-8}$-$10^{-5}$ Torr. Therefore, the predicted BaTiO$_3$ growth window could just barely be accessed at growth temperatures of $T > 900$ °C. However, to achieve a growth rate of just 1 nm per minute at a typical pressure of $P_{AO(g)} = 10^{-8}$ Torr, the growth temperature would have to be $T > 2000$ °C, which is well above the limitations of achievable growth temperatures using MBE techniques, since the perovskite film and substrate materials would melt into the growth chamber.

An elegant way to shift these growth windows to realistically achievable growth temperatures and growth rates is to employ hybrid MBE technique,[67] which incorporates the use a highly volatile metal-organic (MO) based molecule to replace the supply of low-vapor pressure transition metals for the B-site, and the higher-vapor pressure A-site atom is conventionally supplied using a thermal effusion cell. A popularly employed MO precursor material is titanium tetraisopropoxide (TTIP), which has four carbonyl ligands attached to the Ti ion in a tetrahedral arrangement, as shown in Figure 1-26. When the TTIP molecule is evaporated into an MBE chamber during thin film growth, it will decompose into TiO$_x$ and organic byproducts such as propylene, methane, isopropanol, water, and acetone, at the heated growth surface. The organic
byproducts from this reaction are easily pumped away inside of the growth chamber since they have very high vapor pressures,[68] as shown in Figure 1-27, and negligible amounts of carbon contamination are incorporated into grown films.[69] The first demonstration of a growth window for a perovskite material using TTIP was done by Jalan et al.[70], who showed that SrTiO$_3$ films grown on (100)SrTiO$_3$ substrates remained nominally stoichiometric over a broad range of supplied TTIP/Sr flux ratios at growth temperatures of $T = (700, 725, 800)$ °C. Shown in Figure 1-28 are the measured c-axis lattice parameters for each of the films grown in the three temperature series, where the TTIP/Sr flux ratio was systematically adjusted and the films were grown out. The growth window range is defined as the values of TTIP/Sr flux ratios in which the c-axis lattice parameter of the SrTiO$_3$ films are equal to the bulk value, which indicates nominally stoichiometric films. For non-stoichiometric films, lattice expansion will occur due to the formation of either Sr-rich or Ti-rich defects in the films, providing an easy way to locate the boundaries of the growth window range. As seen from Figure 1-28, the growth window range increased at larger growth temperatures of 800 °C, and the growth window shifted to higher TTIP/Sr flux ratios. This seminal work clearly indicated that an adsorption-limited growth condition had been activated at relatively low growth temperatures during MBE growth of SrTiO$_3$ films, and the thermally activated growth windows were facilitated by the volatile TTIP material.

The utility of a hybrid MBE growth window has been demonstrated by the record high electron mobilities $> 50,000$ cm$^2$/V·s in La-doped SrTiO$_3$ films,[71] and device quality factors of $Q = 1/\tan(\delta) > 1000$ in Ba$_x$Sr$_{1-x}$TiO$_3$ films.[72] These recent milestones hallmark the excellent stoichiometry control and low defect concentrations that can be achieved using this growth approach, leading to superior intrinsic material properties in perovskite materials. Similar growth windows have been recently reported for NdTiO$_3$,[73] GdTiO$_3$,[74] BaTiO$_3$,[75] and BaSnO$_3$,[76] as well as vanadate systems such as SrVO$_3$[77] and LaVO$_3$[78] using metal-organic vanadium(V) oxytriisopropoxide, where record high residual resistivity ratios, $\rho_{300K}/\rho_{5K}$, in metal SrVO$_3$ films
were demonstrated, exceeding bulk single crystal values.[79] With the commercial availability of many other transition-metal based metal-organic molecules, different perovskite systems such as zirconates, hafnates, gallates, germinates, chromates, etc., could be explored.
Figure 1-25: The calculated temperature and flux dependent equilibrium curves with the upper boundary (dashed lines) of the growth windows determined by the reaction of AO(s) $\leftrightarrow$ AO(g), and the lower boundary (solid lines) determined by the reaction between AO(g) + TiO$_2$(s) $\leftrightarrow$ ATiO$_3$, where A = (Ca, Sr, Ba, and Pb). Typical growth rates $\sim$ (1-100) nm/min, and growth temperatures $\sim$(600-1000)$^\circ$C are highlighted by the red boxed region.
Figure 1-26: A molecule of titanium tetraisopropoxide (TTIP) with chemical formula Ti-(O-CH(CH$_3$)$_2$)$_4$. Ti, O, C, and H atoms are labeled and indicated by dashed arrows. The Ti atom is in a tetrahedral arrangement with the 4 O atoms, resulting in Ti-O bond angles of ~109.5°.
Figure 1-27: The vapor pressure of titanium tetraisopropoxide (TTIP) shown as the dashed black curve at the bottom with the TTIP molecule shown on the bottom right. The vapor pressures of the organic byproducts after decomposition of the TTIP molecule are also shown, including water, isopropanol, acetone, and propene.
Figure 1-28. The out-of-plane c-axis lattice parameter measured by X-ray diffraction for several series of SrTiO$_3$ films grown on (001)SrTiO$_3$ substrates at growth temperatures of $T = (700, 725, 800)$ °C from bottom to top, where each data point represents the c-axis value for an individual film grown at different TTIP/Sr beam equivalent pressures (BEP). The c-axis value for bulk SrTiO$_3$ is indicated in each panel by the dashed black line, where films grown that had equal c-axis parameters defines the growth window range (highlighted in gray), where to the left and right of this range the films are Sr-rich or Ti-rich, resulting in increased lattice parameter values from bulk. Image adapted from Ref. [70].
1.6 Thesis organization

This thesis mainly focuses on developing the hybrid MBE growth technique for synthesizing high-quality CaTiO$_3$ and SrTiO$_3$ perovskite based films in order to explore how enhanced strain and layering enabled ferroelectric phenomenon can be obtained using stoichiometric growth windows. Chapter 2 discusses the experimental methods used to characterize the thin films grown in this work, such as X-ray diffraction, impedance spectroscopy, and optical second harmonic generation. Chapter 3 introduces the discovery of a growth window for CaTiO$_3$ films grown on (001)LSAT substrates, where the tensile strain-induced ferroelectric and dielectric properties are measured throughout the CaTiO$_3$ growth window, and it is demonstrated that optimal ferroelectric phase transition temperatures ($T \sim 180$ K) and material properties are found only for CaTiO$_3$ films grown inside of the growth window, where outside of the growth window range (i.e. Ca-rich and Ti-rich regimes) properties are greatly reduced. In Chapter 4, the existence of a high-temperature ferroelectric phase transition ($T \sim 800 ^\circ C$) is demonstrated for compressively strained CaTiO$_3$ films on (001)LSAO substrates, where this transition temperature is much higher than what theory currently predicts, and is even higher than the ferroelectric transitions of standard ferroelectric perovskite materials such as BaTiO$_3$ and PbTiO$_3$. In Chapter 5, a stoichiometric growth window for SrTiO$_3$ films which are tensile strained on (001)LSAT substrates is presented, where optical second harmonic generation analysis is used to determine a tetragonal (4$mm$ point group symmetry) symmetry with out-of-plane ferroelectric polarization in the films, and enhanced ferroelectric transition temperature ($T \sim 175$ K) found only for SrTiO$_3$ films grown inside of the growth window. Chapter 6 shows how overlapping growth windows of CaTiO$_3$(001)LSAT and SrTiO$_3$(001)LSAT can be used to construct a series of $n=1$-$10$ (SrTiO$_3$)$_n$/CaTiO$_3$/SrTiO$_3$/LSAT superlattices in a layer-by-layer fashion using in-situ RHEED feedback. The strain-induced ferroelectric properties of the superlattices are measured as a
function of the interface roughness of the grown SL film materials, where it is observed that the
ferroelectric phase found in pure CaTiO$_3$ and SrTiO$_3$ films only emerges for superlattices which
have a critical amount of interface roughness, whereas superlattices with sharp interfaces do not
show transitions.

Going beyond the growth of single phase films and superlattice materials using hybrid MBE,
Chapter 7 includes a detailed calibration methodology for synthesis of an n=4 Sr$_5$Ti$_4$O$_{13}$
Ruddlesden-Popper phase where the doses of SrO and TiO$_2$ layers are sequentially deposited
using TTIP to supply the TiO$_2$ layers, and stoichiometry dependent RHEED characteristics are
used to precisely determine the shuttering times of Sr and TTIP. This is the first demonstration of
an RP film being grown by hybrid MBE, where the advantages of using a very stable TTIP source
to supply Ti is highlighted by the constant RHEED intensity values during the ~5 hour growth
period, and XRD and STEM analysis reveal that the RP film has a very homogenous and periodic
structural quality. Finally, Chapter 8 discusses earlier work done in this thesis on probing strain-
enhanced nonlinear optical properties in BiFeO$_3$ thin films using second harmonic generation
polarimetry analysis techniques developed in this work. A summary of the results and future
outlook for hybrid molecular beam epitaxy growth of high quality complex oxide materials is
given, and how these growth windows can be used to explore enhanced strain-enabled properties
as well as emergent phenomenon in oxide superlattices and RP systems. A brief Appendix is
provided in Chapter 9 for derivations of analytical expressions for transmitted and reflected
second harmonic generation for thin film/substrate boundary conditions in the case of an
absorbing film material, and for the case of birefringence.
1.7 References


Chapter 2

Experimental techniques

2.1 Hybrid molecular beam epitaxy

The films studied in this work were grown inside of a DCA M600 molecular beam epitaxy (MBE) reactor chamber, shown schematically in Figure 2-1. The chamber was held under ultra-high vacuum using a Pfeiffer turbo pump which provided a background pressure of $10^9$ Torr as measured by an ion gauge (IG) positioned next to the turbo pump. During film growth, the chamber walls were cryogenically cooled using liquid nitrogen to condense scattered particles. An electron gun was used to supply a beam of mono-energetic electrons directed onto the film surface for in-situ reflection high-energy electron diffraction (RHEED) at grazing incidence to the film surface. The diffraction patterns were imaged onto a phosphorous screen and recorded using a high-sensitivity low-light-level camera. RHEED data was collected and analyzed using kSpace software.

Thermal effusion cells were used to supply elemental beams of purified 4N (99.99%) Sr and Ca metal charges obtained through Sigma-Aldrich. Figure 2-2(a) shows typical calibration procedures for measuring the Sr and Ca fluxes, which was obtained by systematically adjusting the cell temperatures and measuring the time averaged flux (~5-10 min.) using a quartz crystal microbalance (QCM) which was inserted into the chamber at the growth position. The temperature dependent flux calibration data was fitted using an Arrhenius model in order to determine the temperature setting to supply typical fluxes ranging between $1-3\times10^{13}$ atoms/cm$^2$/s.
The Ti atoms were supplied using 5N (99.999%) Titanium(IV) tetraisopropoxide (TTIP) precursor material (Ti[OCH(CH₃)₂]₄) purchased through Sigma Aldrich. The TTIP material was contained in an ultra-high vacuum bubbler and maintained at a constant temperature (T_{bubbler} ~ 60-70 °C) using heating tape. The TTIP material was supplied via a heated gas inlet system (T_{inlet} ~ 70-80 °C) attached to the chamber, and the TTIP flux was regulated by a motorized leak valve positioned after the bubbler which was throttled in order to maintain a constant capacitance manometer (CM) gauge pressure measured before the TTIP entered the chamber. The TTIP pressure (p_{TTIP}) was measured at the growth position using a beam flux monitor (modified ion gauge) and calibrated with the CM pressure, as shown in Figure 2-2(b). Figure 2-3 shows the stability of the Sr, Ca and TTIP fluxes measured at the growth position inside of the MBE chamber for typical growth time periods (t_{growth} ~ 30 min.) where the fluxes do not drift by more than ±1% throughout a typical growth period.

The majority of substrate crystals used in this work were purchased through MTI Corporation. Prior to growth, the substrates were rinsed using acetone/isopropanol/water and baked at ~200 °C in a load lock chamber (10⁻⁷ Torr) before entering the main MBE chamber. The substrates were mounted onto tantalum pucks which were equipped with notches to hold the substrate crystal in place. A manipulator was used to contain the Ta pucks inside of the growth chamber, which was heated using a SiC resistor element placed just above the puck. The substrates were typically heated and cooled at a rate of ~ 25 °C/min. in the presence of molecular oxygen which was supplied using a gas inlet system. The substrate surfaces were thermally treated prior to growth to remove any organic contaminations by supplying oxygen plasma for ~ 20-30 min at substrate temperatures of T_{sub} ~ 800-900 °C.
Figure 2-1: Hybrid molecular beam epitaxy chamber equipped with a regulated gas inlet system to supply titanium tetraisopropoxide (TTIP) from a heated bubbler source, as well as Sr and Ca effusion cells, and a regulated O₂ gas inlet system. The gas flow of TTIP and O₂ are regulated using PID controlled leak valves positioned downstream to a capacitance manometer (CM) gauge. The Sr and Ca fluxes are calibrated using a quartz crystal microbalance (QCM) and the TTIP flux is calibrated using an ion-gauge, which can both be inserted in the chamber at the growth position. An electron gun is for reflection high energy electron diffraction (RHEED) which is monitored on a photoluminescent screen attached to the chamber. The atomic species are shown on the bottom left.
Figure 2-2: (a) Flux calibrations for Sr (blue dots) and Ca (red dots) effusion cells inside of an MBE chamber. The cells were heated up and the flux was measured at several different temperatures by a quartz crystal microbalance. The flux versus temperature data was fit to an Arrhenius equation which is shown as the black lines. (b) The TTIP pressure measured by the capacitance manometer located outside of the MBE chamber versus the measured ion gauge (IG) pressure (black dots) at the growth position inside of the MBE chamber. The linear relationship is shown by the linear fit (black line).
Figure 2-3: The normalized flux versus time for the TTIP gas (black line) which was measured by an ion gauge, as well as Sr (blue) and Ca (red) fluxes which were measured by a quartz crystal microbalance. The fluxes do not drift more than $\pm 1\%$ over a time period of 30 minutes, as indicated by the shaded gray area.
2.2 Reflection high-energy electron diffraction

Reflection high-energy electron diffraction (RHEED) is one of the most powerful tools available in MBE, in that it allows both qualitative and quantitative real-time feedback during film growth. It can be used to determine several important parameters such as; (1) surface roughness, (2) growth mode, (3) growth rate, (4) structural phase, which will be discussed in this section.[1, 2] RHEED is done by irradiating a thin film sample at grazing incidence (typical angles of only 1-3° with respect to the plane of the sample) with a collimated electron beam which is produced from of an electron gun (typical energy levels of 10 keV) inside an MBE chamber. The resulting RHEED diffraction pattern from the film surface is then projected onto a phosphorous screen attached to the MBE chamber wall, and the intensity of diffracted electrons on the screen are recorded using a camera. The grazing incidence of the electron beam with the sample restricts the diffraction interaction to only the first few planes of a crystal lattice. Therefore, the observed diffraction pattern only represents the two dimensional periodicity of the film surface. Since the sample can be rotated about its azimuth, the film surface can be monitored along different in-plane crystal physics axes, as shown schematically in the bottom of Figure 2-4, with the <100> and <110> directions shown with respect to the out-of-plane <001> axis about which the sample is rotated in the chamber. Also, because of the very low angle of incidence, the irradiated area of the sample is typically 1-3 mm long, therefore the diffraction pattern is an average or sum over a macroscopic area of the sample.

The relationship between the reciprocal space defined by the periodicity of the sample, and the real space the diffracted pattern is observed on a photoluminescent screen as shown in Figure 2-4. An Ewald construction is shown in the figure, where \( k_0 \) is the wavevector of the incident electron wave, and assuming elastic scattering, the diffracted waves \( k_1 \) and \( k_2 \), have the same magnitude as \( k_0 \), and their end points lie within a sphere of radius \( |k_0| \), which is called the
Ewald sphere. The sample can be considered as a periodic array of atoms, where the Fourier transform of the in-plane periodicity of atomic rows (or layers) produces two different series of orthogonal equidistant planes, or reciprocal lattice planes. The intersection of these planes gives rise to the reciprocal rods which are perpendicular to the sample surface. The intersection of these reciprocal rods and the Ewald sphere is what is observed on the RHEED screen as spots arranged around circles, where the smallest circle is called the 0th Laue zone \((L_0)\) and the next largest is called the 1st Laue zone \((L_1)\).[2] Note that only half of the circle will be observable since the transmitted electron beam is shadowed by the sample, which is called the shadow edge.

The quality of the RHEED diffraction patterns provides a great deal of information about the film structure at the growth front. For a perfect single-crystal sample which has an atomically flat surface, the reciprocal lattice rods of the film structure will be extremely sharp and narrow, resulting in very intense circular spots on the RHEED screen, as shown in Figure 2-5(a). However, most films are far from this ideal scenario. If a sample has a flat surface but there are multiple domains, the reciprocal lattice rods will broaden, where the resulting intersection of the Ewald sphere with the thicker rods will produce elongated diffraction spots, or streaks on the RHEED screen, as shown in Figure 2-5(b). If the film surface is rough and has multilevel terraces that have different widths, as shown in Figure 2-5(c) then the reciprocal lattice rods will have modulations that contain nodes of stronger intensity at the on-Bragg points where the waves reflected from the upper and lower terraces interfere constructively, and nodes of weaker intensity at the off-Bragg points.[2] In the worst case scenario during growth, the sample might contain three-dimensional islands, as shown in Figure 2-5(d). For this case, the electron beam will transmit through the islands, and produce transmission like diffraction patterns where the intersections between reciprocal lattice planes in all three directions is observed, resulting in a vertical array of diffraction spots on the RHEED screen.
While the quality of the RHEED pattern can determine the growth mode, the change of the diffraction spot intensities as a function of time during deposition can tell us the rate at which the material is being deposited, as well as the type of surface kinetics involved. If we consider the surface kinetics of atoms at the growth front of a film during deposition, there are two main ways that deposited material can form into a crystal structure which are; (1) step-flow-growth, where the time it takes atoms at the growth front to travel to the next available step edge is smaller than the time it would take an atom to react with other atoms and form an island, and (2) layer-by-layer growth, which is the opposite of step-flow-growth, where the time migration time of atoms at the surface to a step-edge is larger than the time required for island nucleation to occur.[3] In the case of (1), the film surface is always smooth, and the diffracted RHEED spot will be constant with time. For the case of (2), the completion of full layer coverage at the film surface will be smoothest and roughest in between layer completions, resulting in oscillations of the diffracted intensity, as shown in Figure 2-6, giving rise to oscillations which have the same frequency as the layer-by-layer growth rate.
Figure 2-4: An Ewald construction showing the comparison between the reciprocal space and real space of the RHEED process. The Ewald sphere is shown which contains the incident electron beam produced by the electron gun, \( k_0 \) (green), and the diffracted wavevectors, \( k_1 \) (red) and \( k_2 \) (blue) which all have equal magnitudes. The intersection of the Ewald sphere with the reciprocal lattice planes of the sample produce diffractions spots which are detected on a photo luminescent (PL) screen where the top half of the 0th and 1st Laue zones (\( L_0 \) and \( L_1 \), respectively) are observed. The shadow edge above which only the reflected wavevectors are observable is shown. The sample orientation is shown below, with the common directions measured are along the \( <100> \) and \( <110> \) azimuths.
Figure 2-5: A comparison between the real space of a film surface crystal structure (left column), the reciprocal space (middle column), and the observed RHEED pattern (right column), for the cases of (a) flat and single crystalline surface, which result in sharp reciprocal rods and intensity RHEED spots, (b) flat surface with small domains which results in thicker reciprocal rods and RHEED streaks, (c) multilevel stepped surface which gives modulated intensities of the rods and RHEED streaks, and (d) 3D islands which give reciprocal and RHEED spots. Image adapted from Ref. [2].
Figure 2-6: The intensity of a RHEED spot during layer-by-layer growth, where the beginning (a), middle (c) and end (e) of a layer completion result in the max., min., and again mag. in the RHEED intensity oscillation profile shown on the right for each of the layer times. Image adapted from Ref. [3].
2.3 High-resolution X-ray diffraction

X-ray diffraction (XRD) is one of the most powerful tools at hand for thin film growers, as it facilitates the ability to probe the microscopic and macroscopic structural properties of a thin film material. X-ray diffraction is performed by irradiating X-ray light onto a sample in which the diffracted X-ray light from the sample depends on the periodic arrangement as well as the type of atoms in the crystal sample.\textsuperscript{[4, 5]} X-ray light is reflected from atomic planes of atoms, as shown in Figure 2-7, where the reflected light from adjacent atomic planes will interfere with each other. According to Bragg’s Law, they will only constructively interfere with each other upon meeting the condition that,\textsuperscript{[6]}

\begin{equation}
    n\lambda = 2d \sin \theta ,
\end{equation}

where $d$ is the lattice spacing of the atomic planes, and $\theta$ is the angle of incidence between the X-rays and the atomic planes, where the difference in the path length between two reflected X-rays (as shown by the green lines in the figure) has to be an integer multiple of the wavelength.

The majority of XRD data shown in this thesis was performed by 4-circle X-ray diffraction techniques on a Philips X-Pert Pro MRD diffractometer using Cu-K\textsubscript{$\alpha1$} radiation, which has a wavelength of $\lambda=1.54$ nm. Figure 2-8 shows the geometry used for 4-circle X-ray diffraction analysis, where samples are aligned to the incident X-ray beams and are rocked by angles of $\omega$, $\chi$, and $\phi$ about the x, y and z sample axes, where the detected X-rays are detected in the plane of incidence at an angle of $\theta$ with respect to the film surface. By scanning $\omega$ (the incident X-ray) and $\theta$ (the angle of the detector) the spacing between the atomic planes can be measured for different HKL conditions, where H, K and L are the reciprocal lattice vectors of the atomic structure being probed. To measure the out-of-plane lattice parameter (i.e. only scan along 00L direction), 20-$\omega$ scans were performed by rocking $\omega$ and scanning 20, where the
resulting positions of the X-ray peaks in 2θ can be used to calculate the d-spacing of the films for different unit cell geometries using the following equation, [7]

\[
\frac{1}{d^2} = \frac{H^2}{a^2} + \frac{K^2}{b^2} + \frac{L^2}{c^2},
\]

Eq. 2-2

where use of Eq. 2-1 and the known HKL positions, the a, b, and c lattice parameters of the film can be determined.

The positions of the diffracted X-rays can be mapped out as a function of HKL in order to construct reciprocal space maps (RSM), where Figure 2-9(a) shows a typical RSM scan for a thin film that is fully strained to the substrate material, i.e. the same in-plane lattice parameters.[8] For a fully strained film, the HH0 positions of the film and substrate will be equal to each other, although the out-of-plane 00L peak positions will be different. However, if the film does not assume the same in-plane lattice parameters as the substrate, but rather relaxes, meaning that it reconfigures the crystal structure to its bulk parameters (i.e. lowest energy bond lengths and bond coordination), the in-plane lattice parameters of the film will be different than the substrate, and the HH0 diffraction positions will be shifted, as shown in Figure 2-9(b).
Figure 2-7: Bragg’s Law showing the incident X-ray beam (red arrow) on the left at an angle of incidence, $\omega$, with respect to the plane of a periodic array of atoms (blue dots) with lattice spacing of $d$, as shown on the right. The reflected beams will have maximum constructive interference when the difference in their path length is equal to $2d\sin\theta$. 
Figure 2-8: Geometry of 4-circle high-resolution X-ray diffractometer. The incident X-ray beam is at an angle \( \omega \) with respect to the sample plane, where the reflected X-rays are detected at an angle \( \theta \) and in the plane of incidence. The sample can be translated along the \( x \), \( y \) and \( z \) directions, as well as rocked about the \( y \) and \( z \) directions at angles of \( \chi \) and \( \phi \) as shown by the dashed circle arrows.
Figure 2-9: A projection of the three-dimensional reciprocal lattice space (HKL) on the HH0-00L plane, showing the diffraction spots for a film (pink) and substrate (blue) sample where the film is (a) fully strained as shown below the reciprocal space map, resulting in a tetragonal distortion of the film unit cell which has the same HH0 position of the substrate, and (b) a fully relaxed film, where the in-plane lattice parameter of the film is different than the substrate, resulting in different HH0 positions than that of the substrate. Image adapted from Ref. [8].
2.4 Scanning force microscopy techniques

Atomic force microscopy (AFM) is a powerful technique that allows three-dimensional maps of surface morphologies to be generated with nanoscale resolutions by scanning a sharp probe tip over a sample.[9] The surface height resolution can be < 1 nm, while the lateral resolution is typically determined by the size of the probe tip used which is ~10-25 nm. [10] Figure 2-10 shows a schematic of a tapping mode AFM experimental setup. In this technique, the tip/cantilever is oscillated near the resonance frequency using a piezoelectric crystal attached to the end of the cantilever.[11] The tip is lowered towards the sample surface where the amplitude of the oscillation decreases once it makes contact with the sample surface. The oscillating tip will contact and lift off from the surface at ~50-500 thousand cycles per second. The deflection of the tip is monitored by a laser beam which is reflected off the end of the cantilever (positioned above the tip) and onto a 4-quadrant photodetector. When the tip contacts the surface, the reflected beam spot will move on the detector, and the integrated intensity can be used to determine the height of the sample as a function of the position on the sample surface. In the tapping mode, the amplitude is maintained constant by a feedback loop between the piezoelectric, the detector, and the distance between the tip and the sample (z-height). The z-height can then be mapped two-dimensionally and displayed in real time on a monitor. Other mechanical properties, such as the surface adhesion can also be extracted in tapping mode. This technique is superior to conventional AFM modes such as contact AFM since it does less damage the surface during scanning, and it has much better resolution capabilities.

Piezoresponse force microscopy (PFM) is a special mode of atomic force microscopy which allows ferroelectric domains and their polarization direction to be probed at the nanoscale.[12] This technique takes advantage of the converse piezoelectric effect, where a strain ($S$) is induced by an applied electric field ($E$),
where \( d_{ij} \) is the piezoelectric tensor in Voigt notation. It can be shown that for a single-domain ferroelectric, the piezoelectric coefficient relates to the spontaneous polarization \((P_S)\) by the following,

\[
d_{ij} = \varepsilon_{im} Q_{jmk} P_{S,k},
\]

Eq. 2-4

where \( \varepsilon_{im} \) is the dielectric constant and \( Q_{jmk} \) is the electrostriction coefficient. The linear coupling between the ferroelectric and piezoelectric terms means that the polarization direction can be determined from the sign of the strain. Therefore, depending on the direction of the polarization vector, the sample deformation will either elongate, contract, or shear with the electric field, and the direction of the distortion can be determined. A setup of PFM is shown schematically in Figure 2-11. In this technique, a metal tip is driven by an AC voltage, and kept at a constant contact deflection set-point with a ferroelectric sample. If we consider a sample which has a polarization vector that is pointing out of the plane of a sample, when the voltage on the tip is positive, the sample will expand due the converse piezoelectric effect, and the tip will be pushed away from the surface, and when the tip voltage is negative, the sample will contract and the tip will lower towards the sample.

The deflection of the AC biased tip/cantilever is detected on a 4-quadrant detector by a laser beam which is reflected off of the cantilever tip. The oscillation of the laser beam on the detector is then filtered using a lock-in amplifier which can give the phase and amplitude of the tip deflection with the AC voltage. For a polarization pointing out of plane, the phase of the AC bias and the deflection will be in-phase, and for a polarization pointing into the plane of the sample, the deflection and AC bias will be out-of-phase. As the tip is rastered across the sample, the phase and amplitude of the deflection can be imaged in real time to discern the ferroelectric domain polarization directions in a sample. A DC bias can also be applied to the tip (provided
that there is a bottom electrode in close proximity to the tip which is in contact with the sample surface) in order to electrically switch the polarization direction. For PFM switching, the DC bias is ramped and the AC bias on top of the DC is used to probe the piezoelectric deformation of the sample.[13]
Figure 2-10: Schematic of tapping-mode atomic force microscopy (AFM) setup. A laser beam is reflected off a cantilever with a tip on the end which is in contact with the sample, and the laser beam is steered onto a 4-quadrant detector which is monitored by the Nanoscope controller. The cantilever is oscillated using an AC driven piezoelectric actuator and the amplitude of the deflection is kept constant using a feedback loop between the detector, piezoelectric actuator (piezo) and raster stage. The data is analyzed in real time to display the sample surface height as well as other properties such as adhesion.
Figure 2-11: Piezoresponse force microscopy (PFM) experimental setup. A conducting tip is in contact with a polar film sample which can be biased with respect to the tip. An AC voltage is applied to the tip, which will deflect or extend depending on the polarization vector ($P$) orientation of the film area being probed. This causes the reflected laser beam to move up in down on the 4-quadrant photodetector which is then measured using a lock-in amplifier which is part of the Nanoscope controller. The phase and amplitude of the tip deflection with respect to the AC field are extracted and observed on a display screen in real time.
2.5 Photolithography techniques

To probe the electrical properties of the thin film samples studied in this work, photolithography was used to deposit electrodes on top of thin film surfaces. Figure 2-12 shows the entire step-by-step process for depositing electrodes. First, the sample surface is cleaned using ultrasonic rinsing in acetone, then isopropanol (IPA), and then water, in that order. Before transferring the sample from one solvent bath to the next, the sample should be lightly sprayed with the bath solvent to remove any debris near the surface before transferring. After the final water rinsing, the sample is dried by blowing pressurized nitrogen gas and then heated on a hot-plate at ~100 °C to remove any water at the surface before applying the first photoresist layer. Once the sample surface has been thoroughly cleaned, the next step is to deposit a ~500 nm bottom (or undercut) photoresist layer, which is typically LOR5A.[14] The layer is deposited using a spin bench, where the sample is rotated at ~5000 rpm for 30-45 seconds and the sample surface is modestly coated with the LOR5A solution using a pipette. After depositing the LOR5A layer, the sample is then baked at ~180 °C for ~3 minutes. Next, a ~1.3 μm thick photoresist layer of SPR3012,[15] is deposited at ~5000 rpm for 30-45 seconds, and then baked at ~97 °C for 1 minute. Once the LOR5A and SPR3012 photoresist layers are deposited, the sample is ready for UV exposure. To transfer the desired electrode pattern to the sample, a glass/Cr mask is used which has the desired patterns cut out from the Cr layer in the mask. The glass allows the UV light to go through the mask, and the Cr layer absorbs the UV light and stops it from hitting the photoresist layer on the sample. The exposure is done on a MA/BA6 mask aligner which is equipped with a UV lamp. The gap between the sample and the mask is set to ~70-120 μm, and the exposure time is typically ~7-10 seconds long. The gap size and exposure time need to be calibrated in order to ensure optimal exposure of the photoresist layers.
After exposure, the exposed photoresist areas are removed by developing the sample in a bath of CD-26 developer solution for ~ 60-75 seconds.[16] The developing time needs to be calibrated in order to optimize the sharpness of the pattern after the exposure. Once the mask pattern has been successfully transferred to the photoresist layer on the sample surface, the metal electrodes can are deposited. Before metal deposition, the sample surface is first cleaned using oxygen plasma etching to ensure good sample/metal contact. The oxygen plasma etch is done under 50 mTorr of helium and 300 mTorr of oxygen gas with an RF power of ~ 100 W for a time period of ~ 1-3 minutes. After the oxygen plasma etch cleaning, the sample is then loaded into a sputter chamber, where the metal material is deposited onto the sample. The sample is loaded into the sputter chamber by attaching it to a silicon wafer using thermal tape. The metal stack typically used in this work is ~ 30 nm Cr layer, which easily sticks to the sample surface, followed by a ~ 100 nm Au layer, which makes electrical probing easier since it is relatively soft and electrical probe tips can easily contact the Au layer. The final step is to remove the rest of the unwanted photoresist layer. This is done by immersing the sample into a heated bath (~ 70-80 °C) of Nano Remover PG solution for ~ 15-30 minutes.[17] To aid in removal of the leftover photoresist and metal flakes, a pipette can be used to gently agitate the sample surface while it is immersed in the bath solution, or the sample can be carefully sonicated to remove the excess photoresist and metal flakes on the surface. After taking the sample out of the Remover PG solution, it is gently dried using a pressurized nitrogen air gun.
Figure 2-12: The complete process for photolithography deposition of metal electrodes. (a) Rinse cleaning using acetone, isopropanol, and water. (b) Depositing the lift-of-resist layer, (c) depositing the photoresist layer, (d) ultra-violet exposure using a mask, (e) developing or removing the exposed photoresist areas, (f) oxygen plasma etch cleaning the surface before (g) sputtering of the metal electrode material, and finally (h) removing the remaining photoresist layers using remover PG.
2.6 Dielectric measurements

The temperature dependent dielectric properties of samples studied in this work were performed by measuring the capacitance of the film structures using an Agilent E4980 LCR meter, and the samples were cooled inside of a Lake Shore Model TTPX probe station with a Lake Shore 332 temperature controller. The capacitance of a material is given by the general formula,

\[ C = \varepsilon_0 \varepsilon_r \left( \frac{A}{t} \right), \]

where \( C \) is the capacitance (in units of Farads), \( \varepsilon_0 \) is the permittivity of free space (~8.854 \times 10^{-12} \text{ F/m} \), \( \varepsilon_r \) is the relative permittivity, or dielectric constant of the capacitor material, \( A \) is the area of the electrode plates and \( t \) is the thickness of the capacitor material. By measuring the capacitance of a material with known electrode geometries, the out-of-plane dielectric constant can be determined. However, when using interdigitated electrode geometries deposited on a thin film/substrate structure to measure the in-plane dielectric constant, it cannot be directly obtained from this simple equation due to the non-uniform electric-field distribution of the electrodes. To account for the planar electrode geometry as well as the substrate contributions in the composite capacitor material, as shown in Figure 2-13, a conformal mapping technique is typically done which transforms the planar capacitor into a sandwich capacitor,[18-20] which is given by the equation,

\[ C = \varepsilon_0 \varepsilon_r F(k), \]

where \( F(k) \) is a function of the ratio of the total elliptic integral of the first kind of the in-plane and out-of-plane electrode geometry of the transformed sandwich capacitor, and is expressed as,[21]
where \( k \) is the modulus of the elliptic integral form. In this layered composite structure, the total capacitance can be considered as a series of capacitors connected in parallel,[18, 22, 23]

\[
C_{\text{measured}} = C_{\text{air}} + C_{\text{film}} + C_{\text{substrate}},
\]

Eq. 2-8

where, \( C_{\text{air}} \) is the capacitance of the ambient air space between the electrodes, \( C_{\text{film}} \) is the in-plane capacitance of the film, \( C_{\text{substrate}} \) is the capacitance of the substrate material, and \( C_{\text{measured}} \) is the total capacitance measured for the entire capacitor series. The modulus of the elliptic integral, \( k \), for each layer is given by,[19]

\[
k_{\text{air}} = s / l,
\]

\[
k_{\text{film}} = \tanh\left( \pi s / 4t_{\text{film}} \right) / \tanh\left( \pi l / 4t_{\text{film}} \right),
\]

\[
k_{\text{substrate}} = \tanh\left( \pi s / 4(t_{\text{substrate}} + t_{\text{film}}) \right) / \tanh\left( \pi l / 4(t_{\text{substrate}} + t_{\text{film}}) \right).
\]

Eq. 2-9

where, \( t_{\text{film}} \) and \( t_{\text{substrate}} \) are the thickness of the film and substrate layers, respectively, and \( s \) is the gap distance between fingers, and \( l \) is the distance between the edges of two adjacent fingers, as shown in Figure 2-13. The \( F(k) \) functions can be solved for each capacitor section separately, and further mathematical manipulation using a series expansion, the capacitance of each section are determined to be,[19]

\[
C_{\text{air}} = w \cdot \varepsilon_0 \alpha,
\]

\[
C_{\text{film}} = w \cdot \varepsilon_0 (\varepsilon_{\text{film}} - \varepsilon_{\text{substrate}}) \beta,
\]

\[
C_{\text{substrate}} = w \cdot \varepsilon_0 (\varepsilon_{\text{substrate}} - 1) \gamma.
\]

Eq. 2-10

where \( \varepsilon_{\text{film}} \) and \( \varepsilon_{\text{substrate}} \) are the dielectric constant of the film and substrate, respectively, \( w \) is the length of the electrode finger, and the \( \alpha, \beta, \) and \( \gamma \) terms are constants which are given below. The dielectric constant of the film is obtained from the following expression,
\[ e_{\text{film}} = (1/\beta) [C_{\text{measured}} / w\varepsilon_0 + \varepsilon_{\text{sub}}(\beta - \gamma) + (\gamma - \alpha)] , \quad \text{Eq. 2-11} \]

where,
\[
\alpha = (2/\pi) \ln[4l/s],
\]
\[
\beta = 1/((s/t_{\text{film}}) + (4/\pi) \ln[2]),
\]
\[
\gamma = (1/\pi) \ln[16(t_{\text{sub}} - t_{\text{film}})/\alpha].
\]

Note that this expression is generally only applicable if the geometry of the interdigitated electrodes with respect to the dimensions of the film/substrate structure gives the following inequalities; \( s \leq 10 \ t_{\text{film}} \), \( s \leq 0.25 \ l \), \( s \geq \ t_{\text{film}} \), and \( s \leq 0.5 \ t_{\text{sub}} \). For the case where \( s \leq 10 \ t_{\text{film}} \), then the \( \varepsilon_{\text{film}}/\varepsilon_{\text{sub}} > 100 \) ratio inequality must be satisfied.

The dielectric measurements for CaTiO\(_3\) films grown on (001)LSAT substrates in this work (Chapter 3) were done using interdigitated electrode patterns shown in Figure 2-14(a) which shows the electrode design on each sample in the CaTiO\(_3\) film series. The array of interdigitated electrodes on the film surfaces consist of a checkered pattern of different pads with either 6 \( \mu \)m or 10 \( \mu \)m gaps, which are shown in better detail in Figure 2-14(b) and Figure 2-14(c), respectively. The finger widths are 10 \( \mu \)m wide, and the finger lengths are \( \sim 1 \) mm. Using these electrode dimensions, the dielectric properties of the CaTiO\(_3\) films were measured and calculated using the equations provided above.
Figure 2-13: Diagram of a planar capacitor consisting for a thin film (dielectric constant $\varepsilon_{\text{film}}$) on a substrate (dielectric constant $\varepsilon_{\text{sub}}$) with two interdigitated electrode fingers on top of the film. The relevant parameters for describing this structure are the finger gap, $s$, the distance between the ends of the fingers, $l$, and the length of the fingers, $w$. The thickness of the film and substrate, $t_{\text{film}}$ and $t_{\text{sub}}$, respectively, are shown on the right.
Figure 2-14: (a) A photo image of several CaTiO$_3$/[(001)]LSAT substrate samples each showing an array of photolithographically deposited interdigitated electrode patterns (100 nm Au // 30 nm Cr) with alternating pads having different finger gaps of (b) 6 μm and (c) 10 μm. The finger length = 1 mm and the finger width = 10 μm. The number of fingers in (b) is 51, and in (c) 41.
2.7 Second harmonic generation experiments

Optical second harmonic generation (SHG) is a nonlinear optical process where a non-centrosymmetric material (i.e. lack of an inversion center) will convert two photons of light at frequency $\omega$ (wavelength $\lambda$) into one photon of light at frequency $2\omega$ (wavelength $\lambda/2$).[24] This process is shown schematically in Figure 2-15(a). SHG can also be thought of in terms of an energy level scheme, as shown in Figure 2-15(b), where two photons of energy $\hbar \omega$ excite an electron from its ground state into a virtual state, and the electron then decays back to the ground state releasing energy of $2\hbar \omega$ in the form of light. The generated second harmonic polarization ($P_{2\omega}$) is described as,[25]

$$P_{2\omega}^i = d_{ijk} E_{j\omega} E_{k\omega},$$

where $E_{\omega}$ is the fundamental electric field, and $d_{ijk}$ is the nonlinear optical coefficient tensor, which can be expressed as $d_{ij}$ in Voigt notation. For nonpolar materials (i.e. cubic symmetry) the $d_{ij}$ term is equal to zero, and SHG will not occur. But for polar materials, the $d_{ij}$ term is non-zero, and this process will occur. While the creation of SHG indeed indicates that a material lacks an inversion center, it does not necessarily mean that the material is ferroelectric. To determine this, switching of the polarization is necessary. SHG is used extensively in this work to probe the existence of polar phases, as well as the polar symmetry of thin film materials.

A schematic of a typical transmission SHG setup is shown in Figure 2-16. The fundamental beam is generated from a mode-locked Ti:Sapphire laser which typically has a pulse width of ~ 80-100 fs, and a repetition rate of 1-2 kHz for a wavelength of ~ 800 nm. The polarization of the fundamental is cleaned up by using a beam splitter (BS1) which allows p-polarized light to propagate, and s-polarized light to be reflected into a light absorbing dump. The linear polarized fundamental is then steered and aligned using mirrors (M1 and M2) so that it
is well aligned with respect to a sample. The polarization of the fundamental can be rotated by using a zero-order half wave plate (λ/2). A high-pass filter then used to make sure that only 800 nm light is incident to the sample. A lens (L1 focus) is used to focus the fundamental onto a sample, where another lens (L2) is positioned at twice the focal distance away from L1 to collimate the transmitted fundamental as well as SHG from the sample. The L1 and L2 lenses are attached to a motorized translation stage so that the focus point can be moved through the sample. The sample is mounted on a rotation stage, and can be rotated by an angle θ with respect to the incident beam. The SHG is then filtered so that none of the transmitted fundamental light goes to the detector, and an analyzer is used to detect the SHG in any desired direction. A black box is used to house the photomultiplier tube (PMT), where the SHG is steered into the PMT using mirrors M3 and M4, and is then focused onto the PMT using lens L3. A notch filter (NF) is placed just before the PMT to ensure that only the SHG light is allowed to enter the very sensitive PMT detector.

There are two main scan modes for SHG data that is collected in order to determine the polar symmetry of materials. The first type of scan is called a ‘polar plot’, where the sample is fixed at an angle of incidence (θ), and the electric field of the fundamental light, E₀ is rotated by φ=360° using a half waveplate. The SHG is then detected along fixed directions using the analyzer (or beam splitter). The second type of scan is called a ‘tilt scan’ where φ is fixed, and the sample is rotated about one of its crystal physics axes by θ, where θ can be scanned from -90° to +90°, and θ=0° is called normal incidence. Note that in order to perform these SHG polarimetry scans, the incident beam as well as the sample must be very well aligned. The rotation axis of the sample must be exactly perpendicular to the k vector of the incident light. If they are not perpendicular, then rotation of the sample will cause the focal area of the beam on the sample to change as the sample is rotated. This can give erroneous tilt scan data and causes
problems for the modeling procedures. A simple way to make sure that the fundamental is well aligned to the rotation axis, is to use a needle point mounted to the rotation stage axis, and the needle is placed right at the focus point. The needle will shadow the light when it is exactly perpendicular to the fundamental beam, ensuring good alignment for data collecting. Using a combination of polar plots and tilt scan data along with theoretical modelling of the SHG intensity, the polar point group symmetry of a thin film material can be determined, and will be discussed many times throughout this thesis for several different material systems.

For low temperature cryogenic SHG experiments, samples are mounted on a copper finger inside of a vacuum tube which is equipped with transparent windows to allow the fundamental laser beam to irradiate the sample. In order to perform low temperature tilt scans, the sample is rotated by turning the sample holder finger from outside of the cryo tube. This can lead to a ‘wobbling’ of the sample, since the rotation axis of the finger is not exactly along the crystal physics axes of the sample. In order to mitigate this problem, low temperature tilt scans are collected by fixing the angle of incidence $\theta$ and then scanning the focus through the sample as shown in Figure 2-17(a). An example of a low temperature tilt scan for a SrTiO$_3$ film is shown in Figure 2-17(b), where the z-axis is the SHG intensity, the x-axis is the focus distance, and the y-axis is the angle of incidence, $\theta$. The angle of incidence is fixed to $\theta = -45^\circ$, $-30^\circ$, $-15^\circ$, $0^\circ$, $15^\circ$, $30^\circ$, and $45^\circ$, and the focus is moved through the sample in steps of ~0.1 mm. The curves show the SHG intensity measured at each focus point. Figure 2-17(c) shows a projection of the SHG intensity as a function of $\theta$ and the focus, where it is easily seen that the maximum SHG intensity considerable shifts from $\theta=-45^\circ$ to $\theta=+45^\circ$, indicated by the red line. The corrected path is indicated by the dashed white line. This ‘wobble’ is more easily seen in Figure 2-17(d) where the maximum at $\theta=-45^\circ$ and $\theta=+45^\circ$ shifts by about 0.5 mm. By taking the maximum SHG intensity value for each focus scan as a function of $\theta$, a corrected low-temperature SHG tilt scan can be
generated, as shown in Figure 2-17(e), with the uncorrected tilt scan shown for comparison, where the SHG intensity considerable decreases at $\theta=\pm 45^\circ$. Using this method, low temperature SHG polarimetry data can be taken without having systematic errors in the data due to the focal area on the sample changing as the sample is rotated inside of the cryo tube.
Figure 2-15: Nonlinear optical second harmonic generation process, which can be thought of as
(a) the conversion of two photons at frequency $\omega$ (wavelength $\lambda$) which are converted into one
photon of light at frequency $2\omega$ (wavelength $\lambda/2$) by a nonlinear material where the second order
optical susceptibility, $\chi^2 \neq 0$. This process can also be thought of using an energy level diagram
shown in (b) where two photons of energy $\hbar\omega$ excite an electron from the ground state (solid line)
to a virtual state (dashed line), which then emits a single photon with energy $\hbar 2\omega$. 
Figure 2-16: Table top setup for transmission SHG of a sample \((x, y, z)\) which can be rotated by \(\theta\) about a particular axis. The fundamental (80 fs pulse, 1 kHz repetition rate, wavelength \(\lambda=80\text{nm}\)) is aligned using mirrors \(M_1\) and \(M_2\) to be collinear with the sample normal \((z \text{ at } \theta=0^\circ)\). A beam splitter (BS1) allows only \(p\)-polarized light to propagate (s-polarized light is dumped), and a half-wave plate \((\lambda/2)\) is used to rotate the fundamental light field by an angle \(\phi\), where a long pass filter (LPF) stops parasitic wavelengths \((\lambda>700\text{nm})\) from propagating to the sample. The L1 lens focuses the fundamental onto the sample, where the generated \(\lambda=400\) is collimated by L2 lens (attached to L1 by a translation stage). A short-pass filter (SPF) gets rid of red light, and BS2 filters out s-polarized blue light. The p-polarized blue light is steered using mirrors \(M_3\) and \(M_4\), and focused via L3 and filtered \((\lambda=400\pm10\text{nm})\) using a notch filter (NF) before entering the photo-multiplier tube (PMT) which is contained inside of a ‘black box’ indicated by the shaded gray area.
Figure 2-17: (a) Schematic of experimental SHG tilt scan setup where the focus of the incident light ($\omega$) can be varied with respect to the crystal physics axes of a sample ($z_1, z_2, z_3$) which can be rotated about the axis by an angle of incidence $\theta$. (b) Example of a focus series tilt scan on SrTiO$_3$/SrTiO$_3$ film sample where $\theta$ was rocked from -45° to 45° in 15° increments, the focus was scanned from -4 to 4 mm through the center of the film, and the SHG intensity was measured as a function of focus. (c) Contour map of the projected SHG intensity as a function of focus and $\theta$, showing the corrected tilt path by the white dashed line. (d) Change in the focal point at which the maximum SHG intensity is measured for $\theta$=45° and 45°. (e) The corrected (green circles) and uncorrected (dashed red line) tilt scans.
2.8 References

Chapter 3

Unleashing strain-induced ferroelectricity in complex oxide thin films via precise stoichiometry control

3.1 Abstract

Strain tuning has emerged as a powerful means to enhance properties and to induce otherwise unattainable phenomena in complex oxide films. However, by employing strain alone, the predicted properties sometimes fail to emerge. In this chapter, the critical role of precise stoichiometry control for realizing strain-enabled ferroelectricity in CaTiO$_3$ films is demonstrated. An adsorption controlled growth window is discovered for CaTiO$_3$ films grown by hybrid molecular beam epitaxy, which ensures an excellent control over the Ti:Ca atomic percent ratio, with an error of < 0.8% in the films. Superior ferroelectric and dielectric properties are found for films grown inside the stoichiometric growth window, yielding optimal properties. Outside this window, properties are severely deteriorated and ultimately suppressed by defects in the films. This study exemplifies the important role of precise compositional control for achieving strain-induced properties. Untangling the effects of strain and stoichiometry on functional properties will accelerate both fundamental discoveries yet to be made in the vast materials design space of strained complex oxide films, as well as utilization of strain-stabilized phenomena in future devices.

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3.2 Introduction

Intense research efforts have focused on exploiting strain-induced functionality in complex oxide ABO$_3$ perovskite thin film materials.[1] Theory and experiments have shown that epitaxial strain can increase the paraelectric-to-ferroelectric transition temperature ($T_C$) of BaTiO$_3$ by hundreds of degrees,[2] induce room temperature ferroelectricity in the incipient ferroelectric SrTiO$_3$,[3] and even transform the paraelectric antiferromagnetic EuTiO$_3$ into a ferroelectric ferromagnet.[4] While strain engineering has proven to be a powerful strategy for unlocking new functionalities and enhancing performance in complex oxides,[5] achieving controlled and uniform stoichiometry in films is equally important, as defects can destroy ferroic behavior in materials.[6] Although conventional solid state crystal growth routes [7] as well as ultrahigh vacuum growth techniques such as pulsed laser deposition [8] and molecular beam epitaxy (MBE) [9] are capable of producing high quality oxide films, precise control over stoichiometry still remains challenging. Defect formations in perovskites are typically manifest as AO-rich or BO$_x$-rich phases interspersed throughout a material to accommodate deviation from ideal stoichiometric compositions, and have shown to be detrimental to the ferroelectric properties in both thin film [10] and bulk [11] materials. Thus, the ability to accurately control stoichiometry in a material is a critical requirement for exploring intrinsic strain-induced phenomena. For perovskites containing volatile AO species, such as PbO in PbTiO$_3$, stoichiometry in thin films is achieved by accessing an adsorption controlled growth window at low growth temperatures of ~600 °C.[12] However, for less volatile AO species, such as SrO in SrTiO$_3$ or CaO in CaTiO$_3$, the growth windows exist at much higher growth temperatures of > 1500 °C or very low cation flux rates, which are not practicable for the growth of films with tens of nanometer thickness.[13, 14] The absence of a self-regulating growth window limits the level of control over the A:B cation stoichiometry in complex oxides and is dependent on the control of the supplied cation
fluxes. Even in the case of extensive and thorough flux calibrations to ensure a close-to-ideal cation ratio, deviations are quite common and are typically limited by the low vapor pressure B-site transition metal cations (i.e. Ti) which are highly refractory materials and can have flux drifts as high as ~2.5% per hour in the presence of ozone using standard Ti sources.[15, 16]

A promising way to circumvent this limitation was demonstrated by Jalan et al.[14] using a combination of metallic Sr and metal-organic titanium(IV) tetraisopropoxide (TTIP) sources inside an MBE chamber. An adsorption controlled growth window for SrTiO₃ films was accessed at growth temperatures of ~800 °C.[17] Similar growth windows have been recently reported for NdTiO₃,[18] GdTiO₃,[19] BaTiO₃,[20] and BaSnO₃,[21] as well as vanadate systems such as SrVO₃[22] and LaVO₃[23] using metal-organic vanadium(V) oxytriisopropoxide. Using the hybrid MBE approach, record high electron mobilities > 50,000 cm²/Vs in La-doped SrTiO₃ films have been reported,[24] device quality factors of $Q = 1/\tan(\delta) > 1000$ in Ba₃Sr₁₋ₓTiO₃ were achieved,[25] and record high residual resistivity ratios, $\rho_{300K}/\rho_{5K}$, in metal SrVO₃ films were recently demonstrated, exceeding bulk single crystal values.[26] These recent milestones are hallmarks that excellent stoichiometry control and low defect concentrations can be achieved using this growth approach, leading to superior intrinsic material properties in complex oxide materials.

In this work, we report the discovery of a self-regulated adsorption controlled growth window for CaTiO₃ films grown by hybrid MBE. The structural, chemical, nonlinear optical, dielectric, and ferroelectric properties of films grown inside and outside the growth window were comprehensively characterized, namely the out-of-plane $c$-axis lattice parameter, Ti:Ca atomic percent ratio, temperature dependent dielectric and optical properties across the paraelectric-to-ferroelectric phase transition, as well as the magnitude of polarization and polar symmetry in the ferroelectric phase. It is shown that superior properties in strained CaTiO₃ were only present for
films grown within the self-regulated stoichiometric window, whereas films grown outside of the growth window range resulted in dramatically deteriorated ferroelectric and dielectric properties, where ferroelectricity ultimately disappears even with small deviations from ideal stoichiometry. Defects originating from nonstoichiometric growth conditions destabilized the ferroelectric phase accompanied by a reduced saturation polarization and transition temperature. These results demonstrate that excellent stoichiometric control is a mandatory requirement to ensure that strain-induced functional properties are not compromised by unintentional deviations from ideal conditions, and that ideal cation stoichiometry in complex oxides can be achieved using the hybrid MBE growth approach.

3.3 Thin film growth and structural characterization

CaTiO$_3$ is a non-polar paraelectric insulator with a centrosymmetric orthorhombic space group $Pbnm$ in bulk form.[27] Recent calculations of the temperature-strain-phase diagram of CaTiO$_3$ predicted that epitaxial strain can induce ferroelectricity in this material system.[28-30] To explore the role of cation stoichiometry on properties of strained CaTiO$_3$ films, a series of ~20 nm thick films were grown on (001) (LaAlO$_3$)$_{0.3}$(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT) substrates (+1.23% tensile strain) in an MBE chamber with a background pressure of 10$^{-10}$ Torr. Elemental Ca and metal-organic TTIP molecules were co-supplied from an effusion cell and a gas injector, respectively, in the presence of molecular oxygen. The growth temperature, molecular oxygen pressure, and Ca flux were fixed for each film grown in the stoichiometric series to $T_{sub} = 900$ °C, $p_{O_2} = 1 \times 10^{-7}$ Torr, and $\Phi_{Ca} = 2.0 \times 10^{13}$ atoms/cm$^2$·s, respectively. $\Phi_{Ca}$ was calibrated by measuring the Ca flux at several different effusion cell temperatures and extracting the desired flux from an Arrhenius fit. The TTIP precursor material was contained in an ultra-high vacuum.
bubbler, kept at $T_{\text{bubbler}} = (70 \pm 0.2) ^\circ \text{C}$. The TTIP flux was regulated from a PID feedback loop by controlling the flux through a linear leak valve, mounted after the bubbler, using the pressure reading of a capacitance manometer downstream to the linear leak valve. The beam-equivalent TTIP pressure inside of the chamber ($p_{\text{TTIP}}$) was measured using an ion gauge inserted into the chamber at the growth position. The Ca and TTIP fluxes varied less than 1% during the entire 30 minute growth period, ensuring that the cation fluxes were homogenous through the film thicknesses used. By fixing the Ca flux and systematically adjusting the TTIP flux ($p_{\text{TTIP}}$) over a range of $p_{\text{TTIP}} = (21.6 - 41.4) \times 10^{-8}$ Torr, the Ti:Ca cation ratio was controllably varied.

To identify the existence of a growth window, the out-of-plane $c$-axis lattice parameter of each film was determined from X-ray diffraction (XRD) by performing $2\theta$-$\omega$ scans of the 002$_p$ CaTiO$_3$ film peak, as shown in Figure 3-1. The XRD was collected using Cu $K\alpha_1$ radiation on a high-resolution Philips X-Pert Pro MRD diffractometer with a hybrid monochromator on the incident side and a triple axis/rocking curve attachment on the diffracted side. The subscript $p$ denotes the pseudocubic notation. The $c$-axis rapidly increased for Ca-rich (top) and Ti-rich films (bottom) due to lattice expansion caused by defect incorporation into the film, [8] providing a direct way to determine the edges of the stoichiometric growth window. Reciprocal space mapping of the 303$_p$ peak for a stoichiometric CaTiO$_3$ film revealed that the films were commensurately strained to the (001)LSAT substrates for the thicknesses grown here, as shown in Figure 3-2. The surface morphology of the films were determined by atomic force microscopy (AFM) imaging performed on a Bruker Icon instrument operated in peakforce tapping mode. The AFM images are shown in Figure 3-3, revealing that the film morphologies only changed slightly throughout the growth window, and there is no obvious distinction between the Ca-rich and the growth window films as seen from the AFM images. The growth windows films display atomically smooth surfaces with an average RMS roughness of ~0.3 nm, although no clear trend
in changing morphologies is seen throughout the growth window range. In contrast, Ti-rich films were much rougher (RMS ~1.0 nm) exhibiting surface morphologies similar to TiO$_2$ films grown by MBE using TTIP.[31]

During each film growth, time-dependent reflection high-energy electron diffraction (RHEED) intensity oscillations were recorded, as shown in Figure 3-4. The RHEED oscillations indicated a layer-by-layer growth mode, where the maxima corresponded to the completion of an individual CaTiO$_3$ unit cell layer.[32] The RHEED intensity profiles show characteristic features related to the type and degree of deviation from stoichiometric growth conditions. Stoichiometric films exhibited pronounced RHEED oscillations and sharp c(2×2) reconstructions that persisted throughout the entire growth period shown in Figure 3-5. Conversely, for films grown under Ca-rich and Ti-rich conditions the intensity oscillations quickly dampened out after a few minutes, and surfaces revealed a c(4×4) reconstruction for Ca-rich films, and no reconstruction for Ti-rich films.

The extracted c-axis values from the XRD scans in Figure 3-1 are plotted as a function of $p_{TTIP}$ in Figure 3-7(a). The smallest out-of-plane lattice parameter did not significantly vary from an average value of $c = (3.806±0.001)$ Å over a range of $Δp_{TTIP} = (26.6-36.5)×10^{-8}$ Torr, marking the boundaries of the CaTiO$_3$ growth window. The in-situ growth rate for each film was determined from the RHEED oscillation periods, plotted in Figure 3-7(b), which was in good agreement with the growth rate obtained from film thickness measurements extracted from Kiessig fringes around the 002$ _p$ peak in the XRD scans. The change in growth rate with increasing TTIP flux was constant and well within the experimental error for films grown inside the highlighted growth window range. Outside the growth window, a pronounced change in growth rate with $p_{TTIP}$ was found, attributed to the increased rate of defect incorporation. The constant lattice parameter and growth rate found inside the window range confirmed that excess
TTIP molecules arriving at the growth surface were not incorporated into the film and that a self-regulated growth kinetics was at play, enabling the stoichiometric CaTiO$_3$ films occurring for a range of cation flux ratios. This favorable growth mechanism is attributed to the high volatility of the TTIP molecules, which ultimately enabled a growth window at these temperatures.

Compositional analysis of the films was done using energy-dispersive X-ray spectroscopy (EDS) measurements taken on an FEI NanoSEM 600 with an accelerating voltage of 10 kV and a beam current of 1.4 nA using an Oxford X-Max Silicon Drift Detector with an 80 mm$^2$ detection area. The resulting intensities were compared to a standard CaTiO$_3$ bulk crystal from SurfaceNet GmbH. The spectra are shown in Figure 3-6 were analyzed to determine the Ti:Ca atomic percent ratio for each film in the series, and are plotted in Figure 3-7. The Ti:Ca ratio was closest to 1:1 within the growth window, and remained constant throughout the window range to within the error of the measurement. In the Ca-rich and Ti-rich regions, the film compositions rapidly deviated from ideal stoichiometry, which agrees with the expanded c-axis lattice constant and accelerated change in growth rate trends in the nonstoichiometric growth regimes. Defect types formed in nonstoichiometric CaTiO$_3$ films were directly observed in high-resolution transmission electron microscopy (HRTEM) as well as high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images. The samples were prepared in cross section for STEM by mechanical wedge polishing with an Allied Multiprep followed by ion milling at liquid nitrogen temperatures with a Fischione Model 1050. (courtesy of Everett Grimley and James LeBeau at NCSU) Prior to polishing the samples were capped with approximately 25 nm of Al to protect the films during sample preparation and to mitigate charging effects in the STEM. HAADF STEM was conducted on a probe corrected FEI Titan G2 60-300 kV system. The microscope was operated at 200 kV with an inner detector semi-angle of approximately 77 mrad and a probe convergence semi-angle of approximately 20 mrad. Beam currents were
approximately 80 pA for imaging. The plane-view cross section HRTEM images shown in Figure 3-8 reveal that the most Ti-rich film contains a considerable amount of defects and very large surface roughness, which is consistent with the AFM image for this film, whereas the stoichiometric film and Ca-rich are much smoother and do not show any observable defects throughout the film thickness. The HAADF STEM analysis show in Figure 3-9 revealed that CaO rocksalt layers were interspersed throughout the Ca-rich film (Figure 3-9(a)), and TiO$_x$ defect clusters in the Ti-rich film (Figure 3-9(e)). These defect types are expected for nonstoichiometric CaTiO$_3$ compositions according to phase diagram calculations,[33] and are similar to the defects observed for nonstoichiometric SrTiO$_3$ films.[8, 9] The STEM images for the stoichiometric CaTiO$_3$ films grown inside of the growth window, shown in Figure 3-9(b)-(d) did not show these defect inclusions even for the zoomed-in regions shown below in Figure 3-9.

Although the XRD results did not resolve any trends in the film lattice parameter inside the growth window, the EDS measurements revealed a slight change in the Ti:Ca ratio from ~ 0.985 to 1.017 ($\Delta$Ti:Ca = 0.032) throughout the entire growth window range of $\Delta$TTIP $\sim$ 10$\times$10$^{-8}$ Torr. The large error bars in the EDS measurements of $\pm 5\%$ are due to the very thin film thicknesses required to avoid strain relaxation in the films. If the error bars of the EDS measurements are considered, then $\Delta$Ti:Ca = 0.132. The control over the stoichiometry, which we call $\delta$Ti:Ca, afforded by the growth window, can be estimated by considering that for a fixed $p_{TTIP}$ pressure inside of the growth window (i.e. $p_{TTIP} = 31.5 \times 10^{-8}$ Torr), the fluctuation in the TTIP flux is $\delta p_{TTIP} \sim 0.6 \times 10^{-8}$ Torr ($\pm 1\%$). Using these values, the $\delta$Ti:Ca value for a fixed $p_{TTIP}$ pressure can be calculated as $\delta$Ti:Ca = ($\delta p_{TTIP}/\Delta p_{TTIP}$) $\times$ $\Delta$Ti:Ca, as shown in Figure 3-10. This gives a value of $\delta$Ti:Ca = 0.2 % (for $\Delta$Ti:Ca = 0.032), and $\delta$Ti:Ca = 0.8 % if the error bars in the EDS measurement are considered ($\Delta$Ti:Ca = 0.132). This level of stoichiometry control pinpoints the critical advantage of utilizing the self-regulated kinetics inside of a growth window coupled
with the presumption of a line compound. While the large error bars in the EDS measurements on very thin films makes it more difficult to strongly claim trends for the slightly increasing Ti:Ca ratio throughout the growth window range, it would be in agreement with the slight changes in the growth rate obtained from the RHEED oscillations and XRD thickness fringes. The impact of how the stoichiometric growth window affects the material properties is elucidated through temperature dependent nonlinear optical, and polarization measurements for the film series, which is discussed in the next section.

3.4 Optical second harmonic generation characterization

The low temperature polar phase symmetry of the strained CaTiO$_3$ films were determined through optical second harmonic generation (SHG) polarimetry analysis. Recall that SHG is a nonlinear optical process where light at frequency $\omega$ is converted into light at frequency $2\omega$, which can only occur if a material is non-centrosymmetric (i.e. lacks inversion symmetry), as is the case for a ferroelectric. A schematic of the experimental SHG transmission setup is depicted in Figure 3-11(a), showing the geometrical relation between the fundamental electric field vector of light ($E^\omega$) with respect to the film/substrate orientation and the direction of the generated second harmonic field vector ($E^{2\omega}$). The SHG experiments were performed using a femtosecond pulsed laser beam ($\lambda=800$ nm, 80 fs pulse width, 2 kHz repetition rate) which was generated from a Coherent Libra Ti:sapphire amplifier system. The fundamental beam power used for these experiments was 3.0 W/cm$^2$ with a beam waist diameter of 50 $\mu$m at the film surface. The samples were mounted onto a Cu finger using silver paste, and cooled inside of a Janis cryogenic sample holder to $T=77$ K using liquid nitrogen. The sample temperature was monitored and controlled using a LakeShore temperature controller unit. The SHG intensity was detected in the
plane, perpendicular to the [010]p rotation axis used to change the angle of incidence, $\theta$. In general, the SHG intensity can be described as,

$$I_{2\omega ||} = (I_{\omega})^2 \frac{(2\pi L / \lambda_\omega)^2}{\Theta_f} (d_{\text{eff}}^f)^2 \Theta_f,$$

where $L$ is the film thickness, $\lambda_\omega$ and $I_\omega$ are the wavelength and intensity of the fundamental laser beam, respectively, and the $\Theta_f$ term accounts for the transmittance, reflectance, and absorption of the fundamental and SHG fields in the film, which is explicitly defined in Appendix A. The $d_{\text{eff}}^f$ term is the effective $d$ coefficient, which is dependent on the form of the $d_{ij\alpha}$ tensor and the orientation of the fundamental electric field with respect to the crystal physics axes of the film.

Figure 3-11(b) shows SHG polarimetry data taken for a stoichiometric CaTiO$_3$ film ($p_{\text{TTIP}} = 31.5\times10^{-8}$ Torr) measured at $T = 77$ K. The sample was rotated about the [010]p axis at several different $\theta$ values to measure the transmitted SHG intensity for a fixed $E_\omega$ direction of $\phi=0^\circ$. The three top insets in Figure 3-11(b) are polar plots showing the SHG intensities measured at three fixed angles of incidence, $\theta = -45^\circ$, 0°, and 45° (from left-to-right), where $\phi$ was rotated by 360°. SHG modeling analysis [34, 35] of the polarimetry data was performed using the methods described in Appendix A. A monoclinic point group symmetry ($m$) was assumed where the monoclinic domain axes are defined as $z_1 = [001]_p$, $z_2 = [1-10]_p$, and $z_3 = [110]_p$ with respect to the pseudo-cubic orientation. The nonlinear optical $d_{ij}$ tensor coefficient matrix for a monoclinic point group symmetry is,

$$d_{ij} = \begin{pmatrix}
    d_{11} & d_{12} & d_{13} & 0 & d_{15} & 0 \\
    0 & 0 & 0 & d_{24} & 0 & d_{26} \\
    d_{31} & d_{32} & d_{33} & 0 & d_{35} & 0
\end{pmatrix},$$

Eq. 3-2

The general $d_{ij}$ matrix for $m$ point group symmetry was transformed into the crystal physics axes of the two different monoclinic mirror planes (i.e. the two different domain variants, $A_1$ and $A_2$),
which have the relationships: $A_1 \rightarrow (z_1=[001]_p, z_2=[1-10]_p, z_3=[110]_p)$, and $A_2 \rightarrow (z_1=[001]_p, z_2=[110]_p, z_3=[-110]_p)$, an expression for the resulting $d'_{af}$ term in Eq. 3-1 can be derived,

$$d_{af}' / d_{15} = [t_{af}]^2 \cos^2 \phi [\]
\begin{align*}
[A_{21} K_{33} \cos \theta_{2\omega} + (A_{21} K_{13} - K_{12}) \sin \theta_{2\omega}] \cos^2 \theta_{\omega} \\
+ [A_{21} K_{33} \cos \theta_{2\omega} - (A_{21} - 1) K_{11} \sin \theta_{2\omega}] \sin^2 \theta_{\omega} \\
- [(A_{21} K_{31} + K_{26}) \cos \theta_{2\omega} + A_{21} \sin \theta_{2\omega}] \sin 2\theta_{\omega} \\
+ [t_{af}]^2 \sin^2 \phi [A_{21} K_{32} \cos \theta_{2\omega} - (A_{21} K_{12} + K_{13}) \sin 2\theta_{\omega}] \\
+ [t_{af}][t_{af}]^* \sin 2\phi [K_{24} \cos \theta_{2\omega} \cos \theta_{\omega} + \sin \theta_{2\omega} \sin \theta_{\omega}] \tag{3-3}
\end{align*}$$

where $t_{af}$ and $t_{af}^*$ are the standard transmission ($t$) Fresnel coefficients for $p$-polarized (||) and $s$-polarized ($\perp$) light as well as the angles of refraction ($\theta_{\omega}$ and $\theta_{2\omega}$) according to Snell’s law, and are defined in Appendix A. The $K_{ij}=d_j/d_{15}$ parameters as well as the domain area fraction ratio, $A_{21}=A_2/A_1$, were used to fit the SHG polarimetry tilt scan and polar plot data simultaneously.

From the analysis, and the low temperature polar point group symmetry of CaTiO$_3$ agreed well with the multi-domain monoclinic model according to Eq. 3-3, which contains both in-plane and out-of-plane polarization components. Note that assuming an orthorhombic $mm2$ point group symmetry would only allow for symmetric tilt scans about normal incidence, which is not observed for the CaTiO$_3$ film at $T=77$ K. This SHG analysis is in agreement with the predicted monoclinic phase expected to exist at lower temperatures of CaTiO$_3$ for low tensile strain states.[28]

Figure 3-12 shows the temperature dependence of the SHG intensity for the entire film series ($\theta=0^\circ$, $\phi=0^\circ$). SHG is sensitive to the existence of nanopolar regions which can persist above the ferroelectric-to-paraelectric transition temperature and give rise to a residual SHG signal. Therefore, the SHG determined transition temperature is more indicative of the Burns transition temperature ($T_B$) where nanopolar regions disappear.[36] For films grown within the growth window, a transition temperature of $T_B = (192\pm10)$ K was found, which remained high
even for the films with small deviation from ideal stoichiometry (i.e. at the edges of the growth window region) and then drastically decreased for more pronounced deviations from ideal stoichiometry. While the presence of SHG signal indicates that CaTiO$_3$ is indeed polar, electric field switching of the polarization is required to unambiguously identify ferroelectricity.

3.5 Electrical characterization of strained CaTiO$_3$ films

Further analysis of the role of stoichiometry on the electric properties for tensile strained CaTiO$_3$ films was obtained through polarization versus applied electric field (P-E) hysteresis loops, as well as temperature and frequency dependent dielectric measurements to determine the ferroelectric-paraelectric transition temperatures. Prior to the electrical measurements, the films were annealed at 600 °C under O$_2$ gas flow for 1 hour. After annealing, interdigitated electrodes (IDEs) of 20 nm Cr/100 nm Au were deposited on the film surfaces with the following dimensions: finger length = 1000 μm, width = 10 μm, and gap spacing = 10 μm. The dielectric permittivity and loss tangents were measured using an Agilent E4980A high precision LCR meter with a Lake Shore 332 temperature controller. The probe tips used were Beryllium Copper with a 25 μm tip radius. Figure 3-13 shows P-E loops measured at $T = 77$ K using a frequency of 1 kHz for the entire stoichiometric film series. The paraelectric contribution in the P-E loops from the LSAT substrate was removed by subtracting the linear slope from the measured polarization determined at electric field values exceeding the saturation field. Within the growth window, the saturation polarization remained high and independent of p$_{TTIP}$ with clear switching of the polarization hysteresis. With increasing deviation from ideal stoichiometry the P-E loops diminished in size and eventually ferroelectric hysteresis completely disappeared, as shown on the bottom and top of Figure 3-13 for Ca-rich and Ti-rich films, respectively.
The temperature and frequency dependence of the in-plane dielectric constant, $K_{11}$, and loss tangent, tan(δ), are plotted in Figure 3-14(a) and Figure 3-14(b), respectively. The measurements were performed over a temperature range of $T=77-300K$ and a frequency range of 1 kHz - 1 MHz. The $T_C$ was determined from the maximum value of $K_{11}(T)$, which was highest for films inside the growth window. The $T_C$ decreased for Ca-rich and Ti-rich films, and the peak in $K_{11}(T)$ became much broader. Broadening of $K_{11}(T)$ in ferroelectrics is an indicator typical of relaxor-like behavior, attributed to impurities or point defects, such as oxygen vacancies or anti-site defects.[37] This broadening has also been observed for nonstoichiometric tensile strained ferroelectric SrTiO$_3$ films and was related to Sr-rich and Ti-rich defects.[10] Therefore, broadening of the peak in $K_{11}(T)$ for non-stoichiometric CaTiO$_3$ films compared to those grown within the stoichiometric growth window is expected, and is likely due to CaO rocksalt layers in the Ca-rich films and TiO$_x$ regions in the Ti-rich films, as evidenced from the STEM images. Furthermore, the frequency dependence of the films is small but non-zero, also indicating that these films have some relaxor-like ferroelectric behavior. Note that the condensing of $K_{11}$ and tan(δ) curves at both 1 kHz and 1 MHz after the onset of the ferroelectric-to-paraelectric transition (i.e. $K_{11}^{\text{max}}$) indicates that there are negligible space charges in the films which would be associated with oxygen vacancy clusters in the films. Therefore, the annealed films contained very good oxygen stoichiometry. Figure 3-15 shows Curie-Weiss fits of the temperature dependent dielectric constant. The Curie constants extracted from the fits for stoichiometric CaTiO$_3$ films grown inside the window ranged from $(0.9-1.7)\times10^5$ °C, which are typical values for a displacive ferroelectric material.[38] The fact that there is not a sharp discontinuity observed in $K_{11}(T)$ at the transition temperatures indicates that strained CaTiO$_3$ films possess mixed relaxor-like and displacive-like characteristics, which is consistent with the slight frequency dependence of $K_{11}$ and tan(δ) within the ferroelectric phase.
Figure 3-16(a) compiles the transition temperatures from SHG and dielectric characterization for all films in the stoichiometric series. Stoichiometric films had an average $T_C = (175\pm5) \text{ K}$, which is nearly 35 degrees higher than the value reported in Ref.[28]. For Ca-rich and Ti-rich films a pronounced reduction of $T_C$ was found. Defect incorporation into the films destabilized the ferroelectric order even for small deviations from ideal stoichiometry, which was also easily seen by the lattice expansion of the $c$-axis as measured by XRD. No correlation between $T_C$ and the Ti:Ca ratio or growth rate inside the growth window was found, as seen from Figure 3-17.

The transition temperatures extracted from the SHG measurements are plotted in Figure 3-16(a) for comparison, which were in good agreement with the values obtained from dielectric measurements, albeit shifted to higher temperatures. The small, but noticeable increase of the transition temperature was more pronounced towards the edges of the self-regulated growth window as the slight deviation from ideal stoichiometry leads to a larger volume of defect-dipoles in the CaTiO$_3$ film which can also give rise to sizeable SHG signals even after the ferroelectric transition. The impact of stoichiometry was also reflected in the saturation polarization. Stoichiometric films grown inside the window had an average $P_{\text{Sat}} = (8.7 \pm 1.0) \mu \text{C/cm}^2$ as shown in Figure 3-16(b), whereas the values were reduced for slightly nonstoichiometric films. The polarization values were very consistent throughout the growth window range, demonstrating that ferroelectric properties are optimal inside of the growth window. Figure 3-16(c)-(d) show the $K_{11}^{\text{max}}$ and $\tan(\delta)^{\text{max}}$ values, respectively, of each film in the series, displaying slightly less consistent values throughout the window range, though these variations in $K_{11}^{\text{max}}$ and $\tan(\delta)^{\text{max}}$ are due to slightly varying area sizes of the deposited top electrodes. The low dielectric losses of $<3\%$ at all temperatures indicated that the films contained negligible space charge contribution.
3.6 Conclusions

In summary, these results demonstrate that stoichiometry control is a requirement for stabilizing theoretically predicted strain-enabled ferroelectric ground states in oxides. The self-regulated adsorption controlled growth window found in the CaTiO$_3$ system resulted in superior structural and physical properties and found to be independent of the flux ratio of TTIP and Ca species within the growth window range. Deviations from ideal stoichiometry found outside of this growth window completely masked and suppressed the ferroelectric ordering. An order of magnitude improvement in the control of the cation ratio incorporated into the film overcomes existing limits of composition control in commonly employed thin film growth techniques. Given the significant interest and research activity today in the prediction and exploration of strain-enabled functionalities in complex oxide materials precise stoichiometry in strain-stabilized states of matter is demanded, yet sometimes an unsatisfactorily accomplished necessity. This study highlights a missing piece of the puzzle needed to achieve strain-enabled properties predicted by theory. A composition control in films which leaves the targeted functional properties unaffected allows experimental confirmation of theoretical predictions beyond the doubts that unintentional extrinsic effects may either have suppressed the predicted strain-enabled properties or may solely be the cause of the measured response. Untangling the effect of strain and stoichiometry on functional properties, as demonstrated here, will accelerate both, fundamental discoveries to be made in the large materials design space, as well as utilization of strain-stabilized phenomena in future devices. While this study focused on ferroelectric and dielectric properties, it could motivate the large community of complex oxide researchers to seek out similar effects and property enhancements in relation to magnetism, multiferroicity, as well as correlated electronic effects such as metal-insulator transitions, and superconductivity.[39-41]
Figure 3-1: X-ray diffraction 2θ-ω scans around the 002\textsubscript{p} CaTiO\textsubscript{3} film peaks (indicated by arrows) at varying \( p_{\text{TTIP}} \) pressures shown on the right axis. The Ca-rich (bottom) and Ti-rich (top) films are labeled and colored green and red, respectively. The stoichiometric growth window range are indicated on the right side and are shown as blue curves in the XRD scans which yield the largest 2θ film peak values over the range of \( p_{\text{TTIP}} \) values highlighted. The 002 LSAT substrate peak is shown with an asterisk (*).
Figure 3-2: X-ray reciprocal space map around the 303_p peak for a CaTiO_3 film in the middle of the growth window (p_{TTIP} = 31.5\times10^{-8} \text{Torr}). The intensity map is plotted in reciprocal lattice units (r.l.u.) of the LSAT substrate peak located at H=L=3.00. The 303_p CaTiO_3 peak has the same in-plane position along H indicating that the film is coherently strained to the (001)LSAT substrate.
Figure 3-3: Atomic force microscopy (AFM) images for the entire CaTiO$_3$ film series showing the change in surface morphology throughout the stoichiometric growth window indicated by the blue outline, as well as Ca-rich (left) and Ti-rich (right) films. The AFM $z$-height scale bar is in nm and shown on the right side of each image. The $p_{TTIP}$ ($\times 10^{-8}$ Torr) values are shown on the middle axis for each image.
Figure 3-4: Reflection high energy electron diffraction (RHEED) intensity oscillations of the 01 reflection spot recorded along the <110> azimuth from the diffraction patterns shown on the right, where the region of interest being shown is indicated by the dashed white rectangles. The Ca-rich (bottom) and Ti-rich (top) films are labeled with respect to the stoichiometric films (middle), and the $p_{\text{TTIP}}$ values given above each curve on the right side of the panel. Ca-rich films showed c(4x4) reconstructions, indicated by the vertical white dashed arrows, stoichiometric films showed c(2x2) reconstructions, and Ti-rich films showed no reconstructions in the RHEED images.
Figure 3-5: Post-growth RHEED images taken inside of the MBE chamber at $T=200$ °C for each film in the series along the $<100>$ and $<110>$ azimuth as indicated for the images on the left. The most Ca-rich films (highlighted in the green boxed area) showed c(4x4) reconstructions, whereas stoichiometric films showed c(2x2) reconstructions, as indicated by the dashed white arrows. Ti-rich films did not show any reconstructions, with streaky diffraction spots indicating rough surfaces for these films.
Figure 3-6: Energy-dispersive X-ray spectroscopy (EDS) spectra for the CaTiO$_3$ stoichiometric film series. The top panel shows EDS spectra for a bulk CTO reference sample with the Ca K$_\alpha1$, Ca K$_\beta$, and the Ti K$_\alpha1$ peaks labeled on the top panel for bulk CTO, with the dashed vertical lines running through each panel below showing the expected Cad n Ti peaks. The peak on the far right of the spectra is from the La L$_\beta$ of the LSAT substrate. The calculated Ti:Ca ratios from the Ca K$_\alpha1$ and the Ti K$_\alpha1$ peaks are labeled in each panel. Ca-rich films are shown at the bottom (green), Ti-rich films at the top (red), separated by films grown inside the growth window (blue). The error bar for these measurements is ±0.05.
Figure 3-7: (a) Out-of-plane $c$-axis lattice parameter extracted from on-axis XRD measurements. (b) The growth rate determined from RHEED intensity oscillations (filled circles) and XRD thickness fringes (open circles). (c) Ti:Ca atomic percent ratios measured by EDS. The growth window range is highlighted in blue on top, with the Ca-rich and Ti-rich regions labeled. The horizontal shaded orange area with a dashed line in each panel indicates the range of values observed within the growth window including the error bars of the measurement.
Figure 3-8: Plane-view cross-section high-resolution transmission electron microscopy (HRTEM) images for (a) Ti-rich, (b) stoichiometric, and (c) Ca-rich CaTiO$_3$ films. The corresponding Ti:Ca ratios are shown on the top right of each image, and the darker LSAT substrate region is labeled in (c) along with the scale bar shown which applies to all images.
Figure 3-9: HAADF STEM images for (a) Ca-rich, (b)-(d) stoichiometric growth window, and (e) Ti-rich CaTiO₃ films. Below each image are zoomed-in regions indicated by the dashed white rectangles in the top panels. The CaO rocksalt layers in the Ca-rich film are indicated in the bottom panel of (a) by vertical arrows, and a TiOₓ defect cluster is shown in the bottom panel of (c) by the dashed white circle. The corresponding Ti:Ca atomic percent ratios are labeled below each image. The contrast and intensity of each STEM image was adjusted to emphasize the CaTiO₃ features. The scale bar in the bottom panel of (e) applies to all images. The LSAT substrate region at the bottom of the film is shown in the top panel of (a).
Figure 3-10: The atomic percent ratios of Ti:Ca determined from EDS measurements are plotted as a function of $p_{\text{TTIP}}$. The total change in Ti:Ca is $\Delta \text{Ti:Ca} = 0.032$, and the total change in the TTIP flux throughout the window is $\Delta p_{\text{TTIP}} \approx 10 \times 10^{-8}$ Torr. Knowing that the fluctuation in the TTIP flux is $\delta p_{\text{TTIP}} = 0.6 \times 10^{-8}$ Torr, the error in the Ti:Ca ratio is $\delta \text{Ti:Ca} = 0.002$ inside the growth window, highlighted in red. If the error bars are considered, then $\Delta \text{Ti:Ca} = 0.132$ and $\delta \text{Ti:Ca} = 0.008$, highlighted in blue. Note that only the lowest and highest error bars are shown for visual clarity.
Figure 3-11: (a) Experimental SHG geometry showing the linear polarized fundamental field ($E_\omega$) at frequency $\omega$ rotated by an angle $\phi$ and incident to the film normal by an angle $\theta$. The generated second harmonic ($E_{2\omega}$) is detected parallel to the plane of incidence. The pseudo-cubic axes of the film are labeled. (b) SHG intensity as a function of $\theta$ taken at $T=77$ K using a fixed input polarization of $\phi = 0^\circ$. Insets show polar plots taken at fixed angles of incidence $\theta$ and continuously scanning $\phi$ $360^\circ$. The red line is the calculated SHG intensity using a monoclinic point group model ($m$).
Figure 3-12: Temperature dependent SHG scans ($\theta=0^\circ$, $\phi=0^\circ$) of the stoichiometric series with $\rho_{\text{TTIP}}$ values labeled on the top right axis. The SHG transition temperatures, $T_B$, of CaTiO$_3$ are indicated by vertical arrows, the black curve is the SHG intensity of the (001)LSAT substrate. The transition temperature is taken as the intersection of the SHG signal from the substrate and the film.
Figure 3-13: The polarization ($P$) versus electric ($E$)-field ($P$-$E$ loop) applied along [100]$_p$ direction at cryogenic temperature, $T=77$ K, and at a frequency of 1 kHz, for the entire stoichiometric CaTiO$_3$ series with the TTIP flux values labeled on the right axis. The growth window range is highlighted by the blue shaded area on the right. The P-E loops have larger areas for stoichiometric films. Ca-rich (bottom) and Ti-rich (top) films showed linear dielectric behavior with no switching at $T=77$K.
Figure 3-14: The temperature ($T=77-300$ K) and frequency (1 kHz – 1 MHz) dependence of (a) the in-plane dielectric constant, $K_{11}$, and (b) dielectric loss, $\tan(\delta)$. The $T_C$ is determined from the peak in $K_{11}(T)$ and indicated by the dashed black line in both (a) and (b). The temperature range of the ferroelectric phase is highlighted by the shaded areas under each curve. The $P_{TTIP}$ values are labeled on the right axis of (b) and also apply to (a), with the stoichiometric growth window region highlighted in blue.
Figure 3-15: Inverse dielectric constant, $10^4/K_{11}$, for each film grown at $p_{TTIP}$ values shown on the right axis. Curie-Weiss fits are shown as the dotted black lines, with the extracted Curie constants shown on the far right axis.
Figure 3-16:  (a) The ferroelectric transition temperature ($T$) as a function of $p_{TTIP}$ measured from dielectric (filled diamond) and SHG (open circle) experiments. The Ca-rich, growth window, and Ti-rich regions are labeled on top. (b) Saturation polarization, $P_s$, (c), maximum dielectric constant, $K_{11}^{\text{max}}$ and (d), maximum dielectric loss $\tan(\delta)^{\text{max}}$ as a function of $p_{TTIP}$. The average values inside of the growth window are highlighted by the horizontal orange bars with dotted black lines.
Figure 3-17: (a) $T_c$ vs. Ti:Ca and (b), $T_c$ vs growth rate for the CaTiO$_3$ series. The Ca-rich, and Ti-rich sample are labeled, and the growth window area is highlighted in blue. There is no obvious trend of $T_c$ versus either Ti:Ca or growth rate within the stoichiometric growth window range.
3.8 References


Chapter 4

Strain-engineering polar properties in CaTiO\(_3\)

4.1 Abstract

The utility of using a growth window of CaTiO\(_3\) is demonstrated by constructing a series of strained CaTiO\(_3\) films on several different substrate materials in order to induce varying degrees of compressive and tensile strains to map out the effects of strain on the ferroelectric properties of CaTiO\(_3\). While theory predicts that compressive strains up to only 2% result in out-of-plane polarization and below room temperature ferroelectric transitions, compressive strained CaTiO\(_3\) films show polar phenomenon above room temperature with polar transitions for CaTiO\(_3\)/(001)LSAO and CaTiO\(_3\)/(100)LaAlO\(_3\) films at \(T > 600\) K, which is nearly 600 degrees above what theory currently predicts. For tensile strained CaTiO\(_3\)/(110)DyScO\(_3\), a dominantly in-plane polar phase is observed, with a ferroelectric transition at \(T\approx 260\) K which is much closer to what theory predicts. This chapter highlights the potential of strain-engineering polarization in CaTiO\(_3\) films, where unexpectedly large transition temperatures for compressive strained CaTiO\(_3\) suggest that this material could prove useful for high-temperature sensor applications.
4.2 Constructing the strained CaTiO$_3$ series

Using the optical growth window conditions of CaTiO$_3$/LSAT samples discussed in Chapter 3 ($T_{\text{sub}} = 900$ °C, $p_{O_2}=1\times10^{-7}$ Torr, $\Phi_{\text{Ca}}=2.0\times10^{11}$ atoms/cm$^2$/s, $p_{\text{TTIP}} = 31.5\times10^{-8}$ Torr), a series of ~ 14 nm thick CaTiO$_3$ films were grown on several different substrate crystals with different in-plane lattice parameters; (110) YAO, (001) LaSrAlO$_4$ (LSAO), (100) LaAlO$_3$ (LAO), (001) (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT), (100) SrTiO$_3$ (STO), and (110) DyScO$_3$ (DSO). These substrates induce in-plane biaxial strains of (-2.76, -1.68, -0.76, +1.26, +2.23, and +3.23) %, respectively. Figure 4-1(a) shows in-situ reflection high-energy electron diffraction (RHEED) intensity recorded from the 10 streak along the <110> azimuth of each film in the strain series. The RHEED oscillations patterns vary throughout the strained series and are strongest for the tensile strained CaTiO$_3$/LSAT and compressive strained (001)LSAO films, indicating layer-by-layer growth modes for these samples. For larger strain states ($|\epsilon| > 2\%$), i.e. CaTiO$_3$ (CTO) films grown on (110)DSO, (100)STO, and (110)YAO, RHEED oscillations are very weak or do not occur, and the RHEED intensity changes dramatically throughout deposition, suggesting that these films have very rough surfaces and may have undergone structural relaxation.

The strain-induced lattice relaxation was assessed by measuring the in-situ change of in-plane lattice parameter ($\Delta a_{||}$) during the growth of each film. This was done by monitoring the distance between the 10 and -10 diffraction spots (along the <110> azimuth) with respect to the underlying substrate, as shown in Figure 4-1(b). For compressively strained CTO/YAO, during the initial ~2 minutes of growth, the in-plane lattice parameter of the film is equal to the YAO in-plane lattice parameter ($\Delta a_{||} \approx 0$), after which $\Delta a_{||}$ quickly increases to $\Delta a_{||} \approx 0.2$ Å, which is nearly equal to the difference of the in-plane lattice parameter between bulk CTO ($a_{||}=3.822$ Å) and bulk YAO ($a_{||}=3.685$ Å); $\Delta a_{||}=0.137$ Å, indicating that the film has fully relaxed after ~10 monolayers.
For the large tensile strains of CTO/DSO and CTO/STO, the in-plane lattice also changes rapidly after growth was initiated, and the films seem to fully relax to bulk after only 4-6 minutes of growth (~10 monolayers).

For lesser strains, such as CTO/LSAT, CTO/LAO, and CTO/LSAO, the films exhibit oscillations in $\Delta a||$ with time, which has been observed for other thin film materials such as SrTiO$_3$, BaTiO$_3$, GaAs, and various metals,[1-6] and is attributed to ‘breathing’ of the unit-cell layer during layer-by-layer growth. When a unit cell monolayer has been completed, each unit cell will be completely surrounded by neighboring unit cells, effectively clamping them to be equal to the in-plane lattice parameter of the underlying layers. When a unit-cell layer is half-completed, the lattice parameter can expand or contract in-plane in order to minimize elastic strain energy since there are no other adjacent unit-cells to clamp it. Thus the in-plane lattice parameter can oscillate during layer-by-layer growth mode. This is observed for compressive strained CTO/LSAO and CTO/LAO, as well as tensile strained CTO/LSAT, as shown in Figure 4-1(b). However, these oscillations are absent or very weak in the highly strained films. The RHEED oscillations and the in-plane lattice oscillations are strongly dependent on the strain state as shown in Figure 4-2(a) and (b), for compressive CTO/LSAT and tensile CTO/LSAO, respectively. Compressive strain results in the RHEED and in-plane lattice oscillations to be out-of-phase (Figure 4-2(a)), whereas in-phase oscillations will ensue for tensile strain (Figure 4-2(b)). This is because under compressive strain, the in-plane lattice for a half-completed layer will tend to expand, whereas under tensile strain, the in-plane lattice parameter will contract for a half-completed layer.[3]

Figure 4-3 shows post-growth (~ 200 °C) RHEED images taken for each film along the $<100>$ and $<110>$ azimuths. Both compressive and tensile strained films show c(2x2) reconstructions along $<110>$, however compressive strain results in weak 1$^{st}$ and 2$^{nd}$ order Laue rings, whereas tensile strained films show much stronger Laue rings. Along the $<100>$, there are
less discernable strain-related features in the RHEED images, however compressive strain seems to result in more amounts of multilevel stepped surfaces and possible 3D island growth as indicated by the modulated streaks and multiple spots along the streaks.[7]

4.3 Structural analysis of strained CaTiO$_3$ series

The out-of-plane lattice parameter of each CTO film in the strain series was measured from X-ray diffraction (XRD) 2θ-ω scans of the 002 CTO film peaks, as shown in Figure 4-4. The film peaks deviate further from the bulk CTO value (show as the vertical dashed line in Figure 4-4) with increasing strain, however for CTO/YAO and CTO/DSO, the film peaks start to shift back towards bulk CTO indicating severe relaxation has occurred. The film surface morphologies were investigated by atomic force microscopy (AFM) images shown in Figure 4-5. For low strains of CTO/LSAO and CTO/LSAT, the films exhibit single unit cell high step terraces and small root mean square (RMS) roughness values of 0.16 nm and 0.19 nm, respectively. However, delamination events are observed on the CTO/LSAT film surface; whether these holes are induced by the substrate quality or are a result of strain is not clear, and requires further experiments to determine the cause of this. With increasing compressive strain, the surfaces remain relatively smooth for CTO/LSAO and CTO/YAO, although step terraces are not observed in these films. For increased tensile strains, the surface morphologies dramatically change as shown for CTO/STO and CTO/DSO films in Figure 4-5. For CTO/STO films, the surface is much rougher (RMS=0.36 nm) and exhibits circular indentations scattered throughout the surface, which is a strong indication of relaxation. The roughest film surface is observed for CTO/DSO (RMS=0.50 nm) which exhibits very long overlapping rectangular shaped islands along the [100] and [010] directions, which has also been observed for other highly tensile strained oxide thin film materials.[8] Therefore, larger tensile strains are deleterious for surface
morphology features of CTO, whereas compressive strain leads to smooth surfaces. Large area AFM scans are show in Figure 4-6(a) and (b) for CTO/YAO and CTO/DSO, respectively, revealing large cracks in the films surfaces, which readily occurs for tensile strained oxide thin film materials,[9] and is in agreement with the lattice relaxation observed from the RHEED and XRD analysis for the thickness grown here.

The structural quality of compressively strained CTO/LSAO was done using synchrotron-source X-ray diffraction characterization. The out-of-plane lattice parameter for CTO/LSAO was determined to be $c = (3.874\pm0.001)$ Å as measured from the from the 20-0 scan of the 001 CTO film peak about the 004 LSAO substrate peak shown in Figure 4-7(a), and the film thickness was determined to be $\sim 14$ nm from the Kiessig fringes. The in-plane lattice parameter of the film was equal to the substrate ($a = 3.754$ Å) as evidenced by reciprocal space mapping (RSM) of the off-axis 102 CTO film peak about the 106 LSAO substrate peak as shown in Figure 4-7(b). This gives a $c/a$ ratio of $\sim 1.03$, which is comparable to the $c/a$ ratios of ferroelectric BaTiO$_3$ ($c/a = 1.01$) and PbTiO$_3$ ($c/a = 1.06$).[10, 11] However, the 14 nm thick CTO/LSAO film seems to be just on the brink of relaxation since the 102 CTO film diffraction peak is slightly distorted and shifted towards a larger in-plane lattice value. The slight film relaxation is also discerned from the $\omega$-scan rocking curves of the 001 CTO and 002 LSAO peaks shown in Figure 4-7(c), which yield full-width half-maximum (FWHM) values of 36 arcsec and 30 arcsec for the film and substrate, respectively, where the slightly larger FWHM of the film peak indicates small relaxation. The chemical composition of the CTO/LSAO film was measured using energy dispersive X-ray spectroscopy (EDS). A single crystal CTO substrate sample was used as the reference for the EDS spectra measurements as described in Chapter 3. Figure 4-7(d) shows EDS spectra of a bulk CTO crystal as well as spectra taken from three different spots (1-3) of the CTO/LSAO film, which yielded Ti:Ca atomic percent ratios of (0.99, 1.00, and 1.01),
revealing that indeed a ~1:1 Ti:Ca stoichiometry ratio was maintained for the film grown inside of the stoichiometric growth window conditions.

Figure 4-8 shows a STEM HAADF image for the 14 nm thick CTO/LSAO film, where no obvious signs of defects are observed, which is in agreement with the EDS measurements suggesting that the film is nominally stoichiometric. Although preliminary analysis of the STEM image did not reveal displacements above the error of the measurement (~10 pm) between the Ca cations with respect to the Ti cations, further experiments are needed in order to image the O atoms in order to confirm a net polar displacement in the CTO film from STEM analysis for this sample. Furthermore, the interface between the CTO film and the LSAO substrate shows a different type of stacking sequence compared to the underlying bulk layers which may suggest that there is some modification of the substrate surface after thin film growth. Whether this is induced by heating the substrate to high growth temperatures inside of the vacuum chamber or due to chemical reactions between the CTO film and the substrate is unclear. However, the STEM image reveals an overall good structural quality of the strained CTO film throughout the entire thickness.

4.4 Probing polar phases of strained CaTiO₃ film series using SHG

In the next step, optical second harmonic generation (SHG) polarimetry characterization techniques were used to probe the strain-induced polar phases of the CTO strain series. The substrate sides of the samples were polished using a diamond slurry solution, and were mounted inside of a vacuum pumped Janis cryostat and cooled to liquid nitrogen temperatures. Low temperature ($T=77$ K) SHG tilt scans and polar plots for the strain series are show in Figure 4-8 (a) and (b), respectively. The power density of the laser beam on each sample was fixed at ~ 3.0 W/cm². For compressive strained CTO/YAO, CTO/LSAO, and CTO/LAO, the samples show
dominantly out-of-plane polarization as indicated by no SHG signal at normal incidence, and the symmetric tilt scans and 2-lobed polar plots. The CTO/LAO film shows signs of monoclinicity as indicated by the rotated polar plots whose maximum values lie somewhere in-between the [100] and [010] direction. For tensile strained CTO/LSAT, the film shows an asymmetric tilt scan profile with non-zero SHG signal at normal incidence, suggesting that the polarization is likely in the plane made between the <110> and <111> directions, which is in agreement with the results presented in Chapter 3. For the highly tensile strained CTO/DSO, the sample shows dominantly in-plane polarization which is determined by the nearly symmetric tilt scan with maximum signal at normal incidence, and the circular polar plots. The asymmetry of the CTO/DSO tilt scan indicates the film is slightly monoclinic, where the polarization is tilted away from the [110] direction towards the [001] direction. Note that the CTO/STO sample was not measured here, as the substrate showed considerable oxygen vacancy concentrations as indicated by a blue color of the substrate.[12] Although a simple annealing of this sample could considerably decrease the oxygen vacancy concentration, the expected strain-induced ferroelectric transition is not expected to be above room temperature, and this sample was not studied further here.

The samples were then heated from liquid nitrogen temperature ($T=77$ K) too room temperature at a ramp rate of ~ 5 K/minute while measuring the transmitted SHG intensity, as shown in Figure 4-9. The tensile strained CTO/LSAT and CTO/DSO show a continuous decrease in the SHG intensity which reached a minimum value at temperatures of $T_{DSO} \approx 245$ K and $T_{LSAT} \approx 180$ K, indicating the expected transition from a polar phase to a non-polar phase. The SHG intensity from the DSO and LSAT substrates are also shown as black lines, which represent the signal noise-floor for these experiments. These transition values are close to what theory predicts.[13] For the compressive strained films, the SHG intensity persists up to room temperature, with signals that are much larger than the substrate reference materials, indicating
that the polar transitions are higher than what theory predicts.[13] Room temperature SHG polarimetry analysis was performed on the compressively strained CTO films, as shown in Figure 4-11. The SHG tilt scans were performed by rocking the sample by $\theta \sim \pm 60^\circ$ about the [010] axis and continuously measuring the SHG intensity along the plane of incidence with the input polarization of the fundamental fixed at $\phi=0^\circ$. The SHG polar plots were taken at fixed angles of $\theta = (\pm 45^\circ, 0^\circ, +45^\circ)$ and measuring the SHG intensity along the plane of incidence as $\phi$ was rotated $360^\circ$. The room temperature SHG polarimetry data for these samples are extremely similar to the low temperature SHG data. The compressive strained CTO films show dominantly out-of-plane polarization. The CTO/LSAO sample shows very symmetric tilt scans and polar plots, indicating that the polar symmetry is tetragonal 4mm. However, the asymmetric tilt scans for CTO/LAO and CTO/YAO indicate that the polar symmetry is not tetragonal 4mm as theory would predict, but most likely monoclinic (m) where the polarization tilts away from the [001] direction. In order to fit the SHG polarimetry data, a multi-domain monoclinic model was assumed for CTO/LAO and CTO/YAO where the monoclinic mirror planes (m) along (110) and (-110), and a tetragonal 4mm model was assumed for the CTO/LSAO sample with the polar direction along [001]. On the right side of Figure 4-11, schematics of the polar symmetry directions are provided with respect to the film/substrate geometry that was used for the SHG fitting analysis.

The general $d_{ij}$ matrix for the m point group symmetry was transformed into the film axes with the two monoclinic mirror planes (i.e. the two domain variants, $A_1$ and $A_2$) which have the relationships; $A_1 \rightarrow (z_1=[1-10], z_2=[110], z_3=[001])$, and $A_2 \rightarrow (z_1=[110], z_2=[-110], z_3=[001])$. For the 4mm point group symmetry, a single domain model is assumed with the axes relationships $(z_1=[100], z_2=[010], z_3=[001])$. The expression for the effective nonlinear optical coefficient
tensors of the multi-domain monoclinic symmetry \( d_{\text{eff}}^{4mm} \) and the single-domain tetragonal model \( d_{\text{eff}}^{4mm} \) are formulated as,[14, 15]

\[
d_{\text{eff}}^{4mm} \propto [t_{\text{oil}}^{\text{af}}]^{2} \cos^{2} \phi \{ \\
K_{11} \cos \theta_{2\omega} - (A_{21}K_{32} + K_{31}) \sin \theta_{2\omega} \cos^{2} \theta_{\omega} \\
+ [K_{13} \cos \theta_{2\omega} - (A_{21} + 1)K_{33} \sin \theta_{2\omega}] \sin^{2} \theta_{\omega} \\
- [(A_{21}K_{24} + 1) \cos \theta_{2\omega} - K_{35} \sin \theta_{2\omega}] \sin 2\theta_{\omega} \} \\
+ [t_{\text{oil}}^{\text{af}}]^{2} \sin^{2} \phi \{ K_{12} \cos \theta_{2\omega} - (A_{21}K_{32} + K_{31}) \sin 2\theta_{\omega} \} \\
+ [t_{\text{oil}}^{\text{af}}][t_{\text{oil}}^{\text{af}}]A_{21} \sin 2\phi (K_{26} \cos \theta_{2\omega} \cos \theta_{\omega} + K_{35} \sin \theta_{2\omega} \sin \theta_{\omega}) \\
\}
\]

\[
d_{\text{eff}}^{4mm} \propto [t_{\text{oil}}^{\text{af}}]^{2} \cos \theta_{2\omega} \sin 2\theta_{\omega} \\
+ \sin \theta_{2\omega} (K_{31} \cos^{2} \theta_{\omega} + K_{33} \sin^{2} \theta_{\omega}) \cos^{2} \phi, \\
- [t_{\text{oil}}^{\text{af}}]^{2} K_{31} \sin \theta_{2\omega} \sin^{2} \phi
\]

\text{Eq. 4-1}

\[
\]

where \( t_{\text{oil}}^{\text{af}} \) and \( t_{\text{oil}}^{\text{af}} \) are the standard transmission (\( t \)) Fresnel coefficients for \( p \)-polarized (||) and \( s \)-polarized (\( \perp \)) light at the air/film (af) interface, \( \theta_{\omega} \) and \( \theta_{2\omega} \) are the angles of refraction of the fundamental (\( \omega \)) and second harmonic fields (2\( \omega \)), which are explicitly defined in Appendix A.

The \( K_{ij} = d_{ij}/d_{15} \) parameters as well as the domain area fraction ratio, \( A_{21} = A_{2}/A_{1} \), were used to fit the SHG polarimetry tilt scan and polar plot data, which are shown as red lines in Figure 4-11.

The monoclinic model yields very good fits to the SHG polarimetry data for CTO/LAO and CTO/YAO, and the tetragonal model fits well to the CTO/LSAO sample. While the monoclinic polar symmetry of the CTO/YAO could be due to relaxation for the 14 nm thick film, the fact that the relatively low strained CTO/LAO does not show the expected tetragonal symmetry, whereas the higher strained CTO/LSAO does, could be due to the different symmetries of the respective substrate materials. Bulk LaAlO\(_3\) is trigonal (\( R-3m \) space group symmetry) with an octahedral tilt symmetry of \( a'a'a' \) and the octahedral rotations are 6° about the trigonal axis.[16] This distorted ‘pseudo-cubic’ orientation for a (100) oriented substrate crystal could be the reason why the strained CTO film does not adopt the expected tetragonal 4\( \text{mm} \) polar...
symmetry. However, bulk LaSrAlO$_4$ is an \( n=1 \) Ruddlesden-Popper phase with tetragonal (\( P4/mmm \) space group symmetry), with no rotations of the AlO$_6$ octahedra, and it has equal in-plane lattice parameters for an (001) oriented substrate crystal.[17] This might provide a better starting registry for the CTO film to adopt the expected tetragonal polar symmetry under compressive strain. Although the YAO crystal substrate material is orthorhombic (\( Pnma \) space group symmetry) with \( a^\prime \) tilt system,[18] the effects of the YAO symmetry on the asymmetric polar symmetry of the strained CTO film are unclear since this film was highly relaxed, although it is expected that the octahedral rotations already present in YAO substrate material are injected into the CTO film, which could possibly suppress the stabilization of a ferroelectric polarization similar to effects of CTO/(110)NdGaO$_3$ vs CTO/(001)LSAT discussed in Chapter 2, where the rotations in NdGaO$_3$ suppress the tensile strain induced ferroelectric phase whereas the absence of rotations in LSAT bolster the ferroelectric phase by turning of the rotations at the interface. This could also be the reason why CTO/YAO shows much lower SHG signals as compared to CTO/LSAO and CTO/LAO.

Having established that all of the compressive strained CTO films show room temperature polar phenomenon, the next step was to heat them up and measure the polar transition temperatures. Figure 4-12 shows high-temperature SHG intensity scans for each of the compressive strained CTO films. The CTO/LAO film shows a broad peak in the SHG intensity centered around 500 K, and the SHG intensity eventually dies out around 800 K. This broad peak in the SHG intensity at 500 K could be a structural transition from one ferroelectric phase to another, whereas the sharp decrease in the SHG intensity at 800 K could be the ferroelectric-to-paraelectric transition. Above 800 K, the SHG intensity from the CTO film is comparable to the SHG signal measured for a bare LAO substrate, which begins to increase above 900 K and is likely due to optical fluorescence at such high temperatures. Furthermore, it is well known that bulk LAO will undergo a rhombohedral to cubic phase transition at \( \sim 815 \) K where the octahedral
rotations disappear, which is very close to the point at which the SHG signal disappears for the CTO/LAO film sample.[16] This may be a strong indications that the octahedral tilt symmetry of the LAO substrate plays a critical role for the large polar transition temperature even though the strain is relatively small.

The CTO/LSAO sample shows a broad peak in the SHG intensity centered around 400 K, as well as sharper decrease in the SHG intensity around 700 K. Note that there is still considerable SHG intensity observed after the second transition (700 K), meaning that the signal does not decrease to the same value as the LSAO substrate (shown as the black curve). The transition at 700 K is likely the ferroelectric-to-paraelectric transition of the film, and the SHG signal coming from the film after this transition could be due to short-range nanopolar regions in the film. For the CTO/YAO film, a sharp decrease in the SHG intensity is observed at 200 K, and a second sharp transition occurs at 450 K, after which the SHG signal continuously decreases and becomes equal to the SHG signal from the bare YAO substrate signal at 700 K. The relatively lower transition temperatures for the highly strained CTO/YAO sample could be due to the film relaxation which may degrade the polar properties and therefore decrease the transition temperatures. Note that the SHG signal observed above 850 K for both the CTO/YAO film and YAO substrate is likely due to fluorescence of the substrate at elevated temperatures.[19] The polar transitions measured here for compressively strained CTO films, are plotted in Figure 4-13, which are very comparable to prototypical ferroelectric materials such as BaTiO$_3$ ($T_c = 408$ K) and PbTiO$_3$ ($T_c = 763$ K).
4.5 PFM switching of CaTiO$_3$/CaVO$_3$(001)LSAO film

To electrically probe the polar phase of CTO/LSAO, a 5 nm thick conducting CaVO$_3$ bottom electrode was deposited on (001)LSAO, followed by a ~14 nm thick CaTiO$_3$ layer. The optimal growth window conditions for stoichiometric CaVO$_3$ (CVO) material was determined by growing a series of CVO thin films on (001) LSAO substrates with a fixed Ca flux of $\Phi=2.5\times10^{13}$ atoms/cm$^2$/s and systematically varying the pressure of the supplied VTIP flux and measuring the minimum resulting out-of-plane lattice over a range of VTIP pressures (work not shown here), which is the same methodology used for accessing the stoichiometric growth window of CTO/LSAT as discussed in Chapter 3. The CVO perovskite structure has a bulk lattice parameter of 3.77 Å, resulting in compressive in-plane strain for CVO on (001) LSAO of -1.6 %. This large strain was the main reason why the thickness of the CVO film was kept very thin in order to mitigate strain relaxation of the CTO layer. However, this was at the expense of having a much higher sheet resistance for the ~5 nm thick CVO film which is expected to be around 200 $\Omega$$\square$.[20]

An X-ray diffraction 2θ-ω scan of the pure 5 nm thick CVO/(001)LSAO film is plotted in Figure 4-14 showing the 002 CVO peak about the 004 LSAO substrate peak. The 2θ-ω scan of the 14 nm CTO/5 nm CVO/(001)LSAO film shows the same 2θ value as the pure 14 nm CTO/(001)LSAO, indicating that the strain remained commensurate even with the incorporation of the CVO bottom electrode. The film was then annealed at ~300 °C for approximately 1 hour in order to remove oxygen vacancy defects in the film which is needed for electrical probing. Higher annealing temperatures could not be used as this resulted in the CVO bottom electrode layer to become insulating ($R > 1 \Omega$ cm), which has been shown to occur at $T \sim 300-400$ °C for bulk CVO.[21]
Piezoresponse force microscopy (PFM) analysis was performed on the low-temperature annealed CTO/CVO/LSAO stack in order to determine if the out-of-plane polarization is switchable. This technique can resolve nanoscale switching behavior where the phase and amplitude of the piezoresponse can be used to determine the polar direction and symmetry of a ferroelectric material.[22, 23] A thin layer of silver paste was applied to the edges of the sample to contact the CVO bottom layer with the conducting plate that held the sample. The metal probe tip was then brought into contact to the film surface near the center of the sample. The PFM imaging experiments were performed with an AC field of frequency 300 kHz and amplitude of 300 mV. A 10×10 μm area of the film was poled at +3 V DC bias, followed by poling a smaller 5×5 μm area at -3 V DC bias. Subsequently, a 15×15 μm image was scanned to obtain the vertical phase and amplitude of the poled regions, shown in Figure 4-15(a) and (b), respectively. The phase shift between the -3V and +3V poled regions is ~ 180°, as indicated by the line-profile plot in Figure 4-15(c) of the PFM phase along the dashed blue line in Figure 4-15(a). Within the up and down poled regions, the phase remains constant across the line scan, indicating that the polar axis has been switched. Figure 4-15(d) shows that the PFM amplitude across the blue line scan in Figure 4-15(b), which is nearly equal in the oppositely poled regions, and goes to zero at the domain walls between the up and down polar domains. The horizontal PFM response did not show any changes in the phase and amplitude (data not shown here). The 180° vertical phase shifts and equal amplitudes for up and down polar domains indicates that the polar axis is dominantly out-of-plane, which is in agreement with the determined 4mm tetragonal point group symmetry determined by SHG polarimetry analysis.

Figure 4-15(e) and (f) shows PFM images taken approximately 30 minutes after those shown in Figure 4-15(a) and (b), where the PFM phase and amplitude do not significantly change in magnitude over this time period. While there may be a small leakage current in the film, the
polar response does not instantaneously go away in a poled region, suggesting that the response is indeed from a built in out-of-plane polarization of the compressive strained CTO/LSAO film. A PFM switching loop of the vertical phase and amplitude is shown in Figure 4-16(a) and (b), respectively. The PFM hysteresis is indicated by the full 180° phase switch and the saturation of the PFM amplitude, which occurs at approximately ±1 V tip bias. Note that the tip bias was not calibrated for these experiments.

4.6 Conclusions

These results show that the polar properties of CaTiO₃ thin films can be tuned using appropriate substrate crystal strains. While tensile strains are able to induce a polarization with dominantly in-plane polarization, the ferroelectric transition temperatures are quite low, rendering this strain state not particularly useful for devices that operate at useful temperatures, but rather as an important material property parameter for verification of thermodynamically predicted transition temperatures. The discovery of the high temperature polar phase transitions in compressive strained CTO warrants future investigation into this material, both theoretically as well as experimentally.
Figure 4-1: (a) RHEED oscillations recorded from the 01 streak along the <110> azimuth during the first 10 minutes of growth for CaTiO$_3$ films grown on several substrates. The corresponding in-plane strain is shown on the right axis. The substrate crystals are indicated in each sub-panel. (b) The time-dependent change of the in-plane lattice parameter of strained CaTiO$_3$ films.
Figure 4-2: RHEED intensity oscillations (left-axis) and change of the in-plane lattice parameter, $\Delta a_{||}$ (right-axis) for (a) tensile strained CTO/LSAT and (b) compressive strained CTO/LSAO, resulting in in-phase and out-of-phase oscillations, respectively. The dashed red lines show alignment of the maxima in the RHEED oscillations with the oscillations in $\Delta a_{||}$. 
Figure 4-3: Post-growth RHEED images for the strained CaTiO$_3$ films taken at $T_{\text{substrate}} \sim 200$ °C.

The top and bottom rows show RHEED images captured along the $<110>$ and $<100>$ azimuths, respectively, with the in-plane strain of the CaTiO$_3$ films shown on the bottom axis, and the substrate material indicated on the top axis.
Figure 4-4: XRD $2\theta$-$\omega$ scans of the 002 CaTiO$_3$ peaks (indicated by black arrows) around the pseudocubic 002 substrates which are labeled in the graph. The in-plane strain for each film is shown on the right-axis. The expected $2\theta$ position for bulk CaTiO$_3$ is shown as the dashed black line.
Figure 4-5: AFM images taken for (a) compressively and (b) tensile strained CaTiO$_3$ films. The substrate materials and strain are shown above each image, with the vertical height displacement scale bar shown on the right of each image. The scale bars in each image are 300 nm.
Figure 4-6: AFM images for (a) compressive strained 15 nm CaTiO$_3$/(110)YAIO$_3$ and (b) tensile strained 15 nm CaTiO$_3$/(110)DyScO$_3$. The large cracks shown in the AFM image indicate signs of in-plane structural relaxation due to the large strained induced by these substrate materials on CaTiO$_3$ films. The scale bar in each image is 3 \( \mu \)m.
Figure 4-7: (a) Synchrotron-source XRD $2\theta$-\(\omega\) scan about the 004 LSAO substrate peak showing the 001 CaTiO$_3$ peak giving an out-of-plane c-axis lattice parameter of \(c=3.874\) Å for the 15 nm film. (b) RSM scan about the 106 LSAO substrate peak, showing that the 102 CaTiO$_3$ film peak has an equal in-plane lattice parameter to the substrate, but is just on the brink of relaxation. (c) Rocking curves of the 001 CaTiO$_3$ film (blue, left-axis) and 002 LSAO substrate (black, right-axis), which have FWHM values of 36 and 30 arcsec, respectively. (d) EDS spectra taken from three spots on the same CaTiO$_3$/(001)LSAO sample, which revealed Ti:Ca ratios of 0.99, 1.00, and 1.01. The Ca K\(\alpha_1\), Ca K\(\beta\), and Ti K\(\alpha_1\) peaks are shown on top for bulk CaTiO$_3$ sample, with the La L\(\alpha\) substrate peak shown on the right for each film measurement.
Figure 4-8: Room temperature STEM HAADF image of ~ 15 nm thick CaTiO$_3$ film grown on (001)LaSrAlO$_4$ substrate. A zoom in section from the white outlined area shows the Ca (blue) and Ti (green) atoms. The tetragonal unit cell is shown by the black lines, and the red lines indicate the mid-point between the top and bottom of the unit cells. Image courtesy of Jason Lapano at PSU.
Figure 4-9: SHG characterization of CaTiO$_3$ strain series with (a) tilt scans and (b) polar plots taken at $T=77$ K. The tilt scans were generated by rocking the films samples at several values of $\theta$ and measuring the in-plane SHG intensity for a fixed input polarization of $\phi=0^\circ$. The polar plots were generated by fixing $\theta$ and rotating $\phi$ by 360$^\circ$ and measuring the in-plane SHG intensity. The substrate materials are indicated in each subpanel of (a) and (b). The polarization direction for each film is shown as arrow insets in (a).
Figure 4-10. Temperature dependent SHG signal for the strained CaTiO$_3$ series, with the SHG signal from the substrate materials shown as black lines which indicates the noise-floor for the optical measurements. The temperature scans were taken at fixed geometries of $\theta=45^\circ$ and $\phi=0^\circ$. The transition temperatures are indicated by arrows.
Figure 4-11: Room temperature SHG polarimetry for CaTiO$_3$ films grown on (a) LAO, (b) LSAO, and (c) YAO substrates from top to bottom, respectively. Tilt scans were taken at $\phi=0^\circ$ and polar plots shown as top insets were taken at $\theta = (-45, 0, 45)^\circ$. SHG data shown as filled circles and theory fits are shown as red lines. Theory fits were calculated assuming either monoclinic ($m$) or tetragonal (4$mm$) point group symmetries with polarization directions shown schematically on the right with the film axes shown as black arrows, polarization shown as gray arrows, and the mirror planes shown in red.
Figure 4-12. High-temperature SHG intensity measurements ($\phi=0^\circ$, $\theta=45^\circ$), for CaTiO$_3$ films on LAO, LSAO, and YAO substrates from top to bottom, respectively. The SHG signal from the bare substrate is shown as black curves. Transitions are indicated by the stars and the shaded regions.
Figure 4-13. Strain-phase-temperature diagram for CaTiO$_3$ with SHG transition temperatures shown as filled stars. The open stars are transitions observed below the final transition where the SHG signal equals the signal from the bare substrate. The light gray region represent the phase-field theoretical predictions where the strain-induced ferroelectric-to-paraelectric values occur. The $T_C$ values for bulk BaTiO$_3$ and PbTiO$_3$ are shown for comparison.
Figure 4-14: XRD 2θ-ω scans about the 004 LSAO substrate peak showing the 002 film peaks for a 5 nm CaVO$_3$(001)LSAO (black), 14 nm CaTiO$_3$(001)LSAT (red), and a 14 nm CaTiO$_3$/5nm CaVO$_3$(001)LSAT film sample.
Figure 4-15: PFM scans of a 15nm CaTiO$_3$/5nm CaVO$_3$/LSAO sample showing the out-of-plane (a) phase, and (b) amplitude, for an area which was poled at +3V in the inner region (10x10 $\mu$m) with a smaller area poled at -3V in the center (5x5 $\mu$m). (c) A line profile taken from the dashed blue line in (a) showing the phase 180° phase shift between oppositely poled regions, where the amplitude of the PFM response is nearly equal in each region, and decreased sharply at the domain walls. PFM scans of (e) phase, and (f) amplitude, of the film taken 30 minutes after the first scan.
Figure 4-16: PFM switching measurement of the (a) phase and (b) amplitude of the out-of-plane PFM response for the CTO/CVO/LSAO film, where switching occurs at 1.5V tip bias. The tip bias was not calibrated. The dashed red lines in (a) highlight the 180° switching of up and down domains in the film.
4.8 References


Chapter 5

Stoichiometry as key to ferroelectricity in compressively strained SrTiO$_3$*

5.1 Abstract

While strain is a powerful tuning parameter for inducing ferroelectricity in thin film oxides, the role of stoichiometry control is critical, but far less explored. A series of compressively strained SrTiO$_3$ films on (001) LSAT substrates were grown by hybrid molecular beam epitaxy where the Ti cation was supplied using a metal-organic titanium tetraisopropoxide (TTIP) molecule that helps systematically and precisely control Sr:Ti stoichiometry in the resulting films. A stoichiometric growth window is located through X-ray diffraction and in-situ reflection high-energy electron diffraction measurements, which show a minimum out-of-plane lattice parameter as well as constant growth rate within the stoichiometric growth window range. Using temperature dependent optical second harmonic generation (SHG) characterization, a ferroelectric-to-paraelectric transition at $T \sim 180$ K is observed for a stoichiometric SrTiO$_3$ film, as well as a higher temperature structural transition at $T \sim 385$ K. Using SHG polarimetry modeling, the polar point group symmetry is determined to be tetragonal 4mm with the polarization pointing out-of-plane of the film. The SHG coefficients, $d_{31}/d_{15}=3$ and $d_{33}/d_{15}=21$ were determined at 298 K. The ferroelectric transition disappears in films grown outside the

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growth window, thus proving the critical role of stoichiometry control in realizing strain-induced ferroelectricity.

5.2 Introduction

Epitaxial strain engineering has become a powerful technique for unlocking emergent functional properties in complex oxide thin films, such as ferroelectricity, ferromagnetism, or multiferroicity. Large strains induced by lattice mismatched substrate crystals can create or enhance polar distortions by displacing cations in the film, which can drastically alter their ground state energy.\[1, 2\] For example, the incipient ferroelectric SrTiO$_3$ [3] can be turned into a near room temperature ferroelectric when grown as a thin film on a (110)DyScO$_3$ substrate which induces an in-plane tensile strain of ~ 1%, giving rise to an in-plane ferroelectric polarization and a ferroelectric transition temperature of T$_c$ ~ 298 K.\[4\] It has recently been demonstrated that compressively strained SrTiO$_3$ films grown on (001) (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.35}$ (LSAT) substrate (-0.95% strain) exhibits a low temperature ferroelectric phase, where a ferroelectric transition at T ~ 148 K was demonstrated for a 160 nm thick film grown by molecular beam epitaxy,\[5\] and T ~ 155 K for a 60 nm thick film grown by pulsed laser deposition,\[6\] which are close to the theoretically predicted value of T ~ 160 K.\[7, 8\]

While strain is the central tuning parameter for inducing ferroelectricity in oxide thin films, another important variable is stoichiometry of the Sr and Ti cations in the film, which should ideally be 1 Sr for every 1 Ti cation per formula unit. Slight deviations from ideal stoichiometry can lead to reduced ferroelectric and dielectric properties, and has been demonstrated for tensile strained SrTiO$_3$ films on (110)DyScO$_3$ substrate, where intentionally
induced Sr-rich or Ti-rich defects resulted in decreased transition temperatures and smaller dielectric constants.[9]

Controlling stoichiometry in thin films during ultra-high vacuum growth typically requires arduous calibration procedures which are necessary in order to produce high quality samples,[10, 11] and remains challenging since a flux of low vapor pressure materials, such as Ti, can substantially drift during film growth.[12] An effective way to overcome this challenge is to employ a stoichiometric growth window of SrTiO$_3$ using metal-organic titanium tetraisopropoxide to supply the Ti cation,[13, 14] which have resulted in well controlled stoichiometry during growth enabling low temperature carrier mobilities $> 50,000$ cm$^2$/Vs in La-doped SrTiO$_3$ films,[15] and device quality loss factors of $Q = 1$/tan($\delta$) $> 1000$ at room temperature in the tunable dielectric Ba$_x$Sr$_{1-x}$TiO$_3$,[16] hallmarking the low defect concentrations and structural coherency that can be achieved using this growth approach, enabling superior intrinsic material properties to be utilized in strained complex oxide films.

In this work, an adsorption controlled stoichiometric growth window for compressively strained SrTiO$_3$ films on (001) LSAT substrates was located through X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED) measurements. Using optical second harmonic generation (SHG) characterization, the ferroelectric (FE) and antiferrodistortive (AFD) structural transitions of stoichiometric SrTiO$_3$ films were measured to be $T_C \sim 175$ K and $T_{AFD} \sim 385$ K, whereas Sr-rich and Ti-rich films did not show any transitions of the temperature dependent SHG intensity. Using SHG polarimetry characterization measurements, the low temperature ($T = 77$K) ferroelectric point group symmetry was determined to be tetragonal 4$mm$ with out-of-plane polarization. Outside the growth window, the ferroelectric transition was suppressed. These results highlight the importance of a stoichiometric growth window to access intrinsic material properties of strained complex oxides.
5.3 Thin film growth and structural characterization

A series of ~20-nm-thick SrTiO\(_3\)/(001)LSAT films were grown inside of a molecular beam epitaxy (MBE) chamber with a background pressure of 5×10\(^{-10}\) Torr at a growth temperature of \(T_{\text{sub}} = 900\) °C in the presence of molecular oxygen (\(p_{\text{O}_2} = 1×10^{-7}\) Torr). The Sr flux was supplied using a thermal effusion cell and calibrated prior to growth using a quartz crystal microbalance, and the flux was held constant for each film in the series to \(\Phi_{\text{Sr}} = 2.5×10^{13}\) atoms/cm\(^2\)/s. The TTIP pressure (\(p_{\text{TTIP}}\)) was controlled using a PID feedback loop between a capacitance manometer located downstream of a motorized leak valve attached to a TTIP gas inlet system. The \(p_{\text{TTIP}}\) was systematically adjusted and controlled by regulating the gas inlet pressure, which is given as a beam equivalent pressure measured by a beam flux monitor located at the sample position. Figure 5-1(a) shows the growth window of SrTiO\(_3\) films which was determined from the out-of-plane \(c\)-axis lattice parameter of each film measured by X-ray diffraction 20-\(\omega\) scans about the 002 SrTiO\(_3\) film peaks [Figure 5-2(a)] using a Philips X’Pert Panalytical Pro with a CuK\(_{α}\) radiation source. For the beam equivalent pressure of TTIP molecules ranging from (31.5-34.8)×10\(^{-8}\) Torr, highlighted in blue in Figure 5-1(a), films exhibited the smallest \(c\)-axis lattice parameter of \(c = (3.932 \pm 0.002)\) Å, and was irrespective of supplied TTIP flux. Outside of the growth window range, the Sr-rich and Ti-rich films were grown and exhibited defect inclusions as evidenced by the expanded \(c\)-axis values.\(^{[17]}\) Figure 5-1(b) shows the growth rate of each film measured from the XRD thickness fringes (open circles) extracted from the scans shown in Figure 5-2(a), and also from time dependent RHEED intensity oscillations (closed circles) shown in Figure 5-2(b), that were recorded for the 01 diffraction spot along the <110> direction, shown in Figure 5-3. Each RHEED oscillation period corresponds to the completion of a single unit cell layer of SrTiO\(_3\).\(^{[18]}\) Growth rates determined
from XRD and RHEED were found in very good agreement. The constant growth rate for films grown inside the growth window is a direct indication that the desorption of TTIP molecules is the rate determining step, enabling self-regulated stoichiometry at the film surface even in the presence of small amounts of excess TTIP molecules. Outside of the growth window, the growth rate changed with increasing TTIP flux very rapidly in the Sr-rich region, and to a lesser, but significant degree for Ti-rich films.

5.4 Optical second harmonic generation characterization

Having located the stoichiometric growth window of SrTiO$_3$, the ferroelectric phase transition as well as the low-temperature polar phase symmetry was determined by optical second harmonic generation (SHG) characterization. SHG is the conversion of incident photons with frequency $\omega$ into photons at a frequency of $2\omega$ which is only possible if a material has broken inversion symmetry, strongly indicating the presence of a polar phase.[19] Figure 5-4 plots the temperature dependence of the out-of-plane SHG intensity ($\theta=45^\circ$, $\phi=0^\circ$) for the stoichiometric (blue), Ti-rich (red), and Sr-rich (green) films. SHG signal from LSAT substrate only is shown as the black line and represents the lower noise limit for these measurements. A schematic of the experimental SHG geometry is shown as the inset of Figure 5-4, where the fundamental laser beam (~80 fs pulse width, 2 kHz repetition rate, $\lambda=800$ nm) was generated from a Spectra-Physics Ti:sapphire laser system. The fundamental electric field of light ($E_\omega$) can be rotated by an angle $\phi$ using a half-wave plate, and is focused onto the film which can be rocked by an angle $\theta$ about a particular sample axis, and the generated SHG field ($E_{2\omega}$) is detected in the plane of incidence. The stoichiometric films showed a sharp decrease in the SHG intensity at ~ 180 K which was attributed to the ferroelectric transition. The Sr-rich and Ti-rich films did not show
any transitions in this temperature range. Figure 5-6(a) and Figure 5-6(b) show SHG tilt scans and polar plots, respectively, taken at $T=77$K for the films shown in Figure 5-4. The tilt scans were generated by taking the maximum SHG intensity while scanning the focal point of the fundamental laser beam through the sample that was fixed at different angles of $\theta$, as shown in Figure 5-5. Polar plots were taken at fixed angles of incidence $\theta$ while rotating $E_{\omega}$ by $\phi=360^\circ$.

The Sr-rich and Ti-rich films showed very weak SHG signal. Stoichiometric films showed large SHG intensities which was strongest for the film grown at $p_{TTIP}=33.2\times10^{-8}$ Torr. The symmetric tilt scan profiles which is zero at normal incidence ($\theta=0^\circ$) and double-lobed polar plot shapes are a strong indication that the polar direction of the film is out-of-plane. Note that residual SHG signal observed after the ferroelectric transition is likely due to short-range ordering of nano-polar regions throughout the SrTiO$_3$ film matrix, which has been demonstrated in strain free homoepitaxy SrTiO$_3$ thin films.[20] This residual signal is significantly stronger in the stoichiometric films, indicating that strain, stoichiometry and ferroelectric instability strongly couple to each other, even well above the transition temperature.

Figure 5-7 shows the temperature dependence of the out-of-plane SHG intensity ($\theta=45^\circ$ and $\phi=0^\circ$) at high temperatures ($T\sim600$ K) for the stoichiometric SrTiO$_3$ film ($p_{TTIP}=33.2\times10^{-8}$ Torr), with the ferroelectric transition at $\sim175$-180 K highlighted by the shaded blue area. At $T\sim385$ K, another transition in the SHG intensity is found to occur and is attributed to the structural antiferrodistortive (AFD) transition, which has also been observed by Yamada et. al. [6] to occur at $T\sim370$ K for a 60-nm-thick SrTiO$_3$ film grown on (001)LSAT. The anomaly in SHG at the AFD transition clearly indicates that nanopolar regions and AFD octahedral tilts couple to each other. Figure 5-8 shows the SHG tilt scans ($\phi=0^\circ$) for the stoichiometric SrTiO$_3$ film at $T=77$K (open blue circles) and $T=298$ K (open blue squares) with polar plots shown in the top insets for fixed angles of $\theta=-45^\circ$, $0^\circ$, and $45^\circ$. Theory has predicted a tetragonal point group symmetry
4mm for the compressively strained ferroelectric phase of SrTiO$_3$, and was assumed to model the transmitted SHG intensity ($I_{2\omega}$) for a thin film on a substrate sample which is given by the expression,[21, 22]

$$I_{2\omega} = (I_\omega)^2 \left(\frac{2\pi L}{\lambda_\omega}\right)^2 \left(d_{\text{eff}}^{(2)}\right)^2 \Theta_f,$$

where $I_\omega$ and $\lambda_\omega$ are the intensity and wavelength of the fundamental beam, respectively, $L$ is the film thickness, and $\Theta_f$ is a term that depends on the linear optical properties of film and substrate, and the angle of incidence $\theta$. The $d_{\text{eff}}$ term is the effective nonlinear optical coefficient tensor equation which is dependent on the point group symmetry and orientation of the film axes. For 4mm point group symmetry, the $d_{ij}$ tensor, has the following matrix form in the Voigt notation,

$$d_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix},$$

where only the $d_{15}$, $d_{31}$, and $d_{33}$ coefficients are non-zero for tetragonal 4mm point group symmetry.[23] Using Eq. (2), the $d_{\text{eff}}$ term can be expressed as,

$$d_{\text{eff}} \propto \left|t_{0\parallel}^{\text{af}}\right|^2 \{\cos \theta_{2\omega} \sin 2\theta_{\omega} + \sin \theta_{2\omega} (K_{31} \cos^2 \theta_{\omega} + K_{33} \sin^2 \theta_{\omega}) \} \cos^2 \phi,$$

$$-\left|t_{0\perp}^{\text{af}}\right|^2 K_{31} \sin \theta_{2\omega} \sin^2 \phi,$$

where $t_{0\parallel}^{\text{af}}$ and $t_{0\perp}^{\text{af}}$ are the transmission Fresnel coefficients parallel ($||$) and perpendicular ($\perp$) to the plane of incidence at the air/film (af) interface, $\theta_\omega$ and $\theta_{2\omega}$ are the refracted angles of the fundamental and second harmonic light inside of the film, respectively, and $K_{31}=d_{33}/d_{15}$, and $K_{33}=d_{33}/d_{15}$ are the $d_i$ ratios which were used as the fitting parameters to model the experimental data. Theoretical fits using Eq. (3) are shown as red lines on top of the SHG polarimetry data in Figure 5-8 at $T=77$K (open circles) and $T=298$K (open squares). The tetragonal 4mm model fits the SHG polarimetry data very well. At $T=77$ K, the best fitting parameters were determined to
be \( K_{31} = 1.0 \) and \( K_{33} = 3.0 \) and at \( T = 298 \) K, \( K_{31} = 3.0 \) and \( K_{33} = 21.0 \). The SHG signal detected for the SrTiO\(_3\) film in the high temperature paraelectric phase was attributed to short range ordering of nano-polar clusters in the film matrix, which also exhibit tetragonal symmetry. While the space group symmetry for compressively strained SrTiO\(_3\) is predicted to be \( P4mm \),\(^{[24]} \) the symmetry of the AFD phase is predicted to be \( I4/mcm \),\(^{[25]} \) which is likely the case here. However, due to the presence of the out-of-plane SHG signal observed in the paraelectric phase, the AFD structure could have \( I4cm \) symmetry, where the absence of the mirror plane perpendicular to the 4-fold axis results in a non-centrosymmetric symmetry and thus the observation of SHG even after the ferroelectric transition has occurred.

### 5.5 Conclusions

In summary, a demonstration that stoichiometric SrTiO\(_3\) films can be grown on (001)LSAT substrates using hybrid molecular beam epitaxy growth approach has been made, where an adsorption controlled growth window opens up, as determined by a constant \( c \)-axis lattice parameter as well as growth rate inside of the growth window. The stoichiometric films showed an out-of-plane polarization with \( 4mm \) point group symmetry as determined by low temperature SHG polarimetry analysis, with a FE transition at \( \sim 180 \) K, and an AFD transition at \( \sim 385 \) K. Outside this stoichiometric growth window, the ferroelectric transition was suppressed, indicating the importance of stoichiometry control for accessing strain-induced polar properties. A strong coupling of stoichiometry and polar phenomenon is established. As further exploration and investigation of the strain induced ferroelectric phases of SrTiO\(_3\) as well as other complex oxide systems continues to advance, the favorable growth kinetics offered by the hybrid MBE approach
enable intrinsic strain induced properties to be explored with optimal ferroelectric performance for potential incorporation into electronic devices.
5.6 Figures

Figure 5-1: (a) Out-of-plane lattice parameter (c-axis) as a function of TTIP flux ($p_{TTIP}$) for a stoichiometric series of ~20-nm-thick SrTiO$_3$ films on (001)LSAT. The stoichiometric growth window region is highlighted in blue, located between Ca-rich (green-left) and Ti-rich (red-right) growth conditions. (b) Growth rates given in unit cell height per minute as determined by RHEED oscillation periods (filled circles) and XRD thickness fringes (open circles).
Figure 5-2: (a) XRD 2θ-ω scans about the 002 SrTiO$_3$ film peaks (indicated by black arrow), and (b) RHEED intensity oscillations of each film in the stoichiometric series. Corresponding $p_{\text{TTIP}}$ values are shown on the right axis above each curve in (a) and (b).
Figure 5-3: Post-growth RHEED images taken at $T \sim 200$ °C taken along the $<110>$ (top row) and $<100>$ (bottom row) azimuths. The Sr-rich (green-left), stoichiometric growth window (blue-middle), and Ti-rich (red-right) films are labeled on top.
Figure 5-4: Temperature dependent SHG intensity for the stoichiometric (blue), Sr-rich (green), and Ti-rich (red) SrTiO$_3$ films, and the LSAT substrate for comparison (black). The ferroelectric to paraelectric transition is indicated by the dashed blue lines at $T \sim 180$ K. The top inset shows the experimental SHG geometry, where the fundamental (wavelength $\lambda_\omega = 800$ nm) electric field ($E_\omega$) can be rotated about the $x$-$y$ plane by an angle $\phi$, and focused onto the film sample which was rotated by an angle $\theta$ about the $z_1$ crystal physics axes, with $z_3$ lying in the $y$-$z$ plane. The second harmonic light (wavelength $\lambda_{2\omega} = 400$ nm) is detected in the $x$-$z$ plane.
Figure 5-5: (a) Low temperature ($T = 77$ K) focus series tilt scan of a stoichiometric SrTiO$_3$/(001)LSAT film where $\theta$ was rocked from -45° to 45° in 15° increments, and the focus was scanned through the sample from -4 to 4 mm and the SHG intensity was measured as a function of focus. (b) Contour map of the projected SHG intensity as a function of focus distance and $\theta$, showing the corrected tilt path by the white dashed line. (c) The corrected (green circles) and uncorrected (dashed red line) tilt scans generated from the focus series shown in (a).
Figure 5-6: (a) Tilt scans taken at $T = 77$K with $\phi = 0^\circ$ and the angle of incidence $\theta$ scanned from $-45^\circ$ to $+45^\circ$ in $15^\circ$ increments for the stoichiometric (middle), Sr-rich (bottom), and Ti-rich (top) films grown at beam equivalent TTIP pressures $p_{TTIP}$ ($\times 10^{-8}$ Torr) shown on the top right of each sub-panel. (b) Polar plots taken at $T = 77$K with $\theta$ fixed at $-45^\circ$, $0^\circ$, and $+45^\circ$ and $\phi$ scanned $360^\circ$. The $p_{TTIP}$ values ($\times 10^{-8}$ Torr) are shown above each curve in (a) and on the top right of each panel in (b) and (c).
Figure 5-7: Temperature dependent SHG intensity for a stoichiometric (blue) SrTiO$_3$ film and the LSAT substrate (black). The ferroelectric (FE) transition is at ~ 180 K, the discontinuity in the SHG intensity at $T \sim 385$ K marks the antiferrodistortive (AFD) structural transition.
Figure 5-8: SHG polarimetry data taken at $T = 77$ K (open circles) and $T = 298$ K (open squares) showing tilt scans ($\phi = 0^\circ$). The top insets show polar plots taken at $\theta = -45^\circ$, $0^\circ$ and $+45^\circ$.

Theoretical fits to a tetragonal $4mm$ point group symmetry model are shown as red lines on top of the data.
5.7 References


Chapter 6

Overlapping growth windows to build \((\text{SrTiO}_3)_n/(\text{CaTiO}_3)_n\) superlattices*

6.1 Abstract

The synthesis of \((\text{SrTiO}_3)_n/(\text{CaTiO}_3)_n\) superlattices in a layer-by-layer fashion is demonstrated by utilizing overlapping stoichiometric growth windows in hybrid molecular beam epitaxy. The structural quality for a series of 100 nm thick \(n = 1-10\) superlattices was determined through scanning transmission electron microscopy and X-ray diffraction characterization techniques, allowing the ability to quantifiably measure the degree of Sr and Ca cation intermixing at the interfaces by measuring the \(n^{th}\) order satellite peak splitting, revealing a random distribution of \(\Delta n\) throughout the series. A low-temperature ferroelectric phase is found to emerge for \(n \geq 7\) superlattices which had layering thickness above the critical thickness limit for ferroelectricity to emerge, whereas ferroelectricity was destabilized for \(n < 7\) superlattices, except for the \(n = 3\) sample which had a large degree of cation intermixing and the polar phase was attributed to doping. This work exemplifies the importance of assessing structure-property relationships in complex oxide superlattices as thicknesses are scaled towards nanometer dimensions.

*Taken and adapted from work in preparation for journal submission by Haislmaier et al.
6.2 Emergent phenomenon in oxide superlattices

Artificially layered oxide superlattices such as the perovskite-based \((\text{ABO}_3)_n/(\text{A}'\text{B'O}_3)_m\) structure, provide a rich and versatile material template which can lead to novel or emergent functional properties beyond those present in their individual perovskite counterparts.[1, 2] Such functionality arises through the ability to tune the A/A' (typically alkaline or rare earth elements) and B/B' (typically transition metals) chemistries, the layering thickness \((n/m)\), as well as the epitaxial strain imposed by a substrate when superlattices are synthesized as thin films. For example, a superlattice composed of paraelectric SrTiO\(_3\) and SrZrO\(_3\) layers gives rise to ferroelectricity,[3] layering antiferromagnetic LaFeO\(_3\) and LaCrO\(_3\) results in ferromagnetism,[4] combining non-super-conducting BaCuO\(_2\) and SrCuO\(_2\) leads to super-conductivity,[5] enhanced ferroelectricity is found to emerge in bi-color BaTiO\(_3\)/SrTiO\(_3\) and BaTiO\(_3\)/CaTiO\(_3\) superlattices[6, 7] as well as tri-color BaTiO\(_3\)/CaTiO\(_3)/SrTiO\(_3\) superlattices,[8] and new exotic structural phases such as polar vortices have recently been discovered in superlattices of paraelectric SrTiO\(_3\) and ferroelectric PbTiO\(_3\).[9] Additionally, recent theoretical investigations suggest that an improper ferroelectric ground state will emerge for A-site modulated \((\text{ABO}_3)_n/(\text{A}'\text{BO}_3)_n\) superlattices combined from any two non-polar ABO\(_3\) perovskite materials if they both possess an orthorhombic \(Pbnm\) space group symmetry.[10] Clearly, there is a strong impetus for exploration and discovery of emergent phenomenon in oxide superlattice materials. However, constructing oxide superlattices in thin film form requires advanced growth techniques in order to precisely control the layer thicknesses \((n/m)\), interface roughness, and stoichiometry of the A:B and A':B' cations. Controlling these factors in superlattice materials is critical and must be uniform throughout an entire superlattice film; otherwise the targeted material properties may not emerge.[11, 12]
But how are these artificial materials synthesized, and how perfect do they have to be for functional properties to emerge? Current thin film growth techniques employ a sequential shuttering method where individual (A/A')O and (B/B')O$_2$ layers are sequentially deposited using \textit{in-situ} feedback from reflection high energy electron diffraction (RHEED) of the film surface to calibrate the layer deposition times.\cite{13, 14} One of the main limitations for this growth approach is determining the correct shuttering times to deposit precise monolayer doses in stoichiometric proportions, often requiring extensive and time consuming pre-growth calibrations.\cite{15}

Additionally, low vapor pressure sources such as titanium can have large flux drifts over time and can potentially lead to unintentional incorporation of defects throughout a film material.\cite{16} A promising new growth technique for achieving high quality oxide materials has recently been demonstrated by the hybrid MBE approach where Ti is supplied using a volatile metal-organic titanium tetraisopropoxide (TTIP). This opens up self-regulating stoichiometric growth windows for SrTiO$_3$,\cite{17} BaTiO$_3$,\cite{18} and GdTiO$_3$\cite{19}, enabling the synthesis of highly stoichiometric films and superior material properties.

Here, we demonstrate an example of strain-induced ferroelectricity in a ferroelectric superlattice. Our system of choice is (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$, where the individual perovskite components, SrTiO$_3$ and CaTiO$_3$, are not polar in bulk form, but each individually become ferroelectric under a uniform biaxial strain.\cite{20, 21} The synthesis of a series of ~100 nm thick $n = 1$-$10$ (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattice structures grown on (001) (LaAlO$_3$)$_{0.3}$(Sr$_2$TaAlO$_6$)$_{0.35}$ (LSAT) substrates is demonstrated by utilizing overlapping stoichiometric growth windows during hybrid molecular beam epitaxy growth for both SrTiO$_3$ (STO) and CaTiO$_3$ (CTO) films.

The superlattices were grown layer-by-layer where the periodicity ($n$) was controlled by monitoring \textit{in-situ} RHEED intensity oscillations, which are very stable and repeatable over long time periods of $> 2.5$ hours, indicating good flux control of the TTIP and Sr sources during growth. The structural quality and degree of interface mixing in the superlattices were
determined through scanning transmission electron microscopy (STEM) and synchrotron-based X-ray diffraction analysis, revealing a varying degree of intermixing of Sr and Ca atoms at the interfaces in the superlattices. By measuring the degree of splitting of the \( n \)-th order satellite diffraction peak, the deviation from the targeted \( n \) periodicity (\( \Delta n \)) was calculated, revealing that the deviation of \( n \) was not more than 1 unit cell and that \( \Delta n \) had a random distribution throughout the series.

Using optical second harmonic generation (SHG) characterization, the ferroelectric transition temperatures for pure compressive strained \( \text{SrTiO}_3/(001) \text{LSAT} \) and pure tensile strained \( \text{CaTiO}_3/(001) \text{LSAT} \) are both found to occur at \( T \sim 180 \) K, and the \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \) films exhibit tetragonal (4\( mm \)) and monoclinic (\( m \)) polar point group symmetries, as shown schematically, respectively, which is consistent with theoretical predictions and other experimental reports.[22-26] Using SHG, we discover that this strain-induced ferroelectricity in the superlattices is activated above a critical thickness limit (\( n > 6 \)). Below this thickness limit, ferroelectricity is suppressed, but only if there is a low amount of A-site intermixing at the interfaces (\( \Delta n < 0.1 \)). However, for \( n \)-periodicities below the critical thickness limit, a polar ferroelectric can be reactivated when there is a large degree of A-site intermixing at the interfaces (\( \Delta n > 0.2 \)), essentially resulting in a doped \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) film, which is known to exhibit low-temperature relaxor ferroelectricity.[27, 28] This work demonstrates the importance of determining the structural properties of complex oxide superlattices and how it correlates to the emergence of ferroelectricity at nanoscale dimensions.

6.3 Overlapping stoichiometric growth windows of \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \)

Stoichiometric growth window conditions for \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \) were targeted by growing independent series of \( \text{SrTiO}_3/(001) \text{LSAT} \) and \( \text{CaTiO}_3/(001) \text{LSAT} \) using hybrid MBE
where Ti was supplied using metal-organic TTIP molecule.[20, 21] The (001)LSAT substrate material was chosen as it provides an ideal structural template to build the (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattice structures since the in-plane lattice parameter of LSAT ($a = 3.868$ Å) is in between the values for bulk SrTiO$_3$ ($a = 3.905$ Å) and CaTiO$_3$ ($a = 3.82$ Å), inducing a compressive strain of -0.95 % in the SrTiO$_3$ layers, and a tensile strain of +1.26 % in the CaTiO$_3$ layers, as shown in Figure 6-1(a) and (b), respectively. This enables the superlattices to be grown to sufficiently large thicknesses while maintaining a fully strained state, since the alternating tensile and compressive strains in the CaTiO$_3$ and SrTiO$_3$ layers cancel out the net in-plane mechanical tension, shown in Figure 6-1(c).[6]

The first step towards building the (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattice structures is to locate the stoichiometric growth windows of SrTiO$_3$ and CaTiO$_3$ independently. This was achieved by growing different series of 20 nm thick SrTiO$_3$/(001)LSAT and CaTiO$_3$/(001)LSAT films where the Sr flux was fixed at $\Phi_{\text{Sr}} = (2.5 \times 10^{13}, 3.0 \times 10^{13})$ atoms/cm$^2$·s$^{-1}$ and the Ca flux was fixed to $\Phi_{\text{Ca}} = (2.0 \times 10^{13}, 2.5 \times 10^{13})$ atoms/cm$^2$·s$^{-1}$. In each series, the growth temperature (900 °C) and molecular oxygen pressure ($p_{\text{O}_2} = 1 \times 10^{-7}$ Torr) was fixed, and the TTIP flux ($p_{\text{TTIP}}$) was systematically adjusted to determine the growth window boundaries, which is accompanied by an expansion in the out-of-plane lattice parameter ($c$-axis) due to incorporation of either AO-rich (low $p_{\text{TTIP}}$) or BO$_x$-rich (high $p_{\text{TTIP}}$) phases.[29, 30] In order to avoid these nonstoichiometric growth conditions, the optimal $p_{\text{TTIP}}$ value should therefore be chosen near the center of both growth windows, enabling stoichiometric deposition throughout an entire growth period despite any slight fluctuations in the TTIP flux which is < 1% over periods of > 30 minutes for TTIP sources in MBE.

Figure 6-2(a)-(b) shows in-situ RHEED oscillations recorded for the 01 diffraction streak along the <110> azimuth for SrTiO$_3$//(001)LSAT films grown at Sr fluxes of $\Phi_{\text{Sr}} = 2.5 \times 10^{13}$
atoms/cm$^2$s$^{-1}$ and $\Phi_{Sr}=3.0\times10^{13}$ atoms/cm$^2$s$^{-1}$, respectively, and Figure 6-2(c)-(d) shows RHEED oscillations for CaTiO$_3$/|(001)LSAT films grown at Ca fluxes of $\Phi_{Ca}=2.5\times10^{13}$ cm$^2$s$^{-1}$ and (d) $\Phi_{Ca}=2.0\times10^{13}$ cm$^2$s$^{-1}$, respectively. RHEED oscillations during co-deposition indicate a layer-by-layer growth mode, where the maxima in the oscillations correspond to completion of individual SrTiO$_3$ and CaTiO$_3$ unit cells.[31] The corresponding TTIP flux ($p_{TTIP}$) values are shown on the right axis of each graph, and the growth window regions are indicated by the shaded area on the right axis of each panel in Figure 6-2, with the Ti-rich and A-site rich films labeled on top and bottom, respectively. The stoichiometric SrTiO$_3$ and CaTiO$_3$ films showed a steady increase in the RHEED intensity oscillations during the first few minutes of growth after which the oscillations became very consistent and repeatable, indicating well controlled layer-by-layer growth modes for each material. The A-site rich films displayed very weak RHEED oscillations which quickly dampened out. For Ti-rich SrTiO$_3$ films, the RHEED oscillations persisted, however an initial spike in the RHEED intensity was observed, as well as beat patterns in the RHEED oscillation envelope which correspond to the incorporation of extra SrTiO$_3$ unit cells and nonstoichiometry. The Ca-rich CaTiO$_3$ films showed weak RHEED oscillations which damped out quickly after growth was initiated.

X-ray diffraction (XRD) 20-20 scans (X’Pert Panalytical Pro, Cu-K$_{a1}$ radiation source) were measured for each stoichiometric series to determine the c-axis value for the films in each series, as shown in Figure 6-3 for each of the SrTiO$_3$/LSAT and CaTiO$_3$/LSAT series with the corresponding A-site fluxes labeled on top with the corresponding $p_{TTIP}$ values for each series shown on the right axis in each panel. Figure 6-4(a) shows the extracted c-axis values from the XRD measurements for SrTiO$_3$ (left axis) and CaTiO$_3$ (right axis) films, where it is immediately obvious that the growth windows for A-site fluxes of $2.5\times10^{13}$ atoms/cm$^2$s$^{-1}$ do not overlap as a function of $p_{TTIP}$. By increasing the Sr flux to $\Phi_{Sr}=3.0\times10^{13}$ atoms/cm$^2$s$^{-1}$ and decreasing the Ca
flux to $\Phi_{\text{Ca}} = 2.0 \times 10^{13}$ atoms/cm$^2$s$^{-1}$, the growth windows were successfully shifted in order to reposition their centers so that they overlapped as a function of $p_{\text{TTIP}}$. The ability to overlap the stoichiometric growth windows enables an easier way to construct the SL structures where the TTIP flux does not need to be adjusted in between subsequent layer depositions. Note that the size of the growth window ranges for SrTiO$_3$ and CaTiO$_3$ are not the same, which is likely due to the fact that the size of the growth window ranges have different temperature dependences,[17] and a larger SrTiO$_3$ window range might be achieved at higher growth temperatures. Nevertheless, the growth window ranges of SrTiO$_3$ and CaTiO$_3$ used here were sufficiently large in order to maintain a constant $p_{\text{TTIP}}$ which lies within both the SrTiO$_3$ and CaTiO$_3$ growth window ranges.

From the RHEED oscillations ($<110>$ azimuth, 10 diffraction peak), the growth rates of the films in each series were determined, and are plotted as a function of TTIP flux in Figure 6-4(b). Within the highlighted growth window regions, the growth rate becomes constant, which is expected for an adsorption controlled self-regulated stoichiometric growth window. However, the change in the growth rate with the change in the A-site flux is quite different between SrTiO$_3$ and CaTiO$_3$ windows. The change in the growth rate was much larger for the scaled CaTiO$_3$ windows where a change in the A-site flux of $0.5 \times 10^{13}$ atoms/cm$^2$s$^{-1}$ resulted in an increase in the growth rate (inside of the growth window) from ~1.75 to 3.25 unit cells per minute. For the scaled SrTiO$_3$ growth windows, the same change in A-site flux ($0.5 \times 10^{13}$ atoms/cm$^2$s$^{-1}$) only resulted in an increase of the growth rate from ~1.96 to 2.15 unit cells per minute. The reason for this extreme discrepancy of the scalability of the growth rates between SrTiO$_3$ and CaTiO$_3$ growth windows could be due to the difference in desorption rates of SrO and CaO at the growth front, where the higher vapor pressure of SrO might decrease the amount that the growth rate will shift with changing the Sr flux.
6.4 Growth of superlattice films using RHEED oscillations

Having located the overlapping growth windows of SrTiO$_3$ and CaTiO$_3$, a series of $n = 1$-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices were grown to ~100 nm of thickness on (001)LSAT substrates, where the $p_{\text{TTIP}}$ value was fixed at $33.2 \times 10^{-8}$ Torr, and fixed Sr and Ca fluxes of $\Phi_{\text{Sr}} = 3.0 \times 10^{13}$ atoms/cm$^2$s$^{-1}$ and $\Phi_{\text{Ca}} = 2.0 \times 10^{13}$ atoms/cm$^2$s$^{-1}$, respectively. Figure 6-5 shows a schematic of the growth scheme for building an $n = 2$ superlattice using sequential A-site shuttering with codepsition of TTIP, where 2×SrTiO$_3$ layers are deposited by opening and closing the Sr and TTIP sources after the completion of two RHEED oscillations and followed by a pause, with 2×CaTiO$_3$ layers subsequently deposited after two RHEED oscillations are observed. This process was repeated until approximately 100 nm of thickness was synthesized for each superlattice.

In order to accurately control the periodicity ($n$) of the individual SrTiO$_3$ and CaTiO$_3$ layers in the superlattices, time dependent RHEED oscillations were monitored, as shown in Figure 6-6(a) for the $n = 1$-10 superlattice series during the entire ~2.5 hour growth period. The RHEED oscillations indicate a layer-by-layer growth mode during co-deposition, where the maximum in an oscillation corresponds to completion of individual SrTiO$_3$ and CaTiO$_3$ unit cells, and can be used to accurately terminate the layer surfaces.[31] Note that an initial buffer layer of SrTiO$_3$ was deposited first until strong enough RHEED oscillations were observed, enabling the superlattice layering sequence to start on a terminated seed layer. The RHEED oscillations in Figure 6-6(a) show very stable RHEED intensities during the entire growth period, indicating stable fluxes supplied by TTIP and evaporated Sr and Ca metals inside of an MBE chamber. The periodic deposition sequencing throughout the superlattice growth is demonstrated by the qualitatively similar RHEED oscillation profiles at the beginning of growth shown in Figure 6-6(b) and at the end of growth, shown in Figure 6-6(c), although the RHEED oscillations
slightly dampen out during extended growth times. The main advantage for this growth method is that because stoichiometry is self-regulated, the remaining optimization tuning parameter is synchronizing the shuttering events with RHEED oscillations, where the constant flux rates enable superlattices to have a homogenous structure.

6.5 STEM imaging of superlattice interfaces

The structural and interface quality of the superlattices was directly observed from aberration corrected STEM ADF images (Gatan Titan3 operated at 200 kV and a probe convergence semiangle of 29 mrad) shown in Figure 6-7(a) and (b) for the $n=2$ and $n=5$ superlattices, respectively, with the LSAT substrate and SrTiO$_3$ buffer regions labeled. The individual SrTiO$_3$ and CaTiO$_3$ layers are indicated on the right side of the panel in Figure 6-7(b), where the brightest dots in the images are the Sr atoms. Within the $n=2$ and $n=5$ superlattice structures, there are regions where $n$ changes by $\pm 1$ (i.e. $n = 1$, 3 for the $n=2$ sample, and $n = 4$, 6 for the $n=5$ sample), however, $n$ does not vary by more than 1 in any of these regions. High magnification STEM ADF images for the $n=3$ and $n=4$ superlattices are shown in Figure 6-8(a) and (b), respectively. Zoomed-in STEM images are shown in Figure 6-7(c) - (f) for the $n=2$ - 5 superlattices, respectively. Line profiles of the pixel intensity along the dashed red lines are plotted on the right side of each image with alternating Sr and Ca layers highlighted in green and blue shaded areas, respectively. The $n=2$, 4, and 5 superlattices showed a lesser degree of interface mixing as determined by the relatively constant pixel intensities of the Sr and Ca atomic columns throughout layers. The $n=3$ superlattice displayed a larger degree of intermixing at the interface boundaries as indicated by modulated pixel-intensity curve plotted in red on top of the line-profiles. From the STEM image analysis, the superlattices did not show obvious inclusions of defect formations due to nonstoichiometric deposition. The degree of intermixing of Sr and Ca
atoms at the interface of the $n = 3$ superlattice was determined by chemical mapping using energy-dispersive X-ray spectroscopy (EDS) during STEM, as shown in Figure 6-9. The color-coded atomic positions of the Ti (green), Ca (blue), and Sr (red) atoms are shown in Figure 6-9(d) and reveal that the most amount of Sr and Ca intermixing (purple) occurs at the first unit cell layer of each new SrTiO$_3$ and CaTiO$_3$ slab. This is likely due to the fact that when the top-most layer is incomplete, an approximately 1 unit cell thick Sr$_{1-x}$Ca$_x$TiO$_3$ layer will form, where the amount of mixing of this layer is determined by the degree of synchronization between the source shuttering events with the RHEED oscillations, which may be slightly different from one film to the next depending on how well the shuttering times are calibrated.

### 6.6 X-ray diffraction characterization of superlattice structural quality

To determine the macroscopic structural properties of the 100 nm thick superlattice films, synchrotron-based XRD measurements were performed on a Newport six-circle diffractometer using an X-ray energy of 16 KeV on the experimental station 33-ID-D of Advanced Photon Source, Argonne National Laboratory. The total XRD flux was $2 \times 10^{12}$ photons/s and was focused by a pair of Kirkpatrick-Baez mirrors down to a beam size of 50 μm (vertical) by 80 μm (horizontal). The 2D scattering images of the (00L) Bragg rods at each step in the reciprocal lattice were recorded with a Dectric PILATUS 100K pixel area detector using a $\theta$-2$\theta$ scattering geometry. The diffraction intensities were obtained by integrating a narrow slit regions on each 2D scattering images and were background subtracted. Strain relaxation did not occur as evidenced by XRD reciprocal space mapping (RSM) about the 103 LSAT substrate peaks for the $n = 3$ and $n = 8$ superlattice films shown in Figure 6-10(a) and (b), respectively, revealing that the in-plane lattice parameter is equal to that of the LSAT substrates. XRD $2\theta$-$\omega$ scans were taken of the 00L crystal truncation rods for the $n$=1-10 series, as shown in Figure 6-11 and are plotted in
reciprocal lattice units (r.l.u.) of the LSAT substrate. All of the expected superlattice satellite peaks are observed and are labeled accordingly. Figure 6-12(a) displays Kiessig thickness fringes observed around the 00(2n) superlattice peak (which is on top of the 001 LSAT substrate peak) indicating that the film/air and film/substrate interfaces are atomically smooth and that all of the thicknesses are close to 100 nm.

The key feature obtained from the XRD measurements is the degree of splitting of the nth order superlattice satellite peaks, shown in Figure 6-12(b), which directly correlates to the degree of ‘interface-roughness’ in a superlattice film. Peak splitting only occurs in a periodically layered structure if the amount of material deposited in each layer is constant, but is not equal to an integer number of layers.[32, 33] For the case of random variations in the layer thicknesses, the nth order satellite peak linewidths would increase, which is not observed in these films. The separation of the satellite peaks can be used to calculate the non-integral fraction of the layering thicknesses, which is referred to as Δn here. Figure 6-12(c) shows the calculated Δn parameter of the nth order peak splitting for the entire n = 1-10 series. A random variation of Δn parameter is observed, and is associated with the experimental error involved in determining precise deposition times of n×SrTiO₃ and n×CaTiO₃ layers using RHEED oscillations. For the n=4 superlattice, nth order peak splitting is not observed, therefore Δn ~ 0.0 for this particular film, whereas the large nth order peak split observed for the n = 3 superlattice gives a value of Δn ~ 0.22 which is in agreement with the observed intermixing of Ca and Sr in some of the layers for the n = 3 superlattice from EDS STEM analysis, and suggests that the non-integral layer is accumulated in first SrTiO₃ or CaTiO₃ unit cell layers of each slab. In theory, the degree of nth order peak splitting, or interface mixing of Ca and Sr, could be minimized through better refinement of synchronizing the shuttering events with in-situ RHEED oscillations. Figure 6-12(d) shows the calculated out-of-plane c-axis lattice parameter from the positions of the
satellite peak positions, yielding a linear fit given by $c (\text{Å}) = 7.726(n) + 0.032$ with a coefficient of determination of $R^2 = 1.00$. This highly linear trend of the $c$-axis with $n$ indicates that the stoichiometry in the superlattices has been nominally maintained, whereas nonstoichiometric compositions would shift the satellite peak positions, resulting in deviations from the expected $c$-axis lattice parameter. Next, the emergence of a ferroelectric polar phase in the strained superlattice films is demonstrated which is dependent on both the layering thickness ($n$) as well as the degree of interface roughness ($\Delta n$).

**6.7 SHG characterization of strained SrTiO$_3$ and CaTiO$_3$ films**

Nonlinear optical second harmonic generation (SHG) characterization was used to probe the emergence of a strain-induced polar phase in the $(\text{SrTiO}_3)_n/(\text{CaTiO}_3)_n$ superlattices as well as pure SrTiO$_3$/(001)LSAT and CaTiO$_3$/(001)LSAT film samples. SHG is a nonlinear process where two photons of light at frequency $\omega$ (wavelength $\lambda$) are converted into a single photon at a frequency of $2\omega$ (wavelength $\lambda/2$), and only occurs in a non-centrosymmetric material (broken inversion symmetry), such as for a ferroelectric material which has a spontaneous polarization. Figure 6-13(a) shows the configuration of the transmission geometry for the SHG experiments, where the incident laser beam power (800 nm, 80 femtosecond, 2 kHz rep. rate) was fixed to ~3.0 W/cm$^2$ for all SHG measurements. The samples were aligned to a linearly polarized laser beam that was focused onto the film surface, where the incident electric field of light ($E_0$) was rotated by $\phi$. The intensity of the generated second harmonic field ($I_{2\omega}$) was measured in the plane of incidence as the samples were rotated about the [010] axis by $\theta$. The temperature dependence of the SHG intensity was measured for pure SrTiO$_3$ ($p_{\text{TTIP}} = 33.2 \times 10^{-8}$ Torr) and CaTiO$_3$ ($p_{\text{TTIP}} = 31.5 \times 10^{-4}$ Torr) films grown inside of the stoichiometric growth windows, and are
plotted as green and blue curves in Figure 6-13(b), respectively, where the SHG intensity from
the bare LSAT substrate (black curve) defines the noise floor of the SHG measurements. The
pure strained SrTiO$_3$ and CaTiO$_3$ films show transitions in the SHG intensity ($I_{2\omega}$) at $T \sim 180$ K
where hysteresis is observed upon heating and cooling temperature scans. These strain induced
ferroelectric transitions have already been demonstrated in other reports in the literature for
compressive strained SrTiO$_3$/(001) LSAT,[21, 23, 26] and tensile strained
CaTiO$_3$/(001)LSAT,[20, 22] and are theoretically predicted to occur.[24, 25] Note that the
SrTiO$_3$ film shows larger SHG intensity than the bare LSAT substrate above the ferroelectric
transition, which has been observed for strained SrTiO$_3$ films,[21] as well as nonstrained SrTiO$_3$
films grown on SrTiO$_3$ substrates, and is attributed to the formation of nano-polar regions
throughout the SrTiO$_3$ film matrix, which can give sizeable SHG signals.[34]

The polar phase symmetry of the strained films were determined by SHG polarimetry
characterization. Figure 6-14(a) and (c) shows SHG measurements taken at $T = 77$ K for SrTiO$_3$
(green squares) and CaTiO$_3$ (blue circles) films, respectively. The samples were rotated about the
[010] axis at several fixed angles of $\theta$ and the SHG intensity was measured in the plane of
incidence for a fixed $E_\omega$ orientation of $\phi = 0^\circ$ (referred to as tilt scan). The insets of Figure
6-14(a) and (c) show SHG intensity measured taken at fixed angles of $\theta = -45^\circ$, $0^\circ$, and $+45^\circ$
with $\phi$ rotated by $360^\circ$ (referred to as polar plots). Using a combination of tilt scan polar plots, the
symmetry and direction of the polar axis in a film can be determined. For the SrTiO$_3$ film, there
was no in-plane SHG intensity observed, and the symmetric tilt scans and polar plot features
indicate that the polarization is dominantly out-of-plane. The CaTiO$_3$ film shows an asymmetric
tilt scan, indicating that both in-plane and out-of-plane polarization components are present, and
the polarization is tilted somewhere in the (110) plane. To model the SHG data, expressions were
derived for (1) single-domain tetragonal 4$mm$ point group symmetry for compressively strained
SrTiO$_3$ with the out-of-plane polarization along [001], and (2) a multi-domain monoclinic $m$ point group symmetry for tensile strained CaTiO$_3$, with both in-plane and out-of-plane polarization components lying in the (110) and (1-10) mirror planes. [22, 24] The orientation of the assumed domain axes with respect to the film/substrate geometry is shown schematically in Figure 6-14(b) and (d) for SrTiO$_3$ and CaTiO$_3$ films, respectively. The calculated fits based off of these models match well with the measured SHG data. These strain-induced polar building blocks of SrTiO$_3$ and CaTiO$_3$ provides a reference for interpreting the SHG data of the (SrTiO$_3$)$_n$/CaTiO$_3$$_n$ superlattices.

Figure 6-15(a) shows the temperature dependence of the SHG intensity for the $n = 1$-$10$ series. For the $n = 3, 7$-$10$ superlattices, transitions are observed ranging between $T \sim 145$-$180$ K. The $n = 8$ and $n = 9$ superlattices show the strongest SHG intensity and largest degree of hysteresis upon heating and cooling scans, whereas the $n = 3, 7, 10$ superlattices show much less hysteresis and weaker SHG signal. The hysteresis observed in the SHG intensity for the $n = 3, 7$-$10$ superlattices is a clear indication that a ferroelectric-to-paraelectric transition has been stabilized for these particular superlattice samples. In contrast, the $n = 1, 2, 4, 5, 6$ superlattices, shown as black curves in Figure 6-15(a), do not show a transition over this temperature range. Figure 6-15(b) shows SHG polarimetry data taken at $T = 77$ K for the $n = 1$-$10$ superlattices. The $n = 3, 7$-$10$ samples have both in-plane and out-of-plane polarization components, indicated by the asymmetric tilt scan and polar plot curves. The polar symmetry of the superlattices seem to behave like a superposition of the pure SrTiO$_3$ and CaTiO$_3$ films, indicating that the in-plane polar component may be dominantly from the tensile strained CaTiO$_3$ layers and the out-of-plane polar component dominantly from the compressive strained SrTiO$_3$ layers. The $n = 1, 2, 4, 5, 6$ superlattices show very weak SHG signal at $T = 77$ K, which slightly increases at increased angles of $\theta$, similar to the residual SHG observed in the pure
SrTiO$_3$ films grown on LSAT above the ferroelectric transition,[21] and is attributed to the manifestation of nano-polar regions in the films.

6.8 Discussion

In attempting to understand why some of the superlattices show polar activity and others do not, a few considerations must be taken into account. The first consideration is that there is a critical thickness limit for the stabilization of ferroelectricity in a thin film material, which has been experimentally determined to range from $\sim$ (4-7) unit cells (1.6-2.8) nm for BaTiO$_3$ films,[35, 36] and can be as low as 3 unit cells (1.2 nm) in PbTiO$_3$ films.[37] Figure 6-16(a) shows the transition temperatures of the superlattices as a function of $n$, where only the $n = 3, 7$-10 samples showed transitions above $T = 77$ K. The $n = 7$-10 superlattices have unit cell thickness ranging from (5.4-7.7) nm, and considering that the individual layer thickness of ferroelectric SrTiO$_3$ and CaTiO$_3$ slabs are approximately half of the superlattice thickness, thicknesses range from (2.7-3.9) nm for the $n = 7$-10 superlattices, as plotted on the top axis of Figure 6-16. These thickness are above the critical thickness limit for ferroelectricity to emerge and hence polar transitions are observed for $n \geq 7$ superlattices. For the $n = 1, 2, 4, 5$, and 6 superlattices, a polar transition was not observed since the individual layer thicknesses were too thin for ferroelectricity to emerge, i.e. below the critical thickness limit. However, a polar transition was observed for the $n = 3$ superlattice, which is below the critical thickness limit.

To explain this discrepancy, the second point that needs to be considered is that doped Sr$_{1-x}$Ca$_x$TiO$_3$ bulk crystals show ferroelectricity up to $T_C \sim 35$ K for $x \sim 0.04$,[28] and for larger concentrations of $x = 0.2$ the ferroelectric transition occurs at $T_C \sim 125$ K,[27] and for $x = 0.25$, $T_C \sim 160$ K,[38-40] however the ferroelectric transition becomes much more diffuse and the dielectric permittivity dramatically decreases. Therefore, intermixing of Sr and Ca cations in a
superlattice matrix can lead to ferroelectricity, where strain could potentially shift the doping-induced ferroelectric transition to higher temperatures. For the $n = 3$ superlattice, there is a large degree of Sr and Ca intermixing throughout the film as evidenced by STEM-EDS mapping as well as $n^{th}$ order XRD satellite peak splitting, as shown in Figure 6-16(b). Thus, the $n = 3$ superlattice can be considered as a ‘digitally’-doped 100 nm thick Sr$_{1-x}$Ca$_x$TiO$_3$ film, and the emergence of the polar phase is solely due to Sr and Ca cation intermixing since it is below the critical thickness limit for a ferroelectric phase to stabilize. Note that the emergence of a polar phase in the superlattices with $n \geq 7$ which had larger $\Delta n$ values, the observed polar response from SHG measurements is likely a mixture of the polar responses from pure SrTiO$_3$ and CaTiO$_3$ slabs and the intermixed interface regions.

The possibility of a critical thickness limit for ferroelectricity to emerge in superlattices could have important implications. The majority of theoretical investigations of enhanced ferroelectricity in complex oxide superlattices such as (BaTiO$_3$)$_n$/(SrTiO$_3$)$_n$, (BaTiO$_3$)$_n$/(CaTiO$_3$)$_n$, and (BaTiO$_3$)$_n$/(SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ have mainly focused on short period thickness such as $n = 1, 2, and 3$,[41, 42] however, it may be challenging to experimentally realize ferroelectricity for such thin capacitor layers.[43-45] Although ferroelectricity has been reported for $n = 1$ and $n = 2$ (BaTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices grown by pulsed laser deposition,[7, 46] the structural quality of these superlattice films as determined by XRD measurements showed splitting of the $n^{th}$-order satellite peaks, suggesting that the superlattices may have possessed relatively large degrees of A-site mixing, and Ca-doped BaTiO$_3$ is known to be a relaxor ferroelectric albeit decreased transition temperatures with increasing Ca concentrations.[27, 47] These results underscore the critical importance for determining the effects of the structural quality of superlattice film materials (i.e. interface roughness and stoichiometry) and the emergence of ferroelectricity as the dimensionality of superlattices are scaled towards nanometer thicknesses. While this work focused on strain-induced ferroelectricity in (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices grown by
overlapping growth windows in hybrid molecular beam epitaxy, it could motivate future
exploration of emergent novel phenomena in other complex oxide superlattice systems and how
scaling and cation intermixing effect the targeted properties, which would greatly advance the
field of interface engineering in complex oxides.
Figure 6-1: Unit cells of (a) SrTiO$_3$ and (b) CaTiO$_3$, which are under compressive (-0.95 %) and tensile (+1.26 %) strain when grown on (001)LSAT. Arrows indicate the strain direction. (c) The anti-directional strains for SrTiO$_3$ and CaTiO$_3$ layers in the superlattice grown on LSAT substrate.
Figure 6-2: Reflection high energy electron diffraction (RHEED) recorded from the 01 diffraction streak along the <110> azimuth for SrTiO$_3$(001)LSAT films grown at Sr fluxes of (a) $\Phi_{\text{Sr}}=2.5\times10^{13}$ atoms/cm$^2$s$^{-1}$ and (b) $\Phi_{\text{Sr}}=3.0\times10^{13}$ atoms/cm$^2$s$^{-1}$, as well as CaTiO$_3$(001)LSAT films grown at Ca fluxes of (c) $\Phi_{\text{Ca}}=2.5\times10^{13}$ cm$^2$s$^{-1}$ and (d) $\Phi_{\text{Ca}}=2.0\times10^{13}$ cm$^2$s$^{-1}$. Only the first 12 minutes of growth are shown to better emphasize the RHEED oscillations. The corresponding TTIP flux ($p_{\text{TTIP}}$) values are shown on the right axis of each graph. The growth window regions are indicated by the shaded area on the right axis of each panel, with the Ti-rich and A-site rich films labeled in the graphs.
Figure 6-3: X-ray diffraction 2θ-ω scans about the 002_p film peak of SrTiO_3/(001)LSAT films grown at Sr fluxes of (a) Φ_{Sr}=2.5×10^{13} atoms/cm^2s^{-1} and (b) Φ_{Sr}=3.0×10^{13} atoms/cm^2s^{-1}, as well as CaTiO_3/(001)LSAT films grown at Ca fluxes of (c) Φ_{Ca}=2.5×10^{13} cm^2s^{-1} and (d) Φ_{Ca}=2.0×10^{13} cm^2s^{-1}. The corresponding TTIP flux (p_{TTIP}) values are shown on the right axis of each graph. The film peaks are indicated by arrows, and the LSAT substrate peak is indicated by an asterisk (*). The growth window regions are indicated by the shaded area on the right axis of each panel, with the Ti-rich and A-site rich films labeled in the graphs.
Figure 6-4: (a) The out-of-plane c-axis lattice parameter extracted from XRD measurements, and (b) growth rate extracted from RHEED, as a function of TTIP flux ($p_{\text{TTIP}}$) for each SrTiO$_3$/[001]LSAT film series (left-axis) grown at Sr fluxes of $\Phi_{\text{Sr}}=2.5 \times 10^{13}$ atoms/cm$^2$s$^{-1}$ (purple up triangles) and $\Phi_{\text{Sr}}=3.0 \times 10^{13}$ atoms/cm$^2$s$^{-1}$ (green down triangles), as well as CaTiO$_3$/[001]LSAT films (right-axis) grown at Ca fluxes of (c) $\Phi_{\text{Ca}}=2.0 \times 10^{13}$ cm$^2$s$^{-1}$ (blue squares) and (d) $\Phi_{\text{Ca}}=2.5 \times 10^{13}$ cm$^2$s$^{-1}$ (red circles). The growth window regions are indicated by the shaded areas, with the overlapping growth window region highlighted in gray.
Figure 6-5: Schematic of the growth scheme for an n=2 superlattice, showing the deposition sequence where Sr and TTIP sources are both opened to build the SrTiO$_3$ layer, which are then closed and a pause period is allowed, and then Ca and TTIP sources are both opened to build the CaTiO$_3$ layer. This sequence is then repeated to build the superlattice crystal structure shown below. The shuttering times of the sources are determined by RHEED intensity oscillations where the maxima in the oscillations correspond to the completion of individual unit cell layers.
Figure 6-6: (a) Time dependent RHEED intensity oscillations over > 2 hours of growth time for the \( n=1-10 \) (SrTiO\(_3\))\(_n\)/C(TiO\(_3\))\(_n\) superlattices from bottom to top, respectively. The deposition of the individual SrTiO\(_3\) and Ca(TiO\(_3\)) layers for the \( n=10 \) superlattice are indicated on the top curve by green and blue shaded areas, respectively. Zoom-in sections of the time dependent RHEED oscillations shown at (a) the beginning of growth, and (b) the end of growth, which show qualitatively very similar features.
Figure 6-7: STEM ADF images for the (a) \( n=2 \) and (b) \( n=5 \) \((\text{SrTiO}_3)_n/(\text{CaTiO}_3)_n\) superlattices, where the brightest dots correspond to Sr atoms. The initial \( \text{SrTiO}_3 \) buffer layer is labeled in each image, above the LSAT substrate region. The \( \text{SrTiO}_3 \) and \( \text{CaTiO}_3 \) layers are labeled in (b) on the right. The scale bar in (a) and (b) is 10 nm. Zoom in HAADF STEM images for (c) \( n=2 \), (d) \( n=3 \), (e) \( n=4 \), and (f) \( n=5 \) superlattices; the vertical scale bar in each panel is 2 nm. Intensity profiles of the dashed red lines are plotted to the right of each panel, showing the pixel intensity of the Sr and Ca atomic columns.
Figure 6-8: STEM ADF images for (a) $n = 3$ and (b) $n = 4$ (SrTiO$_3$)$_n$/CaTiO$_3$$_n$ superlattices. The SrTiO$_3$ and CaTiO$_3$ layers are shown on the right side of each image, where the brightest dots correspond to the Sr atoms. The white scale bar in each image is 5 nm. Images courtesy of Jason Lapano and Greg Stone at PSU.
Figure 6-9. (a) EDS mapping of (a) Ti, (b) Ca, and (c) Sr atoms in $n = 3$ superlattice. (e) Overlapping EDS maps of Ti, Ca, and Sr atoms. The purple arrows on the right indicate the Sr and Ca intermixing (purple dots) which occur in the first unit cell layer of each SrTiO$_3$ and CaTiO$_3$ slab. Image courtesy of Jason Lapano.
Figure 6-10: Reciprocal space maps around the 103 LSAT substrate peak for (a) $n=3$ and (b) $n=8$ (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices. The 10L superlattice film peaks are indicated with the L index underlines. The RSM plots are in reciprocal lattice units (r.l.u.) of the LSAT substrate.
Figure 6-11: X-ray diffraction $2\theta$-$\omega$ scans of the 00L peaks in reciprocal lattice units (r.l.u.) of the LSAT substrate for the $n = 1$-$10$ $(\text{SrTiO}_3)_n/(\text{CaTiO}_3)_n$ superlattices. The 00(n), 00(2n), 00(3n) and 00(4n) peak positions are labeled on top, with dashed red lines and asterisks corresponding to the 001 and 002 LSAT substrate peaks. The $n^{th}$ order satellite diffraction peaks are highlighted in blue.
Figure 6-12. (a) Zoom-in of the 00(2n) peaks, showing the thickness fringes. (b) Zoom-in of the peak splitting for the 00(3n) peaks, with the error in n determined from the degree of peak splitting which is indicated by the red arrows. (c) The interface roughness parameter, $\Delta n$, and (b) the c-axis lattice parameter for the $n=1$-10 (SrTiO$_3$)$_n$/(CaTiO$_3$)$_n$ superlattices, as determined from the degree of splitting of the 00(3n) peaks and superlattice satellite peak positions with linear fit to the c-axis values in shown as the black line. The linear fit parameters are shown with a coefficient of determination of $R^2=1$. 
Figure 6-13: (a) Schematic of the SHG experimental setup, where the linear polarized electric field of the fundamental laser beam ($E_{\omega}$) can be rotated by an angle $\phi$, and is focused onto the film/substrate sample, and the second harmonic field ($E_{2\omega}$) is measured in the plane of incidence. The film/sample axes are shown, where the sample can be rotated about the [010] axis by $\theta$. (b) Temperature dependent SHG intensity for a stoichiometric SrTiO$_3$ (green) and CaTiO$_3$ (blue) film, with the LSAT substrate signal show as the black line, indicating the noise level for the measurements performed with the sample orientation fixed at $\theta=45^\circ$ and $\phi=0^\circ$. The transitions for the SrTiO$_3$ and CaTiO$_3$ film are indicated by the green and blue arrows, respectively.
Figure 6-14: Low temperature ($T=77K$) SHG intensity as a function of $\theta (\phi = 0^\circ)$ for the (c) SrTiO$_3$ (green squares) and (d) CaTiO$_3$ (blue circles) films, with polar plots shown as the top insets taken at $\theta = -45^\circ$, $0^\circ$, and $+45^\circ$ where $\phi$ was rotated $360^\circ$. Theoretical fits for a tetragonal $4mm$ and monoclinic $m$ point group symmetry are shown as red lines to the SHG data in (c) and (d), respectively. The polarization direction for (e) the SrTiO$_3$ film is assumed to be out-of-plane along the [001] and (f) the CaTiO$_3$ film is in the mirror ($m$) plane and has both an in-plane and out-of-plane polarization component.
Figure 6-15: Temperature dependence of the SHG intensity ($\theta=45^\circ$, $\phi=0^\circ$) for $n=1$-10 $(\text{SrTiO}_3)_n/(\text{CaTiO}_3)_m$ superlattices, with the same incident laser power density of $\sim3.0$ W/cm$^2$.

Transitions for $n=3$, 7-10 are indicated by arrows for the heating (right) and cooling (left) scans, with the SHG intensity for the LSAT substrate shown in each panel as the black line. No transitions are observed for the $n=1$, 2, 4, 5, and 6 superlattices over the measured temperature range (black curves). (b) Low temperature ($T=77$K) SHG tilt scans (bottom), and polar plots (top), for $n = 3$, 7-10 superlattices.
Figure 6-16: (a) Transition temperature determined from SHG experiments and the SHG intensity ($I_{2\omega}$) measured at $T = 77$ K ($\theta = 45^\circ$, $\phi = 0^\circ$) on the left and right axes respectively, for the $n = 1$-10 superlattices. (b) $\Delta n$ parameter for the $n = 1$-10 superlattices. The top axis shows the half $c$-axis unit cell thickness as a function of $n$. The highlighted region around $n = 3$ indicates that the polar transition is caused by A-site intermixing, whereas the highlighted region around $n=6$-$7$ indicates the critical thickness for ferroelectricity to emerge in the superlattices.
6.10 References


Chapter 7

Creating Ruddlesden-Popper phases by hybrid molecular beam epitaxy

7.1 Abstract

The synthesis of a 50 unit cell thick \( n=4 \) \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) (\( \text{Sr}_5\text{Ti}_4\text{O}_{13} \)) Ruddlesden-Popper (RP) phase film is demonstrated by sequentially depositing \( \text{SrO} \) and \( \text{TiO}_2 \) layers in an alternating fashion using hybrid molecular beam epitaxy (MBE), where Ti was supplied using titanium tetraisopropoxide (TTIP). A detailed calibration procedure is outlined for determining the shuttering times to deposit \( \text{SrO} \) and \( \text{TiO}_2 \) layers with precise monolayer doses using \textit{in-situ} reflection high energy electron diffraction (RHEED) as feedback. Using optimized \( \text{Sr} \) and TTIP shuttering times, a fully automated growth of the \( n=4 \) RP phase was carried out over a period of \( >4.5 \) hours. Very stable RHEED intensity oscillations were observed over the entire growth period. The structural characterization by X-ray diffraction and high resolution transmission electron microscopy revealed that a constant periodicity of four \( \text{SrTiO}_3 \) perovskite unit cell blocks separating the double \( \text{SrO} \) rocksalt layer was maintained throughout the entire film thickness with very little amounts of planar faults oriented perpendicular to the growth front direction. These results illustrate that hybrid MBE is capable of layer-by-layer growth with atomic level precision and excellent flux stability.

\*Taken and adapted from work published in Appl. Phys. Lett. 109, 043102 (2016).
7.2 Introduction

Layered complex oxide materials, such as $A_{n+1}B_nO_{3n+1}$ Ruddlesden-Popper (RP) phases,\cite{1} are attracting a great deal of scientific interest. They can be thought of as a simple stacking sequence of AO and BO$_2$ monolayers (MLs) in an alternating fashion with the addition of an extra AO rocksalt layer introduced for every $n$ perovskite unit cells. Depending on the elements occupying the A and B sites this layered structure can possess a broad range of functional properties that are either different or completely absent in the parent ABO$_3$ perovskite compound where ferroelectricity,\cite{2} ferromagnetism,\cite{3} superconductivity,\cite{4, 5} colossal magnetoresistance,\cite{6} high temperature piezoelectricity,\cite{7, 8} as well as photocatalytic properties \cite{9} can emerge or are enhanced in RP phases.

The majority of RP phases have been synthesized through conventional solid state bulk synthesis routes,\cite{10} where only early members of the homologous series ($n < 3$) are phase pure. Stabilization of higher $n$ phases is not possible since this layered material tends to separate into $n<3$ phases as well as the $n=\infty$ end member (ABO$_3$) of the RP series.\cite{1, 11} This presents a serious roadblock when targeted properties only emerge in RP phases with $n > 3$.\cite{12-14} Modern thin film growth techniques such as pulsed laser deposition (PLD) and molecular beam epitaxy (MBE), have overcome this challenge by sequentially depositing individual MLs of AO and BO$_2$.\cite{15-23} Using these growth techniques, $n > 3$ RP films such as Sr$_{n+1}$Ti$_n$O$_{3n+1}$,\cite{14, 17, 24, 25} Sr$_{n+1}$Ru$_n$O$_{3n+1}$,\cite{26} and Ca$_{n+1}$Mn$_n$O$_{3n+1}$,\cite{20} have been demonstrated. In both approaches, the doses needed to deposit AO and BO$_2$ MLs have to be precisely determined. This is commonly achieved using \textit{in-situ} reflection high energy electron diffraction (RHEED) intensity. Characteristic RHEED features provide information about the type and degree of nonstoichiometry arising from small deviations of the ML dosage.\cite{16, 27} However, maintaining correct doses during growth can be challenging. Low vapor pressure sources, such as Ti, have
large flux drifts of ~2.5% per hour [28] which can ultimately lead to nonstoichiometric intergrowths. For example, transmission electron microscopy micrographs of Sr
\(_{n+1}\)Ti\(_n\)O\(_{3n+1}\) RP films revealed a significant increase in the amount of intergrowth regions at the top of RP films in comparison to the film/substrate interface.[29] Incorporation of nonstoichiometric defects and incorrect ML doses due to flux drifts can severely degrade targeted material properties.[30-33] Consequently, there is a strong impetus for new thin film synthesis methodologies with atomic layer precision which provide better flux stability to enable the growth of high quality phase pure layered oxides.

A promising growth technique for achieving high quality oxide films has recently been demonstrated by hybrid molecular beam epitaxy (MBE), which utilizes metal-organic molecules to supply the B-site cation.[34-40] Titanate films grown by hybrid MBE commonly employ titanium tetraisopropoxide (TTIP) [41] to supply the low vapor pressure Ti cation with the higher vapor pressure A-site cation supplied using a standard effusion cell. The high volatility of TTIP allows access to a stoichiometric growth window for SrTiO\(_3\) films for which the Sr:Ti ratio is self-regulated and independent of the supplied Sr and TTIP fluxes.[34] Using the hybrid MBE approach, record high electron mobilities > 50,000 cm\(^2\)/Vs in La-doped SrTiO\(_3\) films have been reported [42] and device quality factors of \(Q = 1/\tan(\delta) > 1000\) in Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\) were achieved,[43] highlighting the low defect concentrations that can be attained using this technique.

In this letter, it is demonstrated how to construct an \(n=4\) Sr\(_5\)Ti\(_4\)O\(_{13}\) RP film, which is otherwise inaccessible through bulk synthesis routes,[11] using hybrid MBE in a layer-by-layer growth fashion by sequentially supplying Sr and TTIP. A detailed calibration procedure is outlined for determining the precise deposition times of SrO and TiO\(_2\) layers using \textit{in-situ} RHEED feedback in order to build the RP film. The RHEED intensity oscillation for the RP film remained very stable with extremely reproducible features throughout the entire ~5 hour growth period, demonstrating the excellent flux stability using this technique. The structural quality of the \(n=4\)
Sr\textsubscript{5}Ti\textsubscript{4}O\textsubscript{13} RP film was characterized using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) which revealed a uniform periodicity of the n=4 unit cell throughout the entire film thickness with low levels of vertically aligned SrO rocksalt layer intergrowths.

### 7.3 Calibrating atomic layer deposition times using RHEED feedback

Films were grown on (100) oriented SrTiO\textsubscript{3} substrates at a growth temperature of $T_{\text{sub}} = 750$ °C inside of a DCA M600 MBE chamber, shown schematically in Figure 7-1. A thermal effusion cell was used to supply elemental Sr, and gas inlet systems were used to supply the TTIP and molecular oxygen ($p_{O_2} = 1 \times 10^{-7}$ Torr). The Sr flux was calibrated to be $2.5 \times 10^{13}$ atoms/cm\textsuperscript{2}/s using a quartz crystal microbalance. The TTIP flux was held constant by maintaining the gas inlet pressure via a motorized leak valve which was PID controlled using a capacitance manometer gauge. Figure 7-2(a) shows a schematic of the growth scheme where SrO and TiO\textsubscript{2} MLs were sequentially deposited by opening and closing the shutters to build up the SrTiO\textsubscript{3} film, shown in Figure 7-2(b), in a layer-by-layer fashion. For the deposition of TiO\textsubscript{2} layers, the TTIP molecule thermally decomposes into TiO\textsubscript{2} and organic byproducts; Ti-[O-CH-(CH\textsubscript{3})\textsubscript{2}]\textsubscript{4}(g) $\rightarrow$ TiO\textsubscript{2}(s) + 4 C\textsubscript{3}H\textsubscript{6}(g) + 2 H\textsubscript{2}O(g).[44] The high vapor pressure of the organic byproducts formed allows them to be effectively pumped away, with small amounts of carbon contamination in the films at the growth temperatures employed here.[45] RHEED intensity oscillations of the 01 diffraction streak taken along the $<1\overline{1}0>$ azimuth were recorded, which is known to show characteristic intensity oscillation profiles depending on the type and degree of Sr:Ti ratio as well as SrO/TiO\textsubscript{2} ML doses.[16, 46] For an ideal dose of single SrO and TiO\textsubscript{2} MLs in stoichiometric ratios, RHEED oscillations exhibit sinusoidal-like oscillations with constant peak amplitudes as shown in Figure 7-2(c).
The calibration procedure to determine single ML dose shutter times using RHEED feedback is discussed next. Figure 7-3(a) shows a parameter space of the Sr and TTIP shutter times for nine different (1-9) growth points. The goal is to quickly find the correct shuttering times for supplying the Sr and TTIP fluxes in an ideal ~ 1:1 Sr:Ti cation ratio (indicated as the dashed red line in Figure 7-3(a)) as well as 1-to-1 SrO-to-TiO$_2$ ML dosage per shutter cycle, which is located at position (7). Deviation from the stoichiometric line can result in Sr-rich (bottom right of Figure 7-3(a)) and Ti-rich (upper left of Figure 7-3(a)) deposition times, and deviation along the ‘stoichiometric line’ could arise from < 1 ML dosages (lower left corner) or for > 1 ML dosages (upper right corner). Navigating to all points (1-9) was done by adjusting the Sr and TTIP shutter times and recording the RHEED oscillation profiles to identify their position in the shutter time parameter space relative to the ideal position, (7). The entire calibration procedure was performed on a single substrate sample. First, two shutter times for Ti rich conditions were determined, one with a longer TTIP shutter time, and one with shorter Sr shutter time with respect to point (7), as indicated by points (1) and (2) in Figure 7-3(a), respectively. For these two Ti-rich shutter times, the amplitude of the RHEED intensity oscillation continuously increased or decreased with subsequent layer depositions, as shown in the top of Figure 7-3(b), corresponding to shutter times (1) and (2) in Figure 7-3(b), respectively.

In the next step, shutter times for two Sr-rich conditions were chosen. Starting from position (1), the Sr shutter time was kept constant and TTIP shutter time was reduced. Conversely, for shutter times of position (2) the TTIP shutter time was fixed and Sr shutter time was increased. The respective shutter times were changed until double peak features appeared in the RHEED intensity profile, as shown in the bottom of Figure 7-3(b), corresponding to the shutter times marked by (3) and (4) in Figure 7-3(a). These four positions (1-4) clearly identify the extreme nonstoichiometric RHEED characteristics. The next shutter time refinement step is to achieve a 1:1 cation ratio, or the ‘stoichiometric line’. This was done by systematically
adjusting the stoichiometric shuttering times in point (7) to obtain four different dosages along the stoichiometry line shown as points (5,6) for < 1-to-1 MLs and points (8,9) for > 1-to-1 MLs. To calibrate precise ML deposition times, the beat frequency of the resulting RHEED oscillation profile is measured, as shown in Figure 7-4. The beating in the RHEED intensity oscillation corresponds to the deposition of either excess or insufficient SrTiO$_3$ unit cells.[16, 27] The longer the time period of the superimposed intensity modulation, the closer the shutter times are to the ideal 1:1 ML dose per cycle. The bottom and top curves in Figure 7-4 show RHEED oscillation patterns where the beat period was approximately ten oscillations, corresponding to a dose of ~ 0.90 [position (5)] and 1.10 MLs [position (9)] per cycle. The beat period then becomes approximately 20 oscillations long for a dose of 0.95 [position (6)] and 1.05 MLs [position (8)] per cycle. Finally, no beating was observed for the stoichiometric dose of a single ML per cycle, position (7), as shown for the middle RHEED oscillation curve in Figure 7-4. Note that these stoichiometry and ML dosage dependent RHEED characteristics are qualitatively the same as those observed for sequentially layered SrTiO$_3$ films grown by conventional MBE where Ti is thermally supplied. This indicates that using TTIP to deposit the TiO$_2$ layers is completely viable for this growth scheme. It may also have an advantage due to the favorable growth kinetics where excess TTIP molecules can desorb from the growth front, avoiding excess Ti from being incorporated into the film. Using the optimized Sr and TTIP shutter times located at position (7) in Fig. 2(a) ($t_{\text{Sr}} = 29.4$ s, $t_{\text{TTIP}} = 31.5$ s), a 30-nm-thick SrTiO$_3$ film was grown on a (100)SrTiO$_3$ substrate. An X-ray diffraction 20-0 scan about the 002 SrTiO$_3$ film peak (Phillips X’Pert Panalytical Pro using CuK$_{\alpha 1}$ radiation) revealed that the film was stoichiometric since no shoulder from the film peak was observed with respect to the substrate peak, as shown in Figure 7-5. A nonstoichiometric Sr:Ti ratio would have resulted in a shift of the SrTiO$_3$ film peak with respect to the SrTiO$_3$ substrate peak towards smaller scattering angles.[46, 47]
7.4 Atomic layer-by-layer deposition of \( n=4 \) \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) RP film

Having found ideal shuttering times using the calibration methodology discussed above, a 50 unit cell thick \( n=4 \) \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) RP film was grown using sequential deposition of SrO and TiO\(_2\) layers in an alternating fashion while adding an additional SrO layer after every 4 SrTiO\(_3\) unit cells, as shown schematically in Figure 7-6. A pause in the growth of ~30 seconds was made before depositing the additional SrO rocksalt layer to provide sufficient time to enable a smooth and abrupt interface. The RHEED intensity oscillation taken during the entire ~5 hour growth time of the RP film is shown in Figure 7-6(a). A 10 unit cell buffer layer of SrTiO\(_3\) was deposited first on (100)SrTiO\(_3\) substrate to provide a well terminated SrO layer to start the first double SrO rocksalt layer in the RP structure. The layer-by-layer RHEED intensity profile was extremely stable throughout the entire growth. Figure 7-6(b) and Figure 7-6(c) shows the RHEED intensity profile at the beginning and end of growth, respectively, which are very consistent to one another. The constant RHEED intensity and similar RHEED oscillation profile features observed throughout the entire growth indicates that both, Sr and TTIP fluxes, were very stable even over extended periods of growth time.

7.5 XRD and HRTEM analysis of RP film structure quality

The structural quality of the \( n=4 \) \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) RP film was determined by XRD 2\( \theta \)-\( \omega \) scans of the 00L film peaks, as well as HRTEM imaging (JOEL 2010F microscope operated at 200 kV) of the entire film structure, as shown in Figure 7-7 and Figure 7-8, respectively. The out of plane \( c \)-axis lattice parameter of the \( n=4 \) RP film was determined to be \( c = (35.7 \pm 0.2) \) Å from the \( 2\theta \) positions of the RP film peaks, which is very close to the \( c \)-axis value of \( 35.6\pm0.2 \) Å reported by Haeni et al. [24] for a \( \text{Sr}_5\text{Ti}_4\text{O}_{13} \) RP film grown on (100)SrTiO\(_3\) substrate by conventional MBE.
Note that the odd numbered 00L peaks are absent due to the reflection condition of \( L=2n \) of the tetragonal \( I4/mmm \) space group symmetry for the \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) RP structure.[1] The HRTEM image showed a consistent and repeated periodicity of four \( \text{SrTiO}_3 \) perovskite unit cell blocks separating the extra \( \text{SrO} \) rocksalt double layer throughout the entire film thickness, albeit with some occurrences of short, vertically aligned double \( \text{SrO} \) rocksalt stacking faults as well. The ratio of vertically aligned \( \text{SrO} \) layers to the desired horizontally aligned \( \text{SrO} \) rocksalt layers is \(< 5\%\). These vertically aligned \( \text{SrO} \) rocksalt layers have been commonly observed for the case of \( n > 3 \) \( \text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1} \) RP thin films reported in literature [14, 29] and are believed to manifest in order to accommodate for very slight imbalances of the local \( \text{Sr}:\text{Ti} \) stoichiometry at the growth front during film growth. These vertically aligned \( \text{SrO} \) rocksalt layers will generally occur with a separation distance of integer multiples of \( n \) (i.e. \( n = 8, 12, \text{etc.} \)), which we also observe in our RP film. Note that in the case of absolute perfect stoichiometric and one-to-one monolayer dose conditions, these vertically aligned \( \text{SrO} \) rocksalt layers would not be observed. Hence, further improvement for refining the \( \text{SrO} \) and \( \text{TiO}_2 \) layer deposition times can be made for this technique, however at the expense of longer and longer calibration times for achieving a beat frequency period of zero as indicated for position (7) in Figure 7-4. Nevertheless, the \( n=4 \) RP film grown here using hybrid MBE approach displayed a high level of structural quality throughout the entire film thickness, rendering this growth scheme as a promising route towards synthesis of high quality layered complex oxide structures.

### 7.6 Conclusions

In summary, the advantages of hybrid MBE for layer-by-layer growth is illustrated through extremely stable fluxes and excellent control over ML dosage using RHEED calibration
methods, as demonstrated by the synthesis of a high quality \( n=4 \) Sr\(_5\)Ti\(_4\)O\(_{13}\) RP film. The accelerated discovery of new growth windows in other complex oxides such as BaSnO\(_3\) [40] BaTiO\(_3\) [48] GdTiO\(_3\) [49] CaTiO\(_3\), SrVO\(_3\) [37] and LaVO\(_3\) [39] along with theoretical predictions of functional properties such as ferroelectricity in artificially layered (Ca/Sr/Ba)\(_{n+1}\)(Sn/Zr/Ge)\(_n\)O\(_{3n+1}\), [50] antiferromagnetism and metal-to-insulator transitions in Sr\(_{n+1}\)Ir\(_n\)O\(_{3n+1}\), [51, 52] and enhanced optical and ferroelectricity properties in Sr\(_{n+1}\)Sn\(_n\)O\(_{3n+1}\), [13, 53] a powerful synergistic coaction between advanced thin film growth techniques and theoretical predictions could potentially lead to the realization of new functional material paradigms in the vast chemical and geometric configurational space offered by layered complex oxides.
Figure 7-1: Schematic of a hybrid MBE chamber used for sequential shuttered growth of layered SrTiO$_3$ films with Sr supplied from a standard effusion cell and TTIP from a gas injector in the presence of molecular oxygen O. The TTIP and O gas inlet pressures are PID controlled using a motorized leak valve (LV) and capacitance manometer gauge (CM).
Figure 7-2: (a) Deposition sequence of alternating SrO and TiO₂ MLs to build (b) the SrTiO₃ perovskite structure. (c) RHEED oscillation profile for precisely one monolayer of SrO and TiO₂ doses.
Figure 7-3: (a) Sr and TTIP shutter time parameter space map for depositing SrTiO$_3$ with 1:1 Sr:Ti cation stoichiometry (red dotted line) and single ML dosage which is located at point 7 (red square). The Ti-rich region (top left corner) and Sr-rich region (bottom right corner) are shaded in blue and green, respectively. (b) RHEED intensity oscillations for Ti-rich (top) and Sr-rich (bottom) with shutter times corresponding to points 1, 2, 3, and 4 in panel (a).
Figure 7-4: RHEED intensity oscillation beating for stoichiometric shutter times and doses systematically adjusted from (0.90, 0.95, 1.00, 1.05, 1.10) MLs corresponding to points (5, 6, 7, 8 and 9) in Figure 7-4(a). The beating periods are indicated by blue arrows, which increase as the 1.0/1.0 SrO/TiO$_2$ ML dosage timing is approached.
Figure 7-5: X-ray diffraction 2θ-ω scan of the 002 SrTiO$_3$ reflection for a 30-nm-thick SrTiO$_3$ film grown on (100)SrTiO$_3$ using sequential shuttering of Sr and TTIP. The good overlap of film and substrate peak, i.e. the absence of a film peak on the substrate peak shoulder towards smaller scattering angles indicates that cation stoichiometric SrTiO$_3$ films can be grown by hybrid MBE in a layer-by-layer fashion.
Figure 7-6: (a) RHEED intensity oscillation profile for entire growth of n=4 Sr₅Ti₄O₁₃ RP film on (100)SrTiO₃ substrate. The RP stack was built by depositing 50 repeat units of the Sr and TTIP shuttering sequence shown in (b) with the corresponding RP crystal structure show above containing the extra SrO rocksalt layer in the middle. The gray regions indicates a pause period where nothing was deposited, enabling a smooth interface for the additional SrO rocksalt layer to be deposited. The initial RHEED in (a) shows the 10 unit cell thick SrTiO₃ buffer layer deposited to ensure a well terminated seed layer for RP film growth. (c) RHEED oscillation profiles of a single RP unit cell at the end of growth (top right inset) has consistent RHEED features compared to the beginning of growth.
Figure 7-7: X-ray diffraction 2θ-ω scan of the 00L peaks of the n=4 Sr$_5$Ti$_4$O$_{13}$ RP film. The out-of-plane c-axis lattice parameter of the n=4 RP film structure was determined to be $c = (35.7 \pm 0.2)$ Å.
Figure 7-8: HRTEM image of the entire RP film with the SrTiO$_3$ buffer layer region labeled on bottom and epoxy on top. The unit cell crystal structure of the RP film is shown on the right, corresponding to the black outlined rectangle area in the image.
7.8 References


Chapter 8

Nonlinear optical properties of strained BiFeO$_3$ thin films

8.1 Large nonlinear optical coefficients in pseudo-tetragonal BiFeO$_3$ films*

8.1.1 Abstract

BiFeO$_3$ (BFO) is one of the most intensely studied multiferroic materials due to the coexistence of a strong ferroelectric polarization ($P_s \sim 90 \mu$C/cm$^2$) and weak ferromagnetism ($\sim 0.02 \mu_B$/unit cell) at room temperature.[1-3] Recently, BFO has also been recognized as a promising candidate for many photonic applications ranging from terahertz wave generation,[4, 5] electro-optical modulation,[6] infrared detection,[7] photoconduction,[8, 9] and ultrafast devices.[10] It has been shown that a structural phase transition from a pseudo-rhombohedral (R) to pseudo-tetragonal (T) phase occurs at ~4.5% compressive strain,[11-14] where increased ferroelectric polarization and electromechanical responses have been reported.[15, 16] as illustrated in the temperature-strain-phase diagram of BFO is shown in Figure 8-1, which was adapted from Ref.[11]. In this chapter, it is shown that using optical second harmonic generation (SHG) analysis, enhanced nonlinear optical (NLO) properties are measured for T-BFO thin films as well as nominally unstrained R-BFO film. As future photonic applications for BFO thin films are realized, the investigation of strain-enhanced nonlinear optical properties could play a vital role for optimizing material performance and functionality.

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In previous works, the nonlinear optical $d_{ij}$ coefficients of R-BFO have been reported, although there are discrepancies in the literature. Using density functional theory, Ju et al. calculated the spectroscopic $d_{ij}$ values for bulk BFO[17] and strained T-BFO[18] systems, which is henceforth referred to as theory. Kumar et al.[19] reported $d_{ij}$ values of a R-BFO thin film at a fundamental wavelength of 800 nm that are not consistent with theory, which can be attributed to an incorrect SHG model (Eq. (4) in Ref. [19]). Yokota et al.[20] measured the $d_{ij}$ coefficient ratios for bulk BFO at 1064 nm, however, their reported values are also inconsistent with theory. There are no reports on the measured $d_{ij}$ coefficient values for T-BFO thin films. In order to address these discrepancies in the literature, a method if formulated to accurately measure the coefficients for a thin film/substrate system, and we report $d_{ij}$ coefficient values at 800 nm and 1550 nm for both R-BFO and T-BFO films which are consistent with theory.

8.1.2 Strain-induced tetragonal phase of BiFeO$_3$

The films studied here were grown by reactive molecular-beam epitaxy,[11] with well-defined orientations of R and T-BFO on (111) SrTiO$_3$ (STO) and (110) YAlO$_3$ (YAO) substrates with lattice misfit strains of -1.1% and -6.9%, respectively. Schematics of the R-BFO and T-BFO unit cells are shown as insets in Figure 8-1. The orientation of the 25 nm thick R-BFO film is (111)$_{p}$BFO on (111)STO and [1-10]$_{p}$BFO || [1-10]STO, with the crystal physics axes defined as: $z_1 = [1-10]_p$, $z_2 = [11-2]_p$, and $z_3 = [111]_p$, where subscript $p$ denotes the pseudo-cubic indices. The orientation of the 25 nm thick T-BFO film is (001)BFO on (110)YAO and [010]BFO || [1-10]YAO, with the crystal physics axes defined as; $z_1 = [100]$, $z_2 = [010]$, and $z_3 = [001]$. X-ray diffraction measurements, shown in Figure 8-2, were performed to determine the lattice parameters of the strained R and T-BFO films. On axis 20-0 scans of the 00L reflections for T-BFO yield an out-of-plane lattice parameter of $c = 4.670 \pm 0.002$ Å, shown in Figure 8-2(a).
Using a combination of off-axis H0L and 0KL reflections, the in-plane lattice parameter of T-BFO was determined to be \( a = 3.751 \pm 0.002 \text{ Å} \). Figure 8-2(c) shows an on-axis 2θ-ω scan of the 111\(_p\) and 222\(_p\) reflections for R-BFO, giving a pseudocubic lattice parameter of \( a_p = 3.958 \pm 0.002 \text{ Å} \). Rocking curves of the 001 T-BFO film reflection and the 110 reflection of the underlying YAO substrate, as shown in Figure 8-2(b), have FWHM values of 0.024° and 0.027°, respectively, showing that the T-BFO film has comparable structural quality to the substrate it was grown on. Shown in Figure 8-2(d) are rocking curves about the 111\(_p\) R-BFO film reflection and the 111 STO substrate reflection, giving FWHM values of 0.37° and 0.024°, respectively. The broadened FWHM value of the R-BFO film is likely due to thermal cycling. The small monoclinic distortions of the films are ignored and are treated as pure tetragonal (4\(mm\) point group symmetry) and rhombohedral (3\(m\) point group symmetry) phases in this analysis, which is later shown to be justified. Piezoresponse force microscopy measurements indicate that the films are single-domain, which is consistent with other reports.[11, 21, 22]

Optical SHG is a process where light at frequency \( \omega \) (electric field \( E^\omega \)) is converted into light at frequency 2\( \omega \) by a nonlinear material, through the creation of a nonlinear polarization, 

\[
P_{1,2\omega} \propto d_{ijk} E_{j,\omega} E_{k,\omega},
\]

where \( d_{ijk} \) is the nonlinear optical coefficient tensor, which can be expressed as \( d_{ij} \) in Voigt notation.[23] To accurately measure the \( d_{ij} \) coefficient values of a nonlinear material, the refractive index (n) and extinction coefficient (k) at the fundamental and SHG wavelengths must be precisely known. The linear optical properties of R-BFO films have already been determined,[19] where n and k for this film are plotted in Figure 8-3. For the T-BFO film, ellipsometric spectra (in \( \Delta, \psi \)) were collected ex-situ at \( \theta_i = 50^\circ, 60^\circ \) and 70° angles of incidence using a variable-angle dual rotating-compensator multichannel spectroscopic ellipsometer[24] with a spectral range from 240 to 1660 nm. Figure 8-3 shows n and k for the T-BFO film as the dashed blue line. The corresponding dielectric function spectra were extracted for the T-BFO
film by using a least squares regression analysis and an unweighted root mean square error[25] to fit the ellipsometric spectra to a four medium optical model consisting of a semi-infinite YAO substrate/bulk film/surface roughness/air ambient structure. The onset of absorption for the R and T-BFO films occurs at approximately 577 nm and 588 nm, respectively, which are near other values reported for BFO thin films.[19, 26] The SHG experiments performed on these films were done using fundamental wavelengths (frequency $\omega$) of $\lambda^\omega = 800$ nm and $\lambda^\omega = 1550$ nm, where the corresponding SHG wavelengths (frequency $2\omega$) are at $\lambda^{2\omega} = 400$ nm and $\lambda^{2\omega} = 775$ nm, respectively. The refractive index and absorption coefficients were determined for the R-BFO film at 800 nm (400 nm) as $n_\omega^R = 2.836$, $k_\omega^R = 0$ ($n_{2\omega}^R = 3.44$, $k_{2\omega}^R = 0.98$), and at 1550 nm (775 nm) $n_\omega^R = 2.72$ and $k_\omega^R = 0$ ($n_{2\omega}^R = 2.85$, $k_{2\omega}^R = 0$), and for the T-BFO film at 800 nm (400 nm) as $n_\omega^R = 2.66$, $k_\omega^R = 0$ ($n_{2\omega}^R = 3.29$, $k_{2\omega}^R = 0.52$), and at 1550 nm (775 nm) $n_\omega^R = 2.53$, $k_\omega^R = 0$ ($n_{2\omega}^R = 2.63$, $k_{2\omega}^R = 0$). The Mueller matrix spectra collected for both films indicate relatively weak optical anisotropy and are treated as being optically isotropic in our analysis. The 800 nm fundamental laser beam (80 f pulse width, 1 kHz repetition rate) was generated by a pumped Spectra-Physics Spitfire Ti:Sapphire amplifier, and the 1550 nm fundamental (120 fs pulse width, 1 kHz repetition rate) was generated from a pumped Spectra-Physics OPA-0800C. The fundamental beam powers used for these experiments was approximately 1.5 W/cm² for a beam waist diameter of 50 $\mu$m. No SHG signal was detected from the STO or YAO substrates at this incident power or wavelengths.

8.1.3 Transmission second harmonic generation polarimetry analysis

The experimental transmission SHG geometry is shown in Figure 8-4(a), where the linearly polarized fundamental electric field, $E_{in}$, is rotated by an angle $\phi$ and incident to the film
normal at an angle $\theta$ in the $x$–$z$ plane. The p-polarized ($||$) transmitted SHG field is denoted as $E_{2\omega||}$. Note that p-polarized refers to the component of the electric field which is parallel to the plane of incidence ($x$–$z$ plane) and the s-polarized component is perpendicular to the plane of incidence ($y$-axis). Two experimental configurations are employed for the SHG characterization: (1) *tilt-scans*, where $\phi$ is fixed and the sample is rotated by $\pm \theta$, and (2) *polar-plots*, where $\theta$ is fixed and $\phi$ is rotated by 360°. The R-BFO film has two unique sample tilt axes due to the anisotropy between the $z_1$ and $z_2$ crystal physics axes for $3m$ point group symmetry, where two unique sample tilt configurations are defined as (1) $z_1 = y$; $z_2 = -x$; $z_3 = z$, henceforth abbreviated as R$_1$, and (2) $z_1 = -y$; $z_2 = x$; $z_3 = z$, abbreviated as R$_2$. The T-BFO film has only one unique sample tilt axis since $z_1$ and $z_2$ are symmetrically equivalent in $4mm$ point group symmetry, and the sample tilt configuration is given as $z_1 = x$; $z_2 = y$; $z_3 = z$, abbreviated as T$_1$.

First, the $d_{ij}$ coefficient ratios ($K_{ij} = d_{ij}/d_{15}$) of the BFO films are determined through transmission SHG polarimetry analysis. A series of tilt scans and polar plots were collected in the configurations described above for the R and T-BFO films, shown in Figure 8-5 and Figure 8-6, respectively. Theoretical fitting of the SHG data was performed using an analytical model for the p-polarized transmitted SHG intensity for an isotropic, absorbing nonlinear thin film (denoted as superscript f) on a substrate, which is defined as,[27]

$$I_{2\omega||} = (I_{\omega})^2 (2\pi L/\lambda_{\omega})^2 (d'_{\omega||}^f)^2 \Theta_f,$$  \hspace{1cm} \text{Eq. 8-1}

where $L$ is the film thickness, $\lambda_{\omega}$ and $I_{\omega}$ are the wavelength and intensity of the fundamental laser beam, respectively, and the $\Theta_f$ term accounts for the transmittance, reflectance, and absorption of the fundamental and SHG fields in the film, which is explicitly defined in Appendix A. The $d'_{\omega||}$ term is the effective $d$ coefficient, which is dependent on the form of the $d_{ik}$ tensor and the orientation of the fundamental electric field with respect to the crystal physics axes of the film, which are given by the following equations,
\[ d^i_{\text{eff}} = \hat{e}_{i,2o||} \cdot d^i_{\text{ijk}} \cdot \hat{e}_{j,\theta} \cdot \hat{e}_{k,\phi}, \]

\[ \hat{e}_{2o||} = (\cos \theta_{2o\alpha} \Omega_x - \sin \theta_{2o\alpha}), \]

\[ \hat{e}_{\alpha} = (t^{af}_{\alpha} \cos \phi \cos \theta_{\alpha}, t^{af}_{\alpha} \sin \phi, -t^{af}_{\alpha} \cos \phi \sin \theta_{\alpha}). \]  

Eq. 8-2

where \( d^i_{\text{ijk}} \) is the transformed \( d_{ij} \) matrix in the \((x,y,z)\) coordinate system shown in Figure 8-4(a), which for the rhombohedral (R) and tetragonal (T) point group symmetries of 3\( m \) and 4\( mm \), respectively, are equal to,

\[
 d^R_{ij} = \begin{pmatrix}
 0 & 0 & 0 & 0 & d_{15} & -d_{22} \\
 -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\
 d_{31} & d_{31} & d_{33} & 0 & 0 & 0 
\end{pmatrix},
\]

\[
 d^T_{ij} = \begin{pmatrix}
 0 & 0 & 0 & 0 & d_{15} & 0 \\
 0 & 0 & 0 & d_{15} & 0 & 0 \\
 d_{31} & d_{31} & d_{33} & 0 & 0 & 0 
\end{pmatrix}. \quad \text{Eq. 8-3}
\]

Note that the only difference between the 3\( m \) and 4\( mm \) \( d_{ij} \) matrix is the \( d_{22} \) coefficient that is nonzero for 3\( m \) symmetry, which gives rise to the in-plane nonlinear component. The standard transmission (\( t \)) Fresnel coefficients for \( p \)-polarized and \( s \)-polarized (\( \perp \)) light as well as the angles of refraction (\( \theta_{\alpha} \) and \( \theta_{2\alpha} \)) according to Snell’s law are given by,

\[
 t^{af}_{\alpha||} = 2 \cos \theta / (\cos \theta_{\alpha} + n_{\alpha} \cos \theta),
\]

\[
 t^{af}_{\alpha\perp} = 2 \cos \theta / (n_{\alpha} \cos \theta_{\alpha} + \cos \theta),
\]

\[
 \sin \theta_{\alpha} = \sin \theta / n_{\alpha},
\]

\[
 \sin \theta_{2\alpha} = \sin \theta / n_{2\alpha}. \quad \text{Eq. 8-4}
\]

An irreducible expression of \( d^i_{\text{eff}} \) is defined as a function of the \( K_{ij} = d_{ij} / d_{15} \) parameters for the R\(_1\), R\(_2\), and T\(_1\) film configurations, where the notation of superscript \( f \rightarrow (R_1, R_2, T_1) \) is used, which were determined to be,
The $K_{ij}$ parameters were extracted from theoretical fits according to Eq. 8-1 to the SHG polarimetry data, and are shown in Table 8-1 with comparison to the ratio values taken from theoretical calculations for bulk R-BFO[17] and strained T-BFO.[18] The values are in very good agreement, however note that other $K_{ij}$ parameter solutions sets exist which yield satisfactory fits to the experimental data; having estimates of the nonlinear optical coefficient values via theoretical calculations a priori is helpful in identifying the correct parameter solution set.

As seen from Eq. 8-1 along with Eq. 8-5, for a $p$-polarized incident field ($\phi=0^\circ$), the SHG intensity for the $R_1$ and $T_1$ configurations go to zero at normal incidence ($\theta=0^\circ$), and should also be symmetric about normal incidence, which is clearly observed in the tilt scans shown in Figure 8-5 for R-BFO and Figure 8-6 for T-BFO. Any significant monoclinicity in the films would result in non-zero SHG intensities at normal incidence and asymmetric tilt scans.[28] This indicates that the films studied here behaving like pure rhombohedral and tetragonal phases.
8.1.4 Determination of nonlinear optical $d_{ij}$ coefficients through reflection second harmonic generation analysis using standard reference

Next, the absolute magnitude of the reflected effective $d$ coefficients, $d_{\text{eff}}$, is measured of the films with respect to a congruently grown $z$-cut LiNbO$_3$ (LNO) reference crystal with well-known linear and nonlinear optical properties.[29] This measurement is made in reflection geometry, shown schematically in Figure 8-4(b) since having to precisely know the thickness of the reference crystal can be avoided, where small errors in the reference thickness can result in large errors of the measured $d_{ij}$ values of the film.[27] By wedging and roughening the backside interface of the reference crystal, the collinear back reflections from that interface are diverted and scattered, where only the SHG reflected from the incident interface is allowed to propagate, and the thickness parameter does not need to be considered. Following the boundary-condition approach outlined in Ref.[27], expressions for the $p$-polarized reflected SHG intensity for an isotropic nonlinear thin film/substrate system and the $p$-polarized reflected SHG intensity from a single interface of a birefringent nonlinear reference (denoted as superscript ref) are derived, and are defined as,

$$I_{20\parallel}^{r,f} = (I_\omega)^2 (2\pi L / \lambda_\omega)^2 (d_{\text{eff}}^{r,f})^2 \Pi_f,$$

$$I_{20\parallel}^{r,ref} = (I_\omega)^2 (d_{\text{eff}}^{r,ref})^2 \Omega_{\text{ref}},$$  \hspace{1cm} \text{Eq. 8-6}

where $\Pi_f$ and $\Omega_{\text{ref}}$ account for the reflectance, transmittance, absorbance, and birefringence of the fundamental and SHG fields in the film and reference sample. Complete definitions are provided in Appendix A. The $z$-cut LNO reference crystal has the same point group symmetry ($3m$) and crystal physics axes orientations as R-BFO, so the same configurations ($R_1, R_2$) apply. In the reflected geometry, $d_{\text{eff}}$ is identical to the expressions in Eq. 8-5 except that the sign in front of
the $\cos \theta_{2\alpha}$ term is reversed. Taking the ratio of the two expressions in Eq. 8-6, $d_{ij}^f$ can be solved for as,

$$
\left| d_{ij}^{R,\text{ref}} \right| = d_{ij}^{T,\text{ref}} \frac{\left( \lambda_{2\alpha} / 2\pi L \right) (I_{2\alpha}^T / I_{2\alpha}^f) (I_{2\alpha}^T, \Omega^\text{ref} / I_{2\alpha}^f, \Pi^f)^{1/2} }{ }.
$$

Eq. 8-7

The values of $I_{2\alpha}^{R,\text{ref}}$, $I_{2\alpha}^{T,\text{ref}}$, and $I_{2\alpha}^{T,\text{ref}}$ were measured at $\theta=45^\circ$ and $\phi=0^\circ$, where the fundamental intensity at the film and reference interfaces was kept constant between subsequent measurements ($I_{2\alpha}^f = I_{2\alpha}^\text{ref}$) by mounting the samples with their incident interfaces lying in the same plane, and translating the samples parallel to the rotation axis. Then, by substituting these measured intensity values and the known linear optical properties of the films and reference into Eq. 8-7, for R-BFO, $|d_{ij}^{R,\text{ref}}| = 10.0 \pm 1.1 \text{ pm/V at } 800 \text{ nm and } |d_{ij}^{R,\text{ref}}| = 3.6 \pm 0.3 \text{ pm/V at } 1550 \text{ nm}$, and for T-BFO, $|d_{ij}^{T,\text{ref}}| = 4.43 \pm 0.4 \text{ pm/V at } 800 \text{ nm and } |d_{ij}^{T,\text{ref}}| = 2.6 \pm 0.2 \text{ pm/V at } 800 \text{ nm}$.

With subsequent use of Eq. 8-5 and the already determined $K_{ij}$ values, for R-BFO $|d_{15}|=2.9 \pm 0.3 \text{ pm/V at } 800 \text{ nm and } |d_{15}|=0.9 \pm 0.1 \text{ pm/V at } 1550 \text{ nm, and for T-BFO that } |d_{15}|=18.4 \pm 2.0 \text{ pm/V at } 800 \text{ nm and } |d_{15}|=47.0 \pm 4.2 \text{ pm/V at } 1550 \text{ nm.}$ The absolute magnitudes of the other $d_{ij}$ coefficients can be directly calculated from the $K_{ij}$ parameters. Note that only the absolute magnitudes of the $d_{ij}$ coefficients can be determined using this technique; only the signs of the $d_{ij}$ coefficient ratios ($K_{ij}$) can be unambiguously resolved. According to the theoretical calculations by Ju et al., $d_{15}=-3.1 \text{ pm/V at } 800 \text{ nm and } d_{15}=-1.0 \text{ pm/V at } 1550 \text{ nm for R-BFO, and } d_{15}=26.9 \text{ pm/V at } 800 \text{ nm and } d_{15}=53.0 \text{ pm/V at } 1550 \text{ nm for T-BFO.}$ Using the $d_{15}$ sign conventions from theory, we have listed in Table 8-1 the measured $d_{ij}$ coefficients for R and T-BFO from this work along with the theoretical values for comparison, which are in very good agreement.

A very large measured $d_{33}$ magnitude is observed at 800 nm of $|d_{33}| = 91.0 \pm 9.0 \text{ pm/V for}$ T-BFO and $|d_{33}| = 55.8 \pm 7.4 \text{ pm/V for R-BFO.}$ These values rival standard nonlinear optical materials such as LiNbO$_3$ ($|d_{33}| = 27.2 \text{ pm/V at } 1064 \text{ nm}$), KNbO$_3$ ($|d_{33}| = 19.6 \text{ pm/V at } 1064 \text{ nm}$),
and BaTiO$_3$ ($|d_{31}| = 14.4$ pm/V at 1064 nm),[29] as shown in a histogram plot in Figure 8-7. The strain-enhanced $d_{ij}$ magnitudes in T-BFO films found here are consistent with other reported property enhancements such as an increased polarization and strong electromechanical responses,[11, 15] which is believed to arise from the strain-induced super-tetragonality in the T-BFO system.[12, 16]

8.1.5 Conclusions

In summary, the measured nonlinear optical $d_{ij}$ coefficients at 800 nm and 1550 nm for R and T-BFO thin films are reported which are very consistent with theory. A general experimental method has been outlined to measure these values for a thin film/substrate system. A very large $d_{ij}$ coefficient magnitude is observed for both the T-BFO and R-BFO films which strongly challenge the standard nonlinear optical materials currently used today. The large $d_{ij}$ magnitudes and low optical absorption in T-BFO films make them potentially useful for optical applications and device integration, where the ability to strain-tune thin films provides an encouraging route for enhancing the nonlinear optical performance of materials.
8.1.6 Figures

Figure 8-1: Temperature-strain-phase diagram of BiFeO$_3$. Compressive strain drives the symmetry of BiFeO$_3$ from the rhombohedral ($R3c$) to tetragonal ($P4mm$) structure which occurs at -4.3% compressive strain at room temperature. The polarization ($P_s$) switched from the $<111>_p$ direction in the $R3c$ phase to $<001>$ in the $P4mm$ phase. Tensile strain drives BiFeO$_3$ from $R3c$ to an orthorhombic $Pmm2$ symmetry. The pseudo-rhombohedral (R) BFO film studied in this work was grown on (111)SrTiO$_3$ substrate and the pseudo-tetragonal (T) BFO film was grown on (110)YAlO$_3$ substrate, where the resulting misfit strains are indicated by arrows in the graph. The R-BFO and T-BFO unit cells are shown with their lattice parameter values labeled.
Figure 8-2: X-ray diffraction data for T-BFO and R-BFO. 2θ-ω scans of (a) the 00L reflections of T-BFO yield an out-of-plane lattice parameter of $c = 4.670 \pm 0.002$ Å, and (c) the 111_p and 222_p reflections for R-BFO yield a pseudo-cubic lattice parameter of $a_p = 3.958 \pm 0.002$ Å. Rocking curves for (b) the 001 reflection of the T-BFO film (blue line) and the 110 reflection of the YAO substrate (black line) yield a FWHM of $0.024^\circ$ and $0.027^\circ$, respectively, and (d) the 111_p reflection of the R-BFO film (red line) and 111 reflection of the STO substrate (black line) yield a FWHM of $0.37^\circ$ and $0.024^\circ$, respectively. The broadened FWHM of the R-BFO film is likely due to thermal cycling. The STO and YAO substrate reflections are marked by an asterisk (*). Films were grown by Alex Melville at Cornell.
Figure 8-3: Refractive index (n) and absorption coefficient (k) over the spectral range from 200 nm to 1690 nm for R-BFO and T-BFO shown as the dashed red and solid blue lines, respectively. The onset of absorption for the R and T-BFO films occurs at approximately 577 nm and 588 nm, respectively.
Figure 8-4: (a) Transmission SHG polarimetry geometry showing the linearly polarized fundamental field, $E_{\omega}$, rotated by an angle $\phi$ and incident to the film normal by an angle $\theta$ in the x-z plane, and the p-polarized ($\parallel$) SHG field, $E_{2\omega\parallel}$ which is detected by a photomultiplier tube (PMT). The (x,y,z) laboratory axes are shown, where the crystal physics axes of the films ($z_1$, $z_2$, $z_3$) are related for the R and T-BFO films as $R_1$ ($z_1 = y$, $z_2 = -x$, $z_3 = z$), $R_2$ ($z_1 = -y$, $z_2 = x$, $z_3 = z$), and $T_1$ ($z_1 = x$, $z_2 = y$, $z_3 = z$) configurations. (b) Reflection SHG polarimetry geometry showing the reference crystal which has the backside interface wedged and roughened to stop reflections.
Figure 8-5: SHG polarimetry data of the R-BFO film showing (a) tilt scans of the transmitted $p$-polarized SHG intensity for a fundamental wavelength of $\lambda=800$ nm as a function of the angle of incidence $\theta$ for a fixed input polarization of $\phi=0^\circ$ in the $R_1$ (blue circles) and $R_2$ (red squares) configurations. Polar plots taken at $\lambda=800$ nm are shown to the right for (b) $R_1$ and (c) $R_2$ configurations, taken at $\theta=45^\circ$ (red circles) and $\theta=-45^\circ$ (green triangles), where $\phi$ was scanned $360^\circ$. Tilt scans and polar plots were also collected for a fundamental wavelength of $\lambda=1550$ nm, shown in (d), (e) and (f), respectively, with the same configurations as (a), (b) and (c) but at a different wavelength. Theoretical fits according to a $3m$ point group symmetry model are shown as black lines.
Figure 8-6: SHG polarimetry data of the T-BFO film showing (a) tilt scan of the transmitted $p$-polarized SHG intensity for a fundamental wavelength of $\lambda=800$ nm as a function of the angle of incidence $\theta$ for a fixed input polarization of $\phi=0^\circ$ in the $T_1$ (blue circles). Polar plots taken at $\lambda=800$ nm are shown to the right for (b) $T_1$ configuration, taken at $\theta=45^\circ$ (red circles) and $\theta=30^\circ$ (green triangles), where $\phi$ was scanned $360^\circ$. Tilt scans and polar plots were also collected for a fundamental wavelength of $\lambda=1550$ nm, shown in (c) and (d), respectively, with the same configurations as (a) and (b). Theoretical fits according to a $4mm$ point group symmetry are shown as black lines.
Figure 8-7: A comparison of the magnitude of $d_{ij}$ nonlinear optical coefficients for several of the best nonlinear optical perovskite materials including LiTaO$_3$, BaTiO$_3$, KNbO$_3$, and LiNbO$_3$, which are all at fundamental wavelengths of 1064 nm, as well as the largest $d_{ij}$ coefficients measured for R-BFO and T-BFO at a fundamental wavelength of 800 nm.
Table 8-1: Nonlinear optical $K_{ij}$ ratios ($d_{ij}/d_{15}$) and $d_{ij}$ (pm/V) coefficient values from experimental work presented here (Expt.) and theoretical values (Theory) reported by Ju et al. for R-BFO[17] and T-BFO[18] at fundamental wavelengths of 800 nm and 1550 nm.

<table>
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<th></th>
<th>R-BFO</th>
<th>T-BFO</th>
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<tbody>
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<td>$\lambda=1550$ nm</td>
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<tr>
<td>$K_{33}$</td>
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<td>-17.4</td>
</tr>
<tr>
<td>$K_{31}$</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>$d_{22}$</td>
<td>-35.8±4.8</td>
<td>-34.7</td>
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8.2 Orthorhombic BiFeO$_3$†

8.2.1 Strain-phase diagram of BiFeO$_3$

In the previous section, it was shown that a pseudo tetragonal phase of BiFeO$_3$ can be stabilized through compressive strain. In this chapter, it is shown that the orthorhombic phase of BiFeO$_3$ can be stabilized through tensile strain, however, the boundary conditions during thin film growth process will greatly affect whether or not this phase can be stabilized.[30] Figure 8-8 shows the calculated strain-phase-temperature diagrams using phase-field simulations for BiFeO$_3$ under two different electrical boundary conditions. The first one is for a short-circuit or closed-circuit electrical boundary conditions, which is the same as shown in Figure 8-1,[11] and is more indicative of the boundary conditions that might be experienced for molecular beam epitaxy growth where a film is typically highly reduced due to oxygen vacancies induced by the ultra-high vacuum conditions. Therefore, an electric current can transfer through the film, effectively screening out the depolarization field. This results in a larger strain needed to transform the otherwise bulk rhombohedral (R) phase into a pure orthorhombic (O) phase with only in-plane polarization, which occurs at ~1.7% tensile strain at room temperature, as shown in Figure 8-8(a). If an open-circuit electrical boundary condition is considered, which is more indicative of pulsed laser deposition performed in much higher oxygen background pressures, this leads to a more insulating film with less oxygen vacancies, and the strain phase diagram changes considerably. In this scenario, the depolarization field suppresses the out-of-plane polarization and more easily promotes the formation of orthorhombic in-plane polarization domains at smaller strains of only ~0.8% at room temperature, as shown in Figure 8-8(b).

8.2.2 Tensile strained BiFeO$_3$ films on (110)NdScO$_3$ and (110)PrScO$_3$ substrates

To test the validity of these two different electrical boundary conditions, thin film BiFeO$_3$ samples were grown by both molecular beam epitaxy (closed-circuit) and pulsed laser deposition (open-circuit). For the MBE sample, a 30 nm thick BiFeO$_3$ film was tensile strained on (110)PrScO$_3$ substrate, which induces $\sim$1.54% tensile strain. For the PLD sample, a 15 nm thick BiFeO$_3$ film was grown on (110)NdScO$_3$ which induces $\sim$1.2% tensile strain.[31] For the PLD grown film on (110)NdScO$_3$ substrate, transmission electron microscopy and piezoresponse force microscopy analysis, as shown in Figure 8-9, reveal that the polarization is in the plane of the film and along the $<1\overline{1}0>$$_p$ directions as evidenced by the striped domain configurations that have different phase intensities, resulting in domain walls that are parallel to the $<100>$$_p$ directions. To further confirm the polar phase symmetry of this film, second harmonic generation polarimetry analysis was performed at a fundamental wavelength of 800 nm with the same experimental configurations shown in the last section for the tetragonal and rhombohedral films. For an orthorhombic $mm2$ point group symmetry, we can derive an irreducible expression of the effective nonlinear optical coefficient, $d_{ij}^\text{eff}$, as a function of the $K_{ij}=d_{ij}/d_{15}$ parameters. However, in this case, the multiple domain variants that will exist for the biaxial tensile strained films needs to be considered. The general $d_{ij}$ matrix orthorhombic (O) $mm2$ point group symmetry is given as,

$$
\begin{pmatrix}
0 & 0 & 0 & 0 & d_{15} & d_{24} \\
0 & 0 & 0 & d_{24} & 0 & 0 \\
d_{31} & d_{32} & d_{33} & 0 & 0 & 0
\end{pmatrix}
$$

Eq. 8-8

and by transforming this matrix into the crystal physics axes orientations of the two different domain variants, O$_1$ ($z_1=[001]_p$, $z_2=[1-10]_p$, $z_3=[110]_p$) and O$_2$ ($z_1=[001]_p$, $z_2=[110]_p$, $z_3=[-110]_p$), and with the use of Eq. 8-2, the following expression is derived for the effective nonlinear optical coefficient for multi-domain orthorhombic $mm2$ symmetry as,
where the $\delta A_{12}$ term is the ratio of the domain area fractions, $\delta A_1$ and $\delta A_2$, and the $d_{ij}$ ratios are equal to $K_0 = d_{ij}/d_{15}$. Using this SHG model, it is shown how the polar phase symmetry of the BiFeO$_3$ film can be determined through SHG polarimetry analysis.

8.2.3 Determination of orthorhombic phase by PFM and SHG analysis

For the nonlinear optical SHG modeling analysis, first the linear optical properties of the 15 nm BiFeO$_3//(110)$NdScO$_3$ sample was determined through spectroscopic ellipsometry using the same methods as described in the last section. Note that the anisotropy of the film/substrate structure was not taken into account. The linear optical properties, $n$ and $k$, are plotted as a function of wavelength in Figure 8-10: With the linear optical properties in hand, next a series of SHG tilt scans and polar plots was obtained, as shown in Figure 8-11:, and fit this SHG data using the model for $d_{\alpha\beta}^O$ in Eq. 8-9 along with Eq. 8-1. From the $mm2$ fits we observe that the multidomain orthorhombic model fits well to the SHG data. Note that the orthorhombic tilt scan is symmetric about normal incidence and has a maximum value at normal incidence, which is to be expected since at normal incidence, the projection of the incident electric field of light will be completely parallel to the in-plane polarization directions, giving rise to the largest SHG response. This projection will decrease symmetrically as the sample is tilted away from normal incidence, resulting in a decreased SHG intensity as the angle of incidence increases. Therefore, based form this SHG polarimetry analysis, the strained BiFeO$_3$ film on (110)NdScO$_3$ substrate
indeed shows orthorhombicity, which is in agreement with the PFM results and the phase field simulations of an open-circuit boundary conditions for the PLD grown film.

Next, the polar symmetry for the MBE grown BiFeO$_3$ film on (110)PrScO$_3$ substrate was determined. PFM analysis of the film, shown in Figure 8-12, reveals that the film has both in-plane and out-of-plane polarization components as evidenced by the phase contrast seen for the out-of-plane PFM response. The striped domain pattern for the in-plane PFM response is similar to that of the BiFeO$_3$ film grown on NdScO$_3$ by pulsed laser deposition. This suggests that the pure in-plane orthorhombic phase of the film has not been stabilized, but rather there is monoclinic type of symmetry where the polarization tilts away from the in-plane direction, towards the out-of-plane direction, which agrees with the closed-circuit boundary conditions of the strain-phase diagram. Second harmonic generation polarimetry analysis also confirms that this film has out-of-plane polarization components as well. The same linear optical properties were used as those found for BiFeO$_3$ on NdScO$_3$ substrate, although the values are likely a little bit different, this will not change the qualitative determination of the polar point group symmetry for the analysis done here. The series of tilt scans and polar plots for the MBE grown BiFeO$_3$ film on PrScO$_3$ substrate were collected at room temperature, and are shown in Figure 8-13. It can immediately see that the tilt scan is asymmetric about normal incidence ($\theta=0^\circ$), which cannot be the case for a pure orthorhombic in-plane symmetry. The figure shows two fits to the SHG tilt scan data, where the $mm2$ theory fit does not fit well to the data as this model can only result in symmetric tilt scans. However, using a multi-domain monoclinic model, the same as described by Eq. 3-3, yields a much better fit, as the monoclinic symmetry can account for the out-of-plane polarization component.
8.2.4 Conclusions

In conclusion, through a combination of theoretical and experimental methods, a way to stabilize and create a new orthorhombic phase in multiferroic BiFeO$_3$ has been demonstrated through strain-engineering. The in-plane polarization of the film greatly depends on the boundary conditions involved during the growth process, where molecular beam epitaxy methods are not able to stabilize the orthorhombic phase, whereas pulsed laser deposition techniques allow this in-plane polarization to manifest. Using SHG polarimetry analysis, the in-plane and out-of-plane polarization component in the films can easily be determined, as well as the polar points group symmetry, showing the powerful advantage of this technique to probe strain-stabilized polar states of matter.
8.2.5 Figures

Figure 8-8: Calculated strain-temperature phase diagrams of BiFeO$_3$ thin films from phase-field simulations for (a) short-circuit or closed-circuit boundary conditions, and (b) under open-circuit boundary conditions. The rhombohedral (R) and orthorhombic (O) phases, which have 3$m$ and $mm2$ point group symmetries, respectively, are labeled, as well as the high temperature cubic phase. The (110) PrScO$_3$ substrate strain and (110)NdScO$_3$ substrate strains are shown in (a) and (b), respectively. An orthorhombic unit cell of BiFeO$_3$ is shown as an inset in (b), with the $a_x$, $a_y$, and $a_z$ lattice parameters, with the polarization direction in the $<110>_p$ direction. The dashed line shows the intersection of the expected polar phase for the substrates in (a) and (b).
Figure 8-9: A TEM micrograph of a BiFeO$_3$ thin film on NdScO$_3$ substrate for (a) high angle annular dark field STEM image with the substrate/film interface shown. (b) Planar-view image showing the striped domain pattern of the film. The crystal physics axes are shown in both (a) and (b). (c) Out-of-plane and (d) in-plane PFM images obtained under a 5 V ac bias of the BiFeO$_3$ film, with the polarizations, $P_1$ and $P_2$ of each domain configuration labeled in (d) with the film axes also shown. Image adapted from Ref. [30].
Figure 8-10: The refractive index, $n$ (left axis), and absorption coefficient, $k$ (right axis), for a 15 nm BiFeO$_3$ film grown on (110)NdScO$_3$ substrate. The linear optical properties of the film were determined through spectroscopic ellipsometry analysis.
Figure 8-11: Second harmonic generation polarimetry analysis at a fundamental wavelength of 800 nm and at room temperature for the 15 nm BiFeO$_3$ film on (110)NdScO$_3$ substrate. The SHG tilt scan shows the SHG intensity as a function of the angle of incidence, $\theta$ where the input polarization of the fundamental field was fixed to $\phi=0^\circ$ with data shown as the blue circles and the theoretical fit according to a multi-domain $mm2$ orthorhombic point group symmetry model shown as red lines. Polar plots are shown above at fixed angles of incidence of $\theta=-45^\circ$, $0^\circ$, and $+45^\circ$, where $\phi$ was rotated by $360^\circ$. 
Figure 8-12: PFM analysis of the 30 nm BiFeO$_3$ film grown on (110)PrScO$_3$ by molecular beam epitaxy. The top panels show the in-plane PFM phase (left) and amplitude (right) response, and the bottom panels show the out-of-plane PFM phase (left) and amplitude (right) response. The color scale bar for the phase is in degrees, and the scale bar for the amplitude is in V. Scale bars for the size of the scan taken are shown in the bottom right of each image.
Figure 8-13: Second harmonic generation polarimetry analysis at a fundamental wavelength of 800 nm and at room temperature for the 30 nm BiFeO$_3$ film on (110)PrScO$_3$ substrate grown by molecular beam epitaxy. The SHG tilt scan shows the SHG intensity as a function of the angle of incidence, $\theta$ where the input polarization of the fundamental field was fixed to $\phi=0^\circ$ with data shown as the green circles and the theoretical fit according to a multi-domain $mm2$ orthorhombic point group symmetry model shown as blue lines, and the theoretical fit for a multi-domain monoclinic $m$ point group symmetry model shown as red. Polar plots are shown above at fixed angles of incidence of $\theta=-45^\circ$, $0^\circ$, and $+45^\circ$, where $\phi$ was rotated by 360$^\circ$. 
8.2.6 References


Chapter 9

Summary, Future Work and Conclusions

The majority of this work focused on investigating strain-induced ferroelectricity in CaTiO$_3$ and SrTiO$_3$ perovskite-based film materials grown by hybrid molecular beam epitaxy. The development of stoichiometric growth windows of CaTiO$_3$ and SrTiO$_3$ enabled the confirmation of theoretically predicted ferroelectric phases to emerge for tensile strained CaTiO$_3$/001)LSAT ($T_C \sim 180$ K) and compressive strained SrTiO$_3$/001)LSAT ($T_C \sim 175$ K). Utilizing the CaTiO$_3$ growth window, the effects of compressive strain on ferroelectricity in CaTiO$_3$ films was also explored, where unexpectedly high-temperature polar phase transitions were observed for ~15 nm thick CaTiO$_3$/001)LAO (strain = -0.8 %) and CaTiO$_3$/001)LSAO (strain = -1.7 %).

Beyond the growth of single-phase CaTiO$_3$ and SrTiO$_3$ films, new growth schemes in the hybrid MBE approach were developed, facilitating the ability to construct (SrTiO$_3$)$_n$/CaTiO$_3$ SLs using overlapping growth windows, as well as SrO(SrTiO$_3$)$_n$ RP phases using half-unit cell deposition sequences, where the self-regulated stoichiometry afforded by the TTIP-induced growth windows, as well as control over the layering periodicity ($n$) using in-situ RHEED oscillations, enabled homogeneously layered oxide structures to be explored.

In going forward, there are several “spin-off” experiments and research projects that could be imagined. The future work “spin-off” proposals are listed below:

(1) Investigation of strain-induced ferroelectric properties in Sr$_{1-x}$Ca$_x$TiO$_3$. How does A-site doping tune ferroelectricity? Since bulk Sr$_{1-x}$Ca$_x$TiO$_3$ exhibits relaxor ferroelectricity at $T \leq$
30 K for Ca concentrations of x < 0.1, and that the transition elevates to T~125 K for x=2. There may be enhanced ferroelectric responses in doped (Sr,Ca)TiO₃ films beyond the individual strained components. [1] By systematically controlling the dopant concentrations for a series of Sr₁ₓCaₓTiO₃ thin films, it might be expected that the polarization could be tuned from out-of-plane in pure compressively strained SrTiO₃, to nearly in-plane for pure tensile strained CaTiO₃. However, it does not seem that there is much gain in ferroelectric transition temperatures with increasing tensile strain in CaTiO₃, or with increased compressive strain in SrTiO₃. [2]

(2) Investigation of compressively strained CaTiO₃ films which showed polar activity above room temperature. This observed response is much different than what theory currently predicts, and the mechanism behind the emergence of a high-temperature polar phase needs to be determined. First, the transition temperatures for compressively strained CaTiO₃ films need to be confirmed using measurement techniques besides PFM and SHG, as shown in this work. This would require further development of chemically and structurally compatible bottom electrode materials. Materials such as SrVO₃ and CaVO₃ are disadvantageous electrode materials due to the fact that they become insulating above T ~ 300-400 °C, which makes it nearly impossible to anneal as-grown films to remove oxygen vacancies while simultaneously retaining conductivity in the electrodes. A promising electrode material could be ruthenates (SrRuO₃, CaRuO₃), although the large difference in lattice parameter between ruthenates and titanates would be problematic when trying to grow useful electrode thicknesses (> 20 nm) without having to worry about structural relaxation effects. Another potential bottom electrode material could be La-doped SrTiO₃ or CaTiO₃, where optimization in the La-concentration, thickness, and sheet resistance would have to be performed on specific substrate materials for the doped films.

To explore the mechanism of the high-temperature polar phase in compressively strained CaTiO₃ films, the tilt symmetry of the films would need to be determined, which could be done using X-ray diffraction to measure a series of half-order peaks that are expected to emerge for
certain tilt patterns, or also by TEM image analysis along different zone axes. By knowing the
degree of tilting and the tilt symmetry of the strained films, i.e. which direction the (+) and (-)
octahedral rotations occur and their magnitude of rotation, may give some insights as to the
driving mechanism, where theory would suggest that turning off the (+) rotation symmetry can
lead to ferroelectric instabilities in orthorhombic structures such as CaTiO₃.[3] Additionally, the
high temperature polar phase transitions could be probed by measuring the temperature
dependence of the out-of-plane and in-plane lattice parameters for the compressively strained
CaTiO₃ films to see when the film transitions from tetragonal to cubic symmetry. The
temperature dependence of the rotation-induced half-order X-ray diffraction peaks could be
measured to see if the transition is accompanied by changes in the degree of tilting as well as the
tilt symmetry.

Since the maximum thickness that can be achieved in compressively strained
CaTiO₃/(001)LaSrAlO₄ is ~15 nm before relaxation occurs, it makes it much more challenging to
probe this system. Therefore, the most likely candidate for further exploration is
CaTiO₃/(100)LaAlO₃ where much thicker films can be grown without relaxation. This would
allow the ability to incorporate thicker bottom electrodes needed to perform good electrical
measurements. It is also expected that the polar properties will change with thickness of the film,
and a thickness series of CaTiO₃/(100)LaAlO₃ could be synthesized to determine if the polar
transition temperature can be tuned by thickness.

For future research experiments on layered (SrTiO₃)ₓ/(CaTiO₃)ₓ superlattices, there are
many questions that need to be answered. Firstly, from an engineering standpoint, while the
layering growth schemes introduced in this work will provide a good starting point for future
hybrid MBE growers, it was done manually, and there is a lot of room for improvement, and a
systematic way of controlling Δn based off of the observed RHEED oscillations will need to be
implemented. Further improvements for controlled growth of layered oxide structures could be
made through software controlled synchronization between in-situ RHEED oscillations and the opening and closing events of the sources in an MBE chamber, allowing better accuracy of atomic layer deposition times. Refinement and optimization of these new layering schemes would enable the synthesis of higher quality layered oxide structures where the layering thickness and interface roughness can be easily controlled in thin film structures, without having to worry about the stoichiometric compositions due to the growth windows.

Since there seems to be a strong correlation between cation mixing at the interfaces of (SrTiO$_3$)$_n$(CaTiO$_3$)$_n$ superlattices and the emergence of ferroelectricity, the obvious next experiment would be to fix $n$ and systematically vary $\Delta n$ to see how the polar phase emerges with increased interface mixing for low $n$ (i.e. $n = 2, 3$) and high $n$ (i.e. $n = 8, 9$), which have layer thicknesses below, and above, the critical thickness limit for ferroelectricity, respectively. Since it is known that Ca-doped SrTiO$_3$ becomes ferroelectric, this could be done for a low $n$ (i.e. $n=2, 3$) where the individual layer thicknesses are below the critical thickness limit for which a material can be ferroelectric (~2 nm), and high $n$ (i.e. $n = 8, 9$) where the layer thicknesses are above this critical thickness limit. It would be expected that for $n = 2, 3$, as $\Delta n$ approaches 0, the low temperature phase will disappear, and as $\Delta n$ is increased, the polar transition and for $n=8$, as $\Delta n$ approaches zero, the polar phase transition will still occur. Another obvious next experiment for (SrTiO$_3$)$_n$(CaTiO$_3$)$_n$ superlattices is to perform electrical measurements to actually probe the ferroelectricity. This would require bottom electrode material to probe the out-of-plane polar component, although inter-digitated electrodes could be used to probe the in-plane ferroelectric properties of the superlattices.

Another interesting idea could be to utilize CaTiO$_3$ in the compressive strained state to build superlattice structures, however, this would require the other perovskite layer to have a smaller pseudo-cubic (subscript $p$) lattice parameter than CaTiO$_3$ ($a_p=3.82$ Å). A possible
perovskite material could be MgTiO$_3$, which has a pseudo-cubic lattice parameter of $a_p=3.726$ Å.[4] Appropriate substrates to grow a (CaTiO$_3$)$_n$/(MgTiO$_3$)$_n$ superlattice could be for instance CeAlO$_3$ ($a_p=3.767$ Å), PrAlO$_3$ ($a_p=3.757$ Å), NdCoO$_3$ ($a_p=3.777$ Å) or YCrO$_3$ ($a_p=3.77$ Å).[5]

Going beyond titanate growth windows, many other perovskite growth windows are yet to be discovered, where the only limitations are the availability of metal-organic (MO) precursor materials. Since the inception of the first MO-induced perovskite growth window of SrTiO$_3$ using titanium tetra-isopropoxide in 2009, other perovskite growth windows have been discovered for SrVO$_3$ using vanadium tri-isopropoxide and BaSnO$_3$ using hexa-dimethyliditin. But what about other perovskite systems such as aluminates, gallates, antimonates, molybdates, chromates, ruthenates, tantalates, niobates, nickelates, germinates, hafnates, tungstates, stannates, manganates, iridates, etc? With the increasing number of high quality commercially available MO precursor materials, growth windows for a vast array of perovskite systems could potentially be discovered in the near future. Synergistic efforts between inorganic chemists and material scientists could lead to the evolution of MO precursor materials that are compatible with hybrid MBE growth of perovskites.
9.1 References


Appendices

Appendix A. Derivation of transmitted and reflected SHG intensity for isotropic absorbing film/substrate interface

The $p$-polarized ($||$) transmitted SHG intensity for an isotropic, absorbing nonlinear thin film (denoted as superscript $f$) on a substrate, are defined as,

$$I^t_{2\omega||} = (I_{\omega})^2 (2\pi L/\lambda_{\omega})^2 (d^f_{\text{eff}})^2 \Theta_f,$$

Eq. A-1

$$I^{r\ell}_{2\omega||} = (I_{\omega})^2 (2\pi L/\lambda_{\omega})^2 (d^{r\ell}_{\text{eff}})^2 \Pi_f,$$

where $L$ is the film thickness, $\lambda_{\omega}$ and $I_{\omega}$ are the wavelength and intensity of the fundamental laser beam, respectively, and the $\Theta_f$ and $\Pi_f$ terms accounts for the transmittance, reflectance, and absorption of the fundamental and SHG fields in the film, which are expressed as,

$$\Theta_f = (8 \cos \theta / c e_0) \{|[r^f_{\omega||}]| r^f_{\omega||} | \exp[-(\delta_{\omega} + \delta_{2\omega})]/n_{2\omega} \cos \theta_{2\omega} \}^2$$

$$\times \{|\sin \tilde{\Psi}/\tilde{\Phi}|^2 + D^2 |r^{af}_{\omega||}|^2 |\sin \tilde{\Phi}/\tilde{\Phi}| \exp(-4\delta_{2\omega})$$

$$- 2D |r^{af}_{\omega||}| \sin \tilde{\Psi}/\tilde{\Phi} | \sin \tilde{\Phi}/\tilde{\Phi} | \exp(-2\delta_{2\omega}) \cos(2\varphi_{2\omega} - \alpha + \beta) \},$$

$$/\{1 + [r^{af}_{\omega||}]^2 [r^{6\ell}_{\omega||}]^2 \exp(-8\delta_{2\omega}) + 2[r^{af}_{\omega||}] [r^{6\ell}_{\omega||}] \exp(-4\delta_{2\omega}) \cos(4\varphi_{2\omega}) \} \}^{\text{Eq. A-2}}$$

$$\Pi_f = (8 \cos \theta / c e_0) \{|[r^f_{\omega||}]| r^f_{\omega||} | \exp[-(\delta_{\omega} - \delta_{2\omega})]/2(\cos \theta_{2\omega} - n_{2\omega} \cos \theta) \}^2$$

$$\times \{|\sin \tilde{\Phi}/\tilde{\Phi}|^2 \exp(-4\delta_{2\omega}) + D^{-2} |r^{6\ell}_{\omega||}|^2 |\sin \tilde{\Psi}/\tilde{\Psi}|$$

$$+ 2D^{-1} |r^{6\ell}_{\omega||}| \sin \tilde{\Phi}/\tilde{\Phi} | \sin \tilde{\Psi}/\tilde{\Psi} | \exp(-2\delta_{2\omega}) \cos(2\varphi_{2\omega} - \alpha + \beta) \},$$

$$/\{1 + [r^{af}_{\omega||}]^2 [r^{6\ell}_{\omega||}]^2 \exp(-8\delta_{2\omega}) + 2[r^{af}_{\omega||}] [r^{6\ell}_{\omega||}] \exp(-4\delta_{2\omega}) \cos(4\varphi_{2\omega}) \} \}$$
where \( c \) is the speed of light, \( \varepsilon_0 \) is the permittivity of free space, and \( \theta \) is the angle of incidence.

The complex terms in Eq. A-2 are expressed as,

\[
\tilde{\Psi} = \Psi + i\chi ,
\]

\[
\Psi = (2\pi L / \lambda_\omega)(n_\omega \cos \theta_\omega - n_{2\omega} \cos \theta_{2\omega}) ,
\]

\[
\chi = (2\pi L / \lambda_\omega)[(k_\omega / \cos \theta_\omega) - (k_{2\omega} / \cos \theta_{2\omega})] ,
\]

\[\widetilde{\Phi} = \Phi + i\Gamma ,\]

\[
\Phi = (2\pi L / \lambda_\omega)(n_\omega \cos \theta_\omega + n_{2\omega} \cos \theta_{2\omega}) ,
\]

\[
\Gamma = (2\pi L / \lambda_\omega)[(k_\omega / \cos \theta_\omega) + (k_{2\omega} / \cos \theta_{2\omega})] .
\]

Eq. A-3

with \( k_\omega \) and \( k_{2\omega} \) being the absorption coefficients at frequency \( \omega \) and \( 2\omega \), respectively.

The conjugated complex terms in Eq. A-2 will therefore simplify to,

\[
|\sin \tilde{\Psi} / \tilde{\Psi}|^2 = (\sin^2 \Psi + \sinh^2 \chi) / (\Psi^2 + \chi^2) ,
\]

\[
|\sin \tilde{\Phi} / \tilde{\Phi}|^2 = (\sin^2 \Phi + \sinh^2 \Gamma) / (\Phi^2 + \Gamma^2) .
\]

Eq. A-3

The additional terms that show up in Eq. A-2 are given by,

\[
\delta_\omega = (2\pi L / \lambda_\omega)(k_\omega / \cos \theta_\omega) ,
\]

\[
\delta_{2\omega} = (2\pi L / \lambda_{2\omega})(k_{2\omega} / \cos \theta_{2\omega}) ,
\]

\[
\varphi_{2\omega} = (2\pi L / \lambda_{2\omega})(n_{2\omega} \cos \theta_{2\omega}) ,
\]

\[
\tan \alpha = (\Psi \tanh \chi - \chi \tan \Psi) / (\Psi \tan \Psi + \chi \tanh \chi) ,
\]

\[
\tan \beta = (\Phi \tanh \Gamma - \Gamma \tan \Phi) / (\Phi \tan \Phi + \Gamma \tanh \Gamma) ,
\]

Eq. A-4

\[
D = d_{\text{eff}}^{t \omega} / d_{\text{eff}}^{r \omega} .
\]

Here, \( d_{\text{eff}}^{t \omega} \) and \( d_{\text{eff}}^{r \omega} \) are the \( p \)-polarized effective transmission and reflection SHG coefficients, respectively, and are further defined as,
\[ d^e_{\text{eff}} = \hat{e}_{i,20||} \cdot \hat{e}_{j,20||} \cdot \hat{e}_{k,20||}, \]
\[ d^{\tau f}_{\text{eff}} = \hat{e}^{\tau}_{i,20||} \cdot \hat{e}^{\tau f}_{j,20||} \cdot \hat{e}^{\tau f}_{k,20||}, \]  
Eq. A-5

where the electric field unit vectors in the primed coordinate system are,
\[ \hat{e}_{20||} = (\cos \theta_{20||}, 0, -\sin \theta_{20||}), \]
\[ \hat{e}^{\tau f}_{20||} = (-\cos \theta_{20||}, 0, -\sin \theta_{20||}), \]  
Eq. A-6

Finally, the standard transmission (\( t \)) and reflection (\( r \)) Fresnel coefficients in Eq. A-2 and Eq. A-6 for \( p \)-polarized (||) and \( s \)-polarized (\( \perp \)) light at the air/film (af), film/substrate (fs), and substrate/air (sa) interfaces are, given by,
\[ t^\text{af}_{20||} = 2\cos \theta (\cos \theta_{20||} + n_{20||} \cos \theta), \]
\[ t^\text{af}_{20||} = 2\cos \theta (n_{20||} \cos \theta_{20||} + \cos \theta), \]
\[ t^\text{af}_{20||} = 2n_{20||} \cos \theta_{20||} (n_{20||}^{\text{sub}} + n_{20||} \cos \theta_{20||}^{\text{sub}}), \]
\[ t^\text{af}_{20||} = 2n_{20||}^{\text{sub}} \cos \theta_{20||}^{\text{sub}} (n_{20||}^{\text{sub}} + \cos \theta_{20||}^{\text{sub}}), \]
\[ t^\text{af}_{20||} = (n_{20||} \cos \theta - \cos \theta_{20||})/(n_{20||} \cos \theta + \cos \theta_{20||}), \]
\[ t^\text{af}_{20||} = (n_{20||}^{\text{sub}} \cos \theta_{20||} - n_{20||} \cos \theta_{20||}^{\text{sub}})/(n_{20||}^{\text{sub}} \cos \theta_{20||} + n_{20||} \cos \theta_{20||}^{\text{sub}}), \]  
Eq. A-7

where using Snell’s law, the refracted angles can be obtained by,
\[ \sin \theta_{20||} = \sin \theta / n_{20||}, \]
\[ \sin \theta_{20||} = \sin \theta / n_{20||}, \]
\[ \sin \theta_{20||} = \sin \theta / n_{20||}^{\text{sub}}, \]  
Eq. A-8
Appendix B. Derivation of reflected SHG intensity for a birefringent non-absorbing single interface

For a uniaxial material with the ordinary (extraordinary) index of refraction, \(n_{i\omega_0}\) (\(n_{i\omega_e}\)), lying parallel (perpendicular) to the plane of the sample at the fundamental \((i=1)\) and SHG \((i=2)\) frequencies, the expression for the reflected SHG intensity from a single interface is given by,

\[
I^r_{2\omega_0} = (I_o)^2 (d^{(l)}_{ee})^2 \Omega ,
\]

where the birefringent reflectance and transmittance of the fundamental and SHG fields in sample are accounted for in the \(\Omega\) term which is defined as,

\[
\Omega = \left(2 \cos \theta / c e_0\right) [n_{2\omega_0}(\theta_\omega) / n_{2\omega_0,0}]^2 \\
\times \left[(n_{\omega_0}(\theta_\omega))^2 - n_{2\omega_0}(\theta_\omega)^2 / (n_{\omega_0}(\theta_\omega)^2 - n_{2\omega_0}(\theta_\omega)^2)\right] \\
\times \left[t_{2\omega_0}^{\text{eff}} \right] / \left[\left(\cos(\theta_{2\omega} - \gamma_{2\omega}) - n_{2\omega_0}(\theta_{2\omega}) \cos \gamma_{2\omega} \cos \theta\right) \right] \\
\times \left[n_{\omega_0}(\theta_\omega) \cos \theta_\omega + n_{2\omega_0}(\theta_{2\omega}) \cos \theta_{2\omega}\right] \right]^2
\]

Eq. B-2

Here, the birefringent indices, \(n_{i\omega_0}(\theta_{i\omega})\) and \(n_{2\omega_0}(\theta_{i\omega})\), as well as the walkoff angle, \(\gamma\), are expressed as,

\[
n_{i\omega_0}(\theta_{i\omega}) = n_{i\omega_0} n_{i\omega_e} / [n_{i\omega_0} \cos^2 \theta_{i\omega_0} + n_{i\omega_e} \sin^2 \theta_{i\omega_0}]^{1/2},
\]

\[
n_{2\omega_0}(\theta_{i\omega}) = n_{2\omega_0} n_{2\omega_e} / [n_{2\omega_0} \cos^2 \theta_{i\omega_0} + n_{2\omega_e} \sin^2 \theta_{i\omega_0}]^{1/2},
\]

\[
\cos \gamma_{i\omega_0} = n_{i\omega_0} n_{i\omega_e} / n_{i\omega_0}(\theta_{i\omega}) [n_{i\omega_0}^2 + n_{i\omega_e}^2 - n_{i\omega_0}(\theta_{i\omega})^2]^{1/2},
\]

Eq. B-3

with the birefringent electric field unit vectors given as,

\[
n_{i\omega_0}(\theta_{i\omega}) = n_{i\omega_0} n_{i\omega_e} / [n_{i\omega_0}^2 \cos^2 \theta_{i\omega_0} + n_{i\omega_e}^2 \sin^2 \theta_{i\omega_0}]^{1/2},
\]

\[
n_{2\omega_0}(\theta_{i\omega}) = n_{2\omega_0} n_{2\omega_e} / [n_{2\omega_0}^2 \cos^2 \theta_{i\omega_0} + n_{2\omega_e}^2 \sin^2 \theta_{i\omega_0}]^{1/2},
\]

\[
\cos \gamma_{i\omega_0} = n_{i\omega_0} n_{i\omega_e} / n_{i\omega_0}(\theta_{i\omega}) [n_{i\omega_0}^2 + n_{i\omega_e}^2 - n_{i\omega_0}(\theta_{i\omega})^2]^{1/2}.
\]

Eq. B-4
The reflected effective $d$ coefficient and electric field unit vectors for a birefringent material become,

$$d_{\text{eff}}^r = \hat{e}_{1,2,2}^r, d_{ijk}^r \hat{e}_{j,\omega} \hat{e}_{k,\omega},$$

$$\hat{e}_{2,\omega}^r = [-\cos(\theta_{2,\omega} - \gamma_{2,\omega}), 0, -\sin(\theta_{2,\omega} - \gamma_{2,\omega})],$$

$$\hat{e}_{\omega} = [t_{o\parallel}^a \cos \phi \cos(\theta_{\omega} - \gamma_{\omega}), t_{o\perp}^a \sin \phi, -t_{o\parallel}^a \cos \phi \sin(\theta_{\omega} - \gamma_{\omega})],$$

Eq. B-5

and the birefringent Fresnel coefficients and refracted angles are,

$$t_{o\parallel}^a = 2 \cos \theta / [\cos(\theta_{\omega} - \gamma_{\omega}) + n_{\omega} (\theta_{\omega}) \cos \gamma_{\omega} \cos \theta],$$

$$t_{o\perp}^a = 2 \cos \theta /[n_{\omega} \cos \theta_{\omega} + \cos \theta],$$

$$r_{2,o\parallel}^a = [n_{2,\omega} (\theta_{2,\omega}) \cos \gamma_{2,\omega} \cos \theta - \cos \theta_{2,\omega}] / [n_{2,\omega} \cos \theta + \cos \theta_{2,\omega}],$$

$$\sin \theta_{\omega} = n_{\omega \omega} \sin \theta /[n_{\omega}^2 (n_{\omega \omega})^2 + (n_{\omega \omega}^2 - n_{\omega \omega}^2) \sin^2 \theta]^{1/2}.$$  

Eq. B-6
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