A STUDY OF STRUCTURE INDUCED PHASE PHENOMENA IN PEROVSKITE OXIDE THIN FILMS

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by
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Abstract

The three core tenants of materials science are theory, synthesis, and characterization. A solid theoretical framework is required for understanding of the problem at hand and using that knowledge to advance new areas of research. Synthesis of pristine materials is required to study the theory in a physical system and prevent misinterpretation of results. Complex structures and compositions are often the most interesting, and when defects and impurities are of interest, "perfectly-imperfect" samples are required which are often the most challenging to synthesize. Characterization of these materials is equally as important and complex, requiring careful sample preparation and experimental setups. Further, it is not always clear how to observe the property of scientific interest, and new characterization techniques must be developed.

This dissertation focuses on using these three tenants to understand and advance the field of transition metal perovskite complex oxides using thin films of the incipient ferroelectrics CaTiO₃ and SrTiO₃ and antiferromagnetic Mott-Insulators LaVO₃ and YVO₃. The knowledge gained in this thesis can be applied to other complex oxide materials in better understanding magnetic and electronic transitions, high Tc superconductivity and quantum hall effect. Coupled with the relatively simple structure and ease of integration of multiple different chemical compounds into a single heterostructure leads to near numerous avenues to design functionality into materials.

The first sections of this thesis begin with (1) an introduction to the basic science and past work in perovskite oxides, followed by (2) exploring the most common and promising synthesis routes, and finally (3) the various characterization methods used. The 4th chapter addresses the
specific challenges of growth of ternary complex oxide thin films in an industrially profitable fashion. The three primary criterion that these deposition methods must adhere to is that they must (a) control film stoichiometry to less than 1% deviations, (b) deposit conformal coatings over standard 8” silicon wafers, (c) and exhibit deposition rates in excess of 1 µm/hr. We show that these can be achieved using a hybrid molecular beam (hMBE) epitaxy approach and outline a route for commercially viable growth of complex oxides on silicon. This method is applied directly to the deposition of SrTiO₃ on silicon for virtual single crystal perovskite substrates.

The 5th chapter of this thesis discusses the effect of epitaxial strain, stoichiometry and interfacial coupling in heterostructures of complex oxides. In the (SrTiO₃)ₙ(CaTiO₃)ₙ series of superlattices grown by hMBE, it is found that interfacial energies play a large role in dictating the macroscopic properties, particularly ferroelectricity. In coherently strained thin films, both CaTiO₃ and SrTiO₃ exhibit relaxor-like ferroelectric behavior below room temperature. However, certain superlattices of these materials show nonpolar behavior when probed using second harmonic generation (SHG). High resolution scanning transmission electron microscopy (STEM) reveals that the symmetry in the superlattice is different from the individual parent compounds at the same strain state. It is found these are directly related to the high density of interfacial layers present in the films. Further, interfacial mixing of the constituent layers on certain superlattices leads to the development of a Ca₁₋ₓSrₓTiO₃ alloy which develops a ferroelectric moment at low temperatures, leading to spurious SHG signals. The findings of this experiment highlight the sensitivity of these complex layered structures to strain, stoichiometry, distortion coupling effects, and interfacial mixing.
Lastly, the growth, characterization, and properties of the rare earth Mott-insulating vanadates, with focus primarily on LaVO$_3$, as well as preliminary work on YVO$_3$ and (LaVO$_3$)$_n$(YVO$_3$)$_n$ heterostructures is discussed. In bulk, the material exhibits the orthorhombic $Pbnm$ crystal structure. It is found that numerous and distinct structural ordering parameters emerge when grown as an epitaxial thin film. Further, these ordered phases are heavily dependent on temperature, as well as substrate symmetry and film thickness, suggesting numerous avenues to design functionality into these materials. This phenomenon is explored using both room temperature and cryogenic STEM, and synchrotron diffraction.
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Chapter 1. Overview

This chapter explores the core principles of structure-property relationships in single-crystalline perovskite oxides in bulk and in thin film forms. The relations are centralized on the tolerance factor and coupling of the oxygen octahedral rotations to the development of a polar ground state in the ferroelectric perovskites, as well as a Mott-insulating state in the correlated electronic systems. This lays the framework for the scope of this thesis, focusing on how manipulating the structure of the titanate and vanadate perovskites can drive different properties using epitaxial growth.

1.1 Theory: The materials by design strategy

Neumann’s law of symmetry states that the symmetry operations of a materials properties reflect the symmetry operations of the point group of that material\(^1\). This seemingly self-evident law has very powerful and far-reaching implications in the study of materials, from understanding the relationship between polar ferroelectrics and nonpolar dielectrics, to dictating the shape of the Fermi surface in metals and superconductors, and explaining hardness of metal through slip systems. In a general sense, this law can be applied to almost any material to explain why it exhibits the properties that it has. However, the converse of this theory asserts that simply by breaking symmetry elements of the crystal structure, the properties can be drastically altered. It is this idea that is currently driving the materials-by-design strategy. Effectively, by manipulating certain symmetry elements, e.g. by imposing epitaxial strain, it is possible to engineer properties and functionality into materials that are otherwise not observable in nature.

The expansion of this strategy has been due primarily to advancements in three major areas: computational modelling and theory, thin film synthesis, and atomic resolution characterization.
Computational methods have always been considered an efficient to studying materials, however, due to the exponential increase in complexity with increasing size of the system, these early trials were limited to relatively simple systems and a very focused approach. With the increased availability of economical processing power as well as machine learning algorithms, there has been a paradigm shift to high-throughput computation. In this approach, thousands of compounds can be modelled and theoretically studied in a very short period of time, with the goal of finding materials that exhibit a certain property such as specific band gaps and work functions for water splitting\(^2\) and energy storage\(^3\), or predicting for ferroelectric or piezoelectrics with enhanced properties\(^4-6\) or materials that combine mutually exclusive properties, such as ferroelectric and ferromagnetic order (multiferroics)\(^7,8\) or optical transparency and metallic conductivity\(^9,10\). Advancements in deposition techniques has allowed single component systems to be deposited with quality exceeding those of bulk single crystals, but also allows, complex heterostructures, and layered superlattices to be deposited with atomically sharp interfaces, vastly expanding the range of possibilities for materials. Finally, these materials are characterized both looking at the macroscopic properties, as well as the atomic scale to confirm the positioning of atoms on the unit cell level. This information is then fed back into the theoretical modeling to improve the predictive capabilities and close the loop constituting a modern approach to the core mission of materials science to elucidate the structure property relationship of materials spanning orders of magnitude from the atomic to the macroscale. Here, structure is manipulated at the atomic level to engineer properties of materials at the macroscale. The three tenants, theory, synthesis and characterization with atomic precision need to be applied together.
1.2 Application to perovskite oxides

The field of perovskite oxides are ideal systems to study the materials by design approach. The typical ABX$_3$ perovskites possess some of the most diverse range of properties, including (anti)-ferroelectricity, piezoelectricity, (anti)-ferromagnetism, multiferroicity, electronic phase transitions, and high-$T_c$ superconductivity (Figure 1-1 a). This is due to the large number of chemical compositions that crystallize in the perovskite structure, exemplified by the periodic table in Figure 1-1 b. This broad arrangement of compositions, as well as potential alloys between two end member compounds, leads to an even greater multitude of electronic and magnetic ground state configurations. Furthermore, as the ionic radii of the incorporated cations and anions change, the crystal structure distorts to accommodate these changes, and thus the structure can vary from cubic to tetragonal, orthorhombic, rhombohedral or monoclinic symmetries, again altering the materials properties and compounding this rich property map.

![Figure 1-1: Properties and compositions of perovskites.](image)

The various properties present in the crystal structure of perovskite oxides is shown (a) exhibiting nearly all properties present in materials, ranging from classical to quantum mechanical in nature. This is primarily due to the wide variety of compounds available, with the available elements that are found in the perovskite crystal structure shown in (b). *Reproduced from reference (97).*

The general configuration of the cubic ABO$_3$ perovskite is shown in the inset of Figure 1-1 a. Here an A-site usually occupied by alkali, alkaline earth or rare earth elements, is located at the
8 corners of the cubic unit cell, oxygen at the 6 face centered positions and the B-site, typically a transition metal element, at the body center of the unit cell. In this sense, the B-site cation is surrounded by an oxygen octahedra. This is shown for prototypical compound SrTiO$_3$ in Figure 1-2. As different elements are added, the crystal structure can deviate from this ideal lattice. This is generally understood by steric arguments, and results in Goldschmidt’s tolerance factor ($t$)$^{11}$ shown in Figure 1-2. It is simple to derive a relation between the radius of the ions to the geometric constraints of cube, particularly the lattice constant to the face diagonal. This then results in Eq. 1, where the radius of the A, B and oxygen ions are given by $r_A$, $r_B$, and $r_O$, respectively.

(Eq. 1) \[
\frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} = t
\]

In the case of a cubic system, the tolerance factor will be roughly 1, such as the case for SrTiO$_3$. However, for different ions where the tolerance factor does not equal 1, it can be seen...
that the above relation no longer holds true just from simple geometric arguments of the ionic radii.

In order for these ions to then fit within the unit cell, the ionic bonding distance must be distorted (a highly energetically unfavorable process) or the bonding angles can distort. This allows a number of ions of different ionic compounds to fit in a derivative of this cubic structure. The distortions of the unit cell depending on tolerance factor are given in Table 1-1.

Table 1-1: Tolerance factors of various perovskite chemical compositions.

<table>
<thead>
<tr>
<th>TOLERANCE FACTOR</th>
<th>STRUCTURE</th>
<th>EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>T &gt; 1</td>
<td>Hexagonal, tetragonal</td>
<td>BaTiO₃, BiFeO₃</td>
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<td>T = 0.91 - 1</td>
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<td>SrTiO₃, SrVO₃</td>
</tr>
<tr>
<td>T = 0.71 – 0.91</td>
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</tr>
<tr>
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<td>Trigonal, different structures</td>
<td>NdAlO₃</td>
</tr>
</tbody>
</table>

These different symmetries differ from their cubic counterparts by various atomic distortions, typically displacement of the A-site cations off the corner sites, displacement of the B-sites off the central position, rotation of the oxygen octahedral along the 3-primary axis, and strain or shearing of the cubic structure. Perhaps the most well studied of these is the cooperative rotation of the oxygen octahedral along the 3 principle axes. For tolerance factors below unity, the BO₆ octahedral network is too large to fit comfortably within the unit cell. The network can accommodate some strain by decreasing the B-O bond length, but this quickly becomes energetically unfavorable. Instead, as the tolerance factor drops below approximately 0.91, the octahedral network rotates to accommodate a smaller unit cell, while maintaining the B-O bond length.

These symmetries differ from their cubic counterparts by various atomic distortions, typically displacement of the A-site cations off the corner sites, displacement of the B-sites off the
central position, rotation of the oxygen octahedral along the 3-primary axis, and strain or shearing of the cubic structure. Perhaps the most well studied of these is the cooperative rotation of the oxygen octahedral along the 3 principle axes. For tolerance factors below unity, the BO$_6$ octahedral network is too large to fit comfortably within the unit cell. The network can accommodate some strain by decreasing the B-O bond length, but this quickly becomes energetically unfavorable. Instead, as the tolerance factor drops below approximately 0.91, the octahedral network rotates to accommodate a smaller unit cell, while maintaining the B-O bond length.

These cooperative rotations have been most famously characterized by A. M. Glazer in his paper titled *The Classification of Tilted Octahedra in Perovskites*\textsuperscript{12}. The nomenclature describes the method to quickly determine direction, magnitude, and phase of the tilting pattern of the oxygen octahedron in the perovskite structure now known as “Glazer notation”, and will be referenced heavily throughout the proceeding manuscript\textsuperscript{13}. Figure 1-3 shows a few examples of this structure for the most common tilt patterns. In this notation, the structure is considered to be *pseudocubic*, that is that the principle axes [100], [010] and [001] are maintained as the symmetry is lowered from cubic to orthorhombic or rhombohedral. To avoid confusion, pseudocubic notation will be following by a subscript $p$, orthorhombic $o$, and rhombohedral $r$. The three letters indicated the axis the octahedral are tilted about, with the first being the [100]$_p$, the second the [010]$_p$, and the third the [001]$_p$. The letter, either $a$, $b$ or $c$, refers to the magnitude of the tilting, with equal magnitudes of tilt (or lack thereof) using the same letter. The third notation is given as a superscript above each letter. This refers to whether the tilting of the adjacent octahedra along that axis are in phase when viewed down that axis and is indicated with a plus (+), or out-of-phase
indicated with a minus (-). Figure 1-3 c and d show the CaTiO₃ unit cell observed along the [100]ₚ and [001]ₚ, respectively. Using Glazer notation, it is clear to see that this material has out-of-phase rotations, equal in magnitude when viewed down the [100]ₚ and [010]ₚ, while an in-phase rotation of opposite magnitude down the [001]ₚ. As can be seen, the central A-site cations displace as well as their position and is driven by the lowest energy location in the network BO₆ octahedra. These displacements are not as succinctly classified, as there are multiple different directions in which they can occur.

In the majority of perovskites, the B-site ion sits in the center of the oxygen octahedra, with approximately equal bond lengths between the six neighboring oxygens. Certain perovskites

**Figure 1-3:** Symmetries and rotations in perovskite oxides. The pseudocubic unit cells of cubic SrTiO₃ (a), tetragonal SrTiO₃ (b), and orthorhombic CaTiO₃ (c & d), to highlight the different rotational tilt patterns. Out-of-phase tilts are given by blue arrows, and in-phase tilts are red.
undergo a *Jahn-Teller* (JT) distortion, in which the oxygen octahedra is elongated in one of the 3 principle axes, lowering the overall crystal symmetry\(^{14}\). Similarly, a *second-order Jahn-Teller* (SOJT), sometimes referred to as a *Pseudo Jahn-Teller* (PJT), also leads to a breaking of the symmetry, however in this case the central cation displaces towards either the apex (6), edge (12) or face (8) of the octahedra\(^{15-17}\). This typically occurs in systems with large, highly polarizable A-site cations relative to the smaller B-site cation, such as the case in BaTiO\(_3\) and PbTiO\(_3\). In this scenario, the B-site cation is small enough to move within the oxygen octahedra towards the neighboring anions to lower the total energy, which creates a permanent dipole moment in the unit cell\(^{18}\). These types of distortions are crucial for piezoelectric and ferroelectric compounds, and will be discussed in further detail in the following section.

1.3 **Ferroelectricity and conductivity in perovskites**

Perovskites are among the most technologically important class of materials as they exhibit multiple functional properties interesting for future memory and computation devices, including field and strain tunable polarizations\(^{19-21}\), correlated electron behavior\(^{22}\), and multiferroic order\(^{8,23,24}\). Though these properties rely on entirely separate mechanisms, they are all intrinsically coupled to the structure of the material. Consider the electronic orbitals of SrTiO\(_3\), shown in Figure 1-4. Sr ionizes to Sr\(^{2+}\) with an empty 5\(s^0\), Ti to Ti\(^{4+}\) and 3\(d^0\), and O to O\(^{-2}\) with a full 2\(p^6\) band. The 5-fold 3\(d\) bands of the Ti\(^{4+}\) ion split when placed in a perovskite crystal as the, the \(d_{z^2}\) and \(d_{x^2-y^2}\) electron orbitals point directly at the neighboring oxygens, raising energy to form the doubly degenerate \(e_g\) bands, while the triply degenerate \(d_{xy}, d_{xz},\) and \(d_{yz}\) form the lower \(t_{2g}\) band. Rotations of the oxygen octahedra as well as changes in the unit cell can further split these bands. Epitaxial strain also serves to split the bands, as tensile strain will shorten the unit cell in
the out-of-plane direction, thus raising the energy levels of the orbitals with a z component \((z^2, xz, yz)\), while lowering orbitals that are in the plane \((xy, x^2-y^2)\), while tensile strain will produce the opposite effect\(^{25,26}\). This splitting allows for multiple electronic and magnetic ground states to exist in materials that are chemically very similar, and can drive diverse properties.

Ferroelectricity is one such property of note that is closely tied to structure. Ferroelectricity is defined as a spontaneous electrical polarization that is reversible under an applied electric field. The most critical consideration for this property is the lack of inversion center, or center of symmetry in the crystal. This is simply understood from Neumann’s law, as by definition an electric polarization has no inversion center. In perovskites, the primary method of symmetry breaking is a SOJT, caused by a displacement of the central cation. Surprisingly, only a small subset of perovskites exhibits this behavior, and ordinarily thought of existing in perovskite structures which do not exhibit rotations, such as the prototypical perovskites \(\text{BaTiO}_3\) and \(\text{PbTiO}_3\).

**Figure 1-4: Evolution of the 3d orbitals in a transition metal perovskite oxide.** From left to right shows the 3d bands in a 5-fold degenerate configuration. Crystal field splitting creates the upper and lower \(e_g\) and \(t_{2g}\) bands in a cubic perovskite. Further splitting of these bands occurs due to octahedral rotations or epitaxial strain. Finally, a Jahn-Teller distortion or monoclinicity of the unit cell can separate the energy levels into 5 nondegenerate orbitals.
Benedek and Fennie have studied this phenomenon, finding that it is not necessarily the rotations that disrupt ferroelectricity, but rather that it is only when the B-site cation is very small relative to the oxygen octahedra that it cannot effectively bond to the 6 nearest neighbor oxygens, and so it displaces off-center of the oxygen octahedra to lower the nearest neighbor bonding distance. This only occurs for situations where the A-site is much larger than the B-site cation, which leads to tolerance factors of \( t \sim 1 \) or \( t > 1 \), and rotations are not stable in these materials\(^{27}\). The lack of ferroelectric perovskites simply arises from the relatively small number of perovskites that exhibit these tolerance factors.

Interestingly, they also discovered that ferroelectricity was possible in perovskites with tolerance factors \( t < 1 \), in which the ferroelectricity would be driven by a displacement of the A-site, rather than the B-site. In most perovskite which exhibit the a’a’c’\(^+\) (Pbnm) rotation pattern, the A-site displacements would order antiferrodistortive (AFD), in which the polar distortion of one A-site cation layer is cancelled out by the opposite polar distortion of the next layer. However, by stabilizing the a’a’a’\(^-\) (R\(\bar{3}\)c) rotational pattern, or by suppressing the octahedral tilts all together, the A-site ferroelectric moment could be stabilized in a large number of perovskites\(^{27}\). Recent predictions have suggested methods to disrupt these rotations through various layering schemes and build in polar moments in a method known as improper ferroelectricity\(^{28,29}\). As this mechanism allows for ferroelectricity in ordinarily nonpolar materials, it has potential to be used in magnetic oxides to create multiferroics\(^{30}\).

As SrTiO\(_3\) when fully ionized has no electrons in the conduction band, it is a traditional conventional d\(^0\) band insulator. The same is true for all the alkali earth titanates, hafnates, and zirconates, as is predicted by traditional band theory. Substitution of the titanium with a group 4
transition metal such as vanadium leads to the addition of one electron into the 3d bands, giving rise to the metallic d\textsuperscript{1} SrVO\textsubscript{3}, CaVO\textsubscript{3} and BaVO\textsubscript{3}. However, not all oxides behave traditional band structure. For instance, the same effect could be achieved instead of substituting the A site with a rare-earth cation such as La to form d\textsuperscript{1} LaTiO\textsubscript{3}, again with single electron in the 3d band, but in this case the material shows insulating behavior. This same is true for the rare-earth d\textsuperscript{2} vanadates, such as LaVO\textsubscript{3}, despite having 2 3d electrons. These materials are known as Mott-insulators, and deviation from traditional band theory is brought on by strong electron-electron correlations that are dictated by 2 parameters, the hopping amplitude (t) which dictate the probability for one electron to hop to the next site, and the onsite Coulomb repulsion (U), which is the effect of the electron “feeling” the electron on the neighboring site. This gives the parameter \( U/t \), which determines if the film is metallic or conducting. In perovskites, t can be modified through rotation of the oxygen octahedral rotations, changing the overlap of the 3d orbitals. Increasing the rotation angle decreases the orbital overlap, decreasing \( t \) and increasing the \( U/t \) parameter. As \( U/t \) increases beyond a critical value, the system undergoes a Mott metal to insulator transition, and goes to an insulating state. This offers a relative straightforward method to drive electron-electron correlations, tune MIT’s, and control other novel electronic phenomenon.

This effect is clearly observed in the rare-earth nickelates perovskites (RNiO\textsubscript{3}, with R = La, Ce, Pr, Nd, etc.) shown in Figure 1-5\textsuperscript{31}. LaNiO\textsubscript{3}, being the most cubic with the least octahedral rotation angle, is paramagnetic metal at all temperatures. Replacing La with the next smaller rare earth cation, Pr, decreases the tolerance factor and increases the octahedral rotation angles, and a bandwidth controlled MIT develops due to a reduction of the hopping integral, \( t \). Substituting in smaller cations further raises the temperature of the MIT, stabilizing the Mott-insulating state as a
direct result of changing the octahedral rotation angles. In the case of the rare-earth vanadates, the rotation angle is never reduced enough to create an MIT transition, and all these materials remain robust Mott-insulators. However, recent predictions have suggested further reduction of the oxygen octahedra rotation angles to a near cubic state in LaVO$_3$ could stabilize a metallic ground state$^{32}$. This unusual coupling between structural parameters and electronic conduction gives the perovskites the wealth of novel electronic properties.

1.4 Effects of epitaxial strain and interface coupling

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**Figure 1-5: Electronic and magnetic phase diagram of the rare-earth nickelates.** $T_{\text{MIT}}$ and $T_N$ is plotted as a function of tolerance factor. As the octahedral rotation angle, decreases, $T_{\text{MIT}}$ also drops due to an increase in the bandwidth $U/t$, until the MIT is completely suppressed for the largest of the rare-earth’s LaNiO$_3$. *Reproduced from Ref. (31).*
This ability to control properties by tuning the structure has led to an exotic array of properties in the bulk. However, there are only a limited number of ways to control the bulk structure. Chemical substitution has proven to be an effective method, but is limited by the availability of elements in the periodic table. For instance, the alkali earth titanates are of particular interest for their high dielectric constants for applications in microwave communications and energy storage capacitors. There is a trend of increasing dielectric constant with increasing A-site cation size up to the ferroelectric BaTiO$_3$. It would be ideal to extend this trend to stabilize higher dielectric constant materials using larger A-site alkali earth cations, however the only larger cation of this series is radioactive, thus putting a hard limit on this trend. Substitution with other divalent cations such as Pb, Zn, or Cd can slightly extend this trend, such as Pb in the case of PbTiO$_3$, but this is not always the case, as ZnTiO$_3$ and CdTiO$_3$ can both crystallize in the illmentite phase. Strain has also been shown to manipulate the various dielectric properties of materials such as BaTiO$_3$ and SrTiO$_3$. However, bulk ceramics can typically only be strained up to approximately 0.1% before fracture and are again limited, due to the inherent brittle fracture of ionically bonded materials.

Epitaxial thin films offer a robust method to stabilize these non-equilibrium states and harness their interesting properties for device applications. This is done by deposition of a thin film on a nearly-lattice matched substrate. Typically, the substrates exhibit the same or similar symmetry, chemical composition, and bonding type, however differ slightly in lattice constant. The atoms of the depositing film will adopt the in-plane lattice constant of the substrate, thus imparting a biaxial strain on the film in either a tensile (+) or compressive (-) direction. One large advantage of this method is that strains of up to a few percent are possible. Additionally, epitaxial
strain is biaxial in nature, and due to Poisson’s ratio an expansion in the in-plane lattice constant leads to a contraction in the out-of-plane lattice constant and vice versa. The highly anisotropic strain can therefore lower cubic symmetries and drive large tetragonal or orthorhombic distortions. The combined result of these is a profound effect on the ferroelectric and piezoelectric properties of perovskites. Figure 1-6 summarizes some of the ferroelectric properties of titanates and BiFeO₃ as a function of epitaxial strain. In all cases there is a significant enhancement of the ferroelectric transition temperature, Tₓ, above the bulk state, and has stabilized a ferroelectric state in the incipient ferroelectrics SrTiO₃ and CaTiO₃.

![Figure 1-6](image)

**Figure 1-6: Effect of strain on ferroelectric transition temperature.** The ferroelectric transition temperature, Tₓ, is due to a changing in symmetry from a polar to nonpolar phase. Here, the relation between Tₓ and epitaxial strain is shown for a variety of perovskite ferroelectrics. In all cases, strain enhances the ferroelectric moment, highlight the potential for strain to be used to tune ferroic order. From references.
Bulk studies of the nickelates mentioned in the previous section have shown that the MIT can be modulated by isostatic pressure as well. The insulating phase can be suppressed entirely in PrNiO₃ with pressures exceeding 11.6 kbar⁴⁶. It was predicted the same could be done for NdNiO₃ at pressure of 31 kbar, however these were unobtainable in the experimental setup⁴⁷. The MIT modulation by application of pressure is due to a decreasing degree of oxygen octahedral rotation, thus increasing the system bandwidth (W) and stabilizing the metallic state⁴⁷.

This type of behavior can be replicated in thin films. Lui et. al. have grown a series of epitaxial NdNiO₃ thin films on substrates of various lattice constants, leading to strain states ranging from $\varepsilon \sim +4\%$ to $-2.9\%$⁴⁸. The results showed that MIT could be tuned to higher temperatures up to approximately 250 K at positive strain values. Conversely, the MIT is entirely suppressed for all negative strain. Interestingly, the MIT is suppressed below bulk even for nominally zero strain state, suggesting that film thickness, interface effects, and structural defects can play a substantial role in the electronic structure of these materials as well.

A second route to controlling a materials structure and properties through epitaxy is the use of interfacial coupling of oxygen octahedra. In a fully coherent epitaxial film, bond lengths can extend and contract, and bond angles can change, however the bonds themselves cannot break. Therefore, when two perovskites with different oxygen octahedral rotational patterns are joined through an epitaxial interface, there must be a continuous change in the bonding environment to maintain octahedral connectivity across the interface. This effect can be observed in its most basic form at the interface between a cubic $(LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7}$ (LSAT) substrate $(a₀a₀a₀)$ and an orthorhombic CaTiO₃ film $(a‘a‘c‘)$. 

The LSAT unit cell exhibits oxygens at the face-centered positions in the unit cell. In CaTiO$_3$ the oxygens are displaced from these positions due to the rotations of the oxygen octahedra. In order to maintain a continuous transition across the interface, it was observed that the rotations are suppressed in the first 4 monolayers of the CaTiO$_3$ film, with the rotations increasing at each successive monolayer until a bulk value of $\sim 10^\circ$ was reached, which can be seen in Figure 1-7$^{49}$. Additionally, it was discovered that the rotations from the film were also imprinted in the last 2 monolayers of the LSAT substrate. To show that these effects were not simply due to strain, a second CaTiO$_3$ film was deposited on NdGaO$_3$ (a’a–c’), which has a nearly identical pseudocubic lattice constant to LSAT, however exhibits the same octahedral rotation pattern as CaTiO$_3$. It was found that the rotational pattern was uninterrupted between the film at the interface, showing that the suppressed rotations for the CaTiO$_3$ film on LSAT in the proximity of the substrate film interface was due maintaining octahedral connectivity.

The effect of these rotations are visible in ferroelectric properties of the film. It was observed that while both CaTiO$_3$ films were ferroelectric at low temperatures, CaTiO$_3$ on LSAT showed a greatly enhanced remnant polarization ($5 \mu$C/cm$^2$) and $T_c$ (140 K) than films on NdGaO$_3$ ($1.5 \mu$C/cm$^2$ and $T_c = 70$ K)$^{49}$. This discrepancy is attributed to the suppression of the octahedral rotations at the interface, leading to a more symmetric structure with lower octahedral tilts, allowing for displacement of the cations and a more robust ferroelectric state.
In addition to altering interfacial bond angles, substrate driven octahedral rotations can be used to control film orientation and induce metastable rotational patterns in perovskites. Choquette et al. have studied a series of EuFeO$_3$ films grown on substrates under both tensile and compressive strain, as well as various octahedral rotational patterns. It was found that in the absence of rotations, EuFeO$_3$ films adopted a mixed $a^-a^-c^+$ and $a^+a^-c^-$ rotational pattern under epitaxial compressive strain, and $a^-a^-c^+$ pattern in tensile strain. However, when grown on GdScO$_3$ (110), the film reorients to a single-phase $a^-a^+c^-$ pattern despite being in tensile strain, so that the films octahedral rotation pattern matches that of the substrate. Therefore, just by choosing a specific cut of a substrate, the structure and orientation of the film’s octahedral rotation pattern can be altered.
This process of symmetry control through substrate coupling is broadly applicable to thin films in the field of perovskites. First principle calculations of various perovskite compounds of interest in different rotational symmetries was performed by Chen et. al\textsuperscript{51} (Figure 1-8). As can be seen, while the \textit{Pbnm} \textit{a'}\textit{\textit{a}}'\textit{c}\textsuperscript{+} state is the lowest energy state for the majority of perovskites studied, there are numerous nearly-degenerate rotational patterns, in many cases less than 25 meV. This suggests the possibility for phase coexistence in thin films, as well as the possibility to stabilize these metastable states that cannot be synthesized in bulk using strain and interfacial coupling.

![Figure 1-8: Energies of perovskite oxide symmetries from first-principles.](image)

(a) The energy differences between the oxygen octahedral rotational patterns are calculated for numerous perovskite oxides. The \textit{a'}\textit{\textit{a}}'\textit{a'} structure is taken as the zero energy. The amplitude of the octahedral tilting shown with respect to tolerance factor (b) is given for the tilt patterns studied in (c-d). While most perovskites favor the \textit{Pbnm} (\textit{a'}\textit{\textit{a}}'\textit{c}\textsuperscript{+}) pattern, the energy difference can be small, seen in the lanthanum and strontium containing perovskites studied here. Reproduced from reference (51).
Chapter 2. Synthesis

Thin film deposition is the process by which a thin layer of material, usually on the order of a few micrometers down to a single layer of atoms, is applied to a substrate. This can be generally divided into two distinct cases. The first being the case where the substrate is the device of interest, and the film is used as a coating to enhance a specific property of the material. These could be considered thermal barrier coatings\(^5^2\), passivation layers and anti-corrosive coatings\(^5^3,5^4\), as well as coatings for increasing hardness and wear resistance\(^5^5,5^6\). The second application is where the added functionality of the film is the material of interest\(^5^7,5^8\), and the substrate provides a rigid support with specific properties to complement the desired application of the film. This is typically what is used in electronic and optical applications, and will be the topic of this thesis.

In this chapter the fundamentals of oxide thin film growth are explored in relation to surface energies, film nucleation, and subsequent growth. The oxide deposition techniques of molecular beam epitaxy, pulsed laser deposition, sputtering, and hybrid molecular beam epitaxy are discussed with emphasis on minimization of defects through low-energy deposition methods and development of a self-regulated growth mechanism for deposition of stoichiometric, ABO\(_3\) perovskite thin films.

2.1 Science of Surfaces, Thin Films and Epitaxy

In an ideal bulk crystal, all atoms have their bonds fully satisfied, with translation symmetry preserved between the unit cells. At surfaces, this periodicity is broken, leaving configurational degrees of freedom to minimize the free energy of the surface, e.g. by the structural rearrangement of dangling bonds. These dangling bonds are highly energetically unfavorable, and the surface will undergo drastic changes in order to lower their energy, either by bonding to
contaminant gaseous molecules or by reconstructing their atomic arrangement to minimize the number of unsatisfied bonds. It is incredibly difficult to predict how these surfaces will reconstruct as the reconstructions can be exceedingly complex for relatively simple materials system, posing a challenge but also a tremendous opportunity to stabilize surface states with exotic properties that cannot be found in bulk. For example the Si (111) is a simple hexagonal close packed surface with six-fold symmetry, but undergoes a 7x7 reconstruction to a much more complex geometry show in Figure 2-1\textsuperscript{59–61}. Further, these reconstructions are sensitive to factors such as partial pressures of gases, defects present within the crystal, and angle of the surface relative to the crystalline lattice.

**Figure 2-1: 7x7 surface reconstructions on clean Si (111).** (a) The silicon surface reconstruction shown in top-view the different adatom positions on the surface. (b) A cross sectional schematic reveals the adatoms sit at the locations with the higher number of dangling bonds on the surface. (c) This reconstruction appears as triangles in a close-packing configuration in STM, revealing the long range ordering on the surface. (d) These reconstructions give rise to a 7x7 reconstructed RHEED pattern. *Reproduced from references \textsuperscript{59–61}.*
Surfaces become even more complex for the case of SrTiO$_3$, in which the ternary compound can undergo various different reconstructions based on factors such as not only oxygen partial pressure and temperature, but also stoichiometry considerations. Numerous different surface reconstructions have been reported just for the SrTiO$_3$(001) interface, including the (1x1)$^{62-67}$, (2x1)$^{65-70}$, (2x2)$^{64,65,71-73}$, c(4x2)$^{64,67,70,72-74}$, c(4x4)$^{67,72}$, (4x4)$^{72}$, c(6x2)$^{64,66,68,75,76}$, ($\sqrt{5}x\sqrt{5}$)R26.6°$^{62,72,77,78}$, ($\sqrt{2}x\sqrt{2}$)R45°$^{79}$ and ($\sqrt{13}x\sqrt{13}$)R33.7°$^{72,80}$. The sensitivity of the surface is evident as different reconstructions have been reported for nominally similar surface treatments$^{73}$, and fully understanding the science behind each individual reconstruction is well beyond the scope of this thesis. However, information on the pertinent surface reconstructions for this thesis is given in the relevant chapters pertaining to each materials system.

This complex surface energy can be largely ignored for bulk materials, as the total ratio of surface atoms to bulk atoms is negligible for sizes over 1 mm$^3$. For instance, if we assume a spherical particle of 1mm diameter and a surface layer of approximately 1 nm, the ratio of bulk atoms to surface atoms exceeds 10$^6$. However, if we take that same volume of material, and stretch it over a 6” wafer, it will form a film approximately 15 nm thick, and the surface region exceeds 10% of the total volume of the film. Thus, while bulk synthesis primarily focuses on achieving the most thermodynamically favorable state, thin films are often metastable and synthesis of a crystalline film is dependent on various surface effects, which are discussed below.

The process for deposition from the gaseous phase onto a surface is outlined in Figure 2-2 a in which a schematic of a gaseous atom element $A$ film being deposited on a substrate of element $S$ is given. The reaction follows as:

(Eq. 2) \[ A_g + S_s \leftrightarrow A_s + S_s \rightarrow AS_s \]
The atom A first physisorbs to the substrate, and diffuses across the surface. If the atom finds a suitable bonding site it can chemisorb to the surface, forming a permanent A-S bond. It can also thermally desorb from the surface, going back to the gas phase. Once the entire substrate has been coated by the film, the reaction then proceeds as:

\[(\text{Eq. 3})\]

\[A_g + A_s \leftrightarrow A_s + A_s \rightarrow A A_s\]

This view gets more complex when we consider nucleation, surface energies and strain. When a film deposits from the vapor phase, there is a change in the free energy per unit volume, \(\Delta G_v\), given by:

\[(\text{Eq. 4})\]

\[\Delta G_v = -\frac{k_B T}{V} \ln \left( \frac{P_v}{P_s} \right)\]

In which \(V\) is the atomic volume, \(P_s\) is the vapor pressure above the film, and \(P_v\) is the vapor pressure of the supersaturated vapor. In case where \(P_v > P_s\), \(\Delta G_v\) is negative and the film will deposit. However, in the case where \(P_v < P_s\), \(\Delta G_v\) is positive. In this case, the rate of thermal desorption is greater than the rate of chemisorption, and the film will not nucleate. The surface/interfacial energies must be factored into the equation. Figure 2-2 a shows a film (red) at the early stages of deposition on a substrate (green). There are three interfaces. The interface between the substrate and atmosphere (\(\gamma_{sv}\)), between the atmosphere and film (\(\gamma_{fv}\)), and the interface between the film and substrate (\(\gamma_{sf}\)). If we assume the particles deposit as semi-spherical droplets, the contact angle (\(\theta\)) of the droplet to the surface is approximated by 81,82:

\[(\text{Eq. 5})\]

\[\cos(\theta) = \frac{\gamma_{fv} - \gamma_{sv}}{\gamma_{sf}}\]
If the energy difference between atmosphere-film-surface to atmosphere-substrate-surface is positive, \( \gamma_{fv} > \gamma_{sv} \) then \( \theta \) is less than 90° and the film will wet the surface and will deposit in a conformal, layer-by-layer fashion (Figure 2-2 b, c). If the opposite is true \( \gamma_{fv} < \gamma_{sv} \), then \( \theta \) will be less than 90° and the film will most likely ball up on the surface and form a roughened film, known as Volmer-Weber growth. There is also the situation where the film will wet the surface forming a conformal layer, then inclusion of strain or defects change the surface energy and the film roughens, known as Stranski-Krastanov growth. At this point, we can consider the total energy of the system as:

\[
\Delta G = V_f \Delta G_v + \gamma_{fv} A_{fv} + (\gamma_{fs} - \gamma_{sv}) A_{sf}
\]

(Eq. 6)

where \( V_f \) is the volume of the deposited material, and \( A_{fv} \) and \( A_{sf} \) are the surface areas of the film-atmosphere and surface-atmosphere interfaces. Replacing these terms with the radius of the deposited particle, \( r \), the equation becomes:

\[
\Delta G = \left[ \frac{\pi}{3} r^3 \Delta G_v + 4\pi r^2 \gamma_{sv} \right] + \left[ \frac{2 - 3\cos(\theta) + \cos^3(\theta)}{4} \right]
\]

(Eq. 7)

This equation presents the barrier for nucleation. In this case, if \( \Delta G_v \) is still negative, growth is possible. However, steps must be taken to lower the surface energy, such as the use of a seed layer.

The last energy consideration occurs for the case of epitaxial deposition. For epitaxial films, a material is deposited on a substrate with a similar structure and lattice constant. Rather than form interfacial defects, which would be energetically unfavorable, the film distorts to adopt the lattice constant of the underlying substrate and form a “defect-free” interface. This method is
useful to stabilize metastable states and grow single crystalline thin films, free of grain boundaries and other structural defects. The disadvantage to this method is that it is thickness limited. While surface energy is fixed, the total strain energy of the film increases with increasing thickness. At a critical thickness, the cost of the strain energy outweighs that of the interfacial energy, and the film relaxes back to the bulk lattice constant through the formation of defects. This phenomenon has been well explored in SrTiO$_3$ films grown by hMBE on LSAT$^{83}$, in which it was found that coherent, fully strained films could be grown to 180 nm before the onset of relaxation occurred, and films needed to be grown in excess of 600 nm until they fully relaxed. Interestingly, using the theoretical Matthews and Blakeslee equation$^{84}$, which only considers the strain energy, and energy due to misfit dislocation formation, the critical thickness should be limited to 12 nm, over 10x smaller than the experimental value, suggesting that other factors such as such as ferroelectric domains, oxygen vacancies, or other defects may contribute to strain relaxation and the ultimate critical thickness of the film$^{83}$. 
2.2 Deposition techniques of complex oxides

Nearly all classes of materials have been made into thin films of some form using the various physical and chemical vapor deposition techniques developed and perfected over the past decades. While each materials system has their own specific challenges, transition metal complex
oxides are known for being notoriously difficult. One difficulty can be clearly seen from the phase diagrams in Figure 2-3 a of the prototypical perovskite SrTiO$_3$ and the transparent conductor SrVO$_3$. In the SrO-TiO$_2$ binary phase diagram, SrTiO$_3$ is a line compound and only forms for the exact 1:1 stoichiometric ratio. Any deviations from this will lead to the formation of undesirable 2$^{nd}$ phases that can have drastic negative effects on the properties. Figure 2-4 shows the dielectric constant of Sr$_{1+x}$TiO$_{3+\delta}$ films grown on DyScO$_3$ substrates by molecular beam epitaxy. The figure shows the dielectric constant peaks for the stoichiometric sample, while the non-stoichiometric samples show a diffuse peak and relaxor-like behavior.

![Figure 2-3: Compositional phase diagrams of perovskite oxides.](image)

As can be seen any deviation from the stoichiometric phase leads to precipitation of unwanted 2$^{nd}$ phases that deteriorate the targeted properties. Reproduced from references (85, 86).

A plot of the out-of-plane lattice constant for homoepitaxial SrTiO$_3$ films grown using various deposition methods is shown in Figure 2-4 b. The incorporation of defects leads to local
strain fields that cause an expansion of the lattice. These defects can be seen in accompanying microstructures\textsuperscript{88} (Figure 2-4 d-g).

While A:B cation stoichiometry is critical in SrTiO\textsubscript{3} and need to be controlled precisely during growth, oxygen concentration is not as problematic. Sr is robustly 2\textsuperscript{+} in the oxidation state, and Ti may adopt a mixed 3\textsuperscript{+} to 4\textsuperscript{+} oxidation state, the structure remains as a perovskite and oxygen vacancies can simply be annealed out after the growth. The formation energy and diffusion of oxygen vacancies in SrTiO\textsubscript{3} has been well studied\textsuperscript{89–94}. The defect formation equation of an oxygen vacancy in SrTiO\textsubscript{3} thin films is fairly simple, given by Eq. 8, and reveals that each oxygen vacancy can contribute 2 carriers to the conduction band.

\textbf{Eq. 8} \[ O_{o}^{x} \leftrightarrow \frac{1}{2} O_{2} + V_{o}^{+} + 2e' \]

Fortunately, the oxygen diffusivity increases with increasing oxygen vacancy concentration\textsuperscript{93}, with an enthalpy of formation for an oxygen vacancy of \( \sim 0.51 \text{ eV} \) at as low as 2 mTorr \( pO_{2} \textsuperscript{91}, \) thus there is a large thermodynamic and kinetic driving force to remove oxygen vacancies at atmospheric \( pO_{2} \). This is further supported through O\textsubscript{18} tracer experiments in which O\textsubscript{18} was found to migrate microns through the sample under these annealing conditions, as well as by reducing carrier concentrations by 6 orders of magnitude for SrTiO\textsubscript{3} films on silicon by an atmospheric anneal in dry air at 500\textdegree C\textsuperscript{94}.

In other perovskite oxides this is not so simple, as is the case of the vanadates. The ternary phase diagram for SrO-VO\textsubscript{2}-V\textsubscript{2}O\textsubscript{5} is shown in Figure 2-3 b\textsuperscript{86}. The binary line between the SrO and VO\textsubscript{2} shows that nonstoichiometries from the ideal 1:1 Sr:V ratio leads to precipitation of 2\textsuperscript{nd} phase, causing an increase in the out-of-plane lattice constant, as well as an increase in the low temperature resistivity due to defect scattering (Figure 2-5 a, b)\textsuperscript{95}. These 2\textsuperscript{nd} phases can be seen in
the film microstructures in Figure 2-5 c-e, and appear very similar to SrTiO₃. Although, in SrVO₃, vanadium is in the 4⁺ state, the 5⁺ oxidation state is more favorable at atmospheric pressures. This means that a low oxygen partial pressure must be maintained in the deposition system to prevent the formation of oxygen rich phases, such as the pyrochlore Sr₂V₂O₇.

![Graphs and micrographs showing dielectric constant and lattice constant](image)

**Figure 2-4**: Effect of stoichiometry on the temperature dependent dielectric constant of SrₓTiO₃₊δ (a). The dielectric constant peaks for stoichiometric samples, while nonstoichiometric samples show a diffuse peak and relaxor-like behavior. Non-stoichiometry also leads to an expansion in the out-of-plane lattice constant (b). The non-stoichiometric faults for the Ti-rich (c, d) and Sr-rich (f, g) can be seen in the HR-STEM micrographs, while the stoichiometric sample appears with little to no defects. *Reproduced from references (87, 88).*
It is for this reason that a host of synthesis techniques have been used to deposit oxide thin films. In general, deposition techniques can be broken down into two classes, either physical vapor deposition (PVD) or chemical vapor deposition (CVD). This classification is based on how the material is delivered to the substrate. In PVD, constituent elements of the films are supplied in physical form by volatilizing the constituent elements, either through thermal evaporation or sublimation, or by high-energy ablation. In chemical deposition, elemental source material is contained in a volatile chemical precursor, and the film precipitates via a chemical reaction on the substrate surface. These two classes can be further split into a variety of unique deposition techniques, each with their own array of advantages and drawbacks which will be discussed in the following section. As such, there is no one technique that is superior for all scenarios, and instead

Figure 2-5: Stoichiometry of SrVO₃ films grown by hMBE. (a) For stoichiometric compounds, there is a constant and minimal out of plane lattice spacing, (b) and a large ratio in the resistivities between room temperature and 5 K. This is cause by the inclusion of nonstoichiometric defects, as can seen in the accompanying microstructures (c, d, e). Reproduced from references (95, 96).
the best technique must be chosen for each application in terms of required film quality, economic feasibility, adaptability, utilization, and material deposited.

2.3 **Molecular Beam Epitaxy**

Molecular beam epitaxy (MBE) is perhaps the simplest deposition technique conceptually, but is technically very complex and elaborate, making it one of the most difficult to synthesize high quality films. Its invention is credited to Alfred Cho at Bell Labs with the goal of developing a deposition technique that is capable of depositing a single layer of atoms for atomically sharp interfaces in heterostructures and superlattices. A schematic of an MBE system is shown in Figure 2-697. The elemental source material is placed in an effusion cell, which is heated until the material evaporates or sublimates and a stable flux of atoms towards the substrate develops. Cryogenic adsorption (cryo) and turbomolecular (turbo) pumps are used to lower the pressure in the chamber to down to $10^{-7}$ to $10^{-11}$ Torr, well into the molecular flow and ultra-high vacuum (UHV) regimes. Additional pumping speed can be obtained through the use of cryogenic panels which are cooled with either chilled ethanol or liquid nitrogen to lower the base pressure of the chamber. At UHV pressures, the evaporate elements behave like a beam of molecules rather than a gas in, and it is this property for which the technique receives its namesake. Actual fluxes emanating from the cells are measured using a quartz crystal monitor, which is a quartz crystal that is driven near its resonant frequency. As material builds up on the quartz the oscillating mass of the quartz crystal is increased by the amount of material received, resulting in a frequency change. The rate of change of mass can then be converted to flux through the atomic weight and density of the material. The substrate is mounted on the sample manipulator, which is heated to aid in the crystallization of the thin film.
Using evaporated elemental source material proved very advantageous for deposition of a multitude of materials. The effusion cells are able to maintain a constant temperature with precisions of < 1° using carefully tuned PID controllers, providing a very stable flux of material over a long periods at very low fluxes leading to low growth rates (10-100 nm/hr). Mechanical shutters block the atomic flux from the substrate with actuation times on the order of 0.1s, allowing for very precise and repeatable control of deposited material. Further, the atoms impinge on the substrate with energies on the order of 0.01 – 0.1eV which can be approximated roughly from the equipartition theorem of gases for elements that volatilize in the range of 100°C - 2000°C, well below the energy required to penetrate the film and form defects. By depositing in UHV condition, and using high purity elemental source material, nearly all contaminates can be removed from the growth front, and it is possible to deposit thin films with defect concentrations approaching the thermodynamic limit.

However, this method has a few intrinsic drawbacks. The first and most notorious being the cost of maintaining a functional molecular beam epitaxy system. The combined costs of the pumps and liquid nitrogen cooling to maintain low pressure, as well as effusion cells and vacuum sample transfer can put the cost of even a small MBE system to over $1 Million, as the abbreviation of molecular beam epitaxy MBE has fittingly been referred to as “mega buck equipment”.

Further, MBE works by evaporating elemental source material for the precise amount of time and in the exact stoichiometric ratio of the desired film. Unintentional deviation from the amount of constituent elements greater than 1% can already greatly affect film properties. This makes control of both cation and anion stoichiometry difficult. Effusion cells are typically calibrated by using beam flux monitor or quartz crystal monitor, which are only accurate to about
1-5%. In addition, the flux of the effusion cell will drift over time, requiring additional

Figure 2-6: Schematic of a typical molecular beam epitaxy system. The sample sits in the sample manipulator facing down. Effusion cells are arranged in a circle near the bottom of the MBE, directed toward the substrate. The flux measurements are taken using QCM which can be extended to the sample position and retracted during growth. Pumping is provided via a turbomolecular (turbo) pump and cryogenic adsorption (cryo) pump. Additional pumping speed during deposition is supplied from cryogenic panels cooled by liquid nitrogen. Reproduced from reference (97).
There have been methods to further increase the accuracy of these measurements such as by using RHEED oscillations to determine the monolayer formation time to less than 1% accuracy\textsuperscript{100,101} as well as using atomic absorption spectroscopy to monitor drifts in the atomic flux during deposition\textsuperscript{102}, however these measurements are often tedious or add additional complexity to the growth process. Finally, many refractory materials don’t develop a significant vapor pressure until well beyond the maximum operating temperature of an effusion cell. These materials can be deposited using an e-beam evaporator, however these are subject to more extreme flux drifts.
2.4 Pulsed Laser Deposition

Figure 2-7: Pulsed Layer Deposition system. The laser pulse incident on the target (center) ablates material creating the high energy plasma plume. This deposits target material on the substrate (left) which is directly exposed to the plume containing material ablated from the target. Courtesy: Maria Group at Penn State.

Pulsed laser deposition is another PVD deposition technique that is used to deposit a multitude of different materials. In this process, a target made of the desired material bombarded with high-energy laser pulses in the visible to ultra-violet range. These pulses cause rapid heating of the local target surface, leading to melting, vaporization, and ablation of target material which manifests as a plume of plasma, seen in Figure 2-7 emanating from the target. The ejected material then travels towards the substrate, and condenses to form a film on the substrate.
Typically, the target is rotated during the deposition process to keep the surface uniform and ensure each pulse produces a nearly identical plume.

PLD is very widespread in the field of materials research and synthesis due to its simplicity of operation. Q-switched Nd:YAG and excimer laser produce extremely high peak power output pulse capable of ablating any material including refractories and other low vapor pressure materials that otherwise cannot be easily evaporated\textsuperscript{103}. Multiple-component targets are commonly used, as the plume and resulting film will have a composition largely similar to the target surface. This allows for the synthesis of complex thin films from a single target. As there are no specific constraints on the environmental conditions within the chamber, deposition can occur in pressures ranging from UHV to ambient, and any gas can be added to the chamber to favor the formation of oxides\textsuperscript{104}, nitrides\textsuperscript{105}, carbides\textsuperscript{106,107}, fluorides\textsuperscript{108}, or any other desired composition. The amount of material deposited per pulse is calibrated before growth, and remains fairly consistent. This makes deposition of a single, atomically sharp monolayer fairly simple, and even sub-monolayer coverages can be targeted by careful calibration of the pulses. For these reasons, PLD has been used extensively to fabricate complex heterostructures and superlattices of oxides and other materials.

The cost of PLD is typically much less than comparatively to MBE, with the bulk of it being in the initial purchase of the laser. However, a single laser can be used to deposit from multiple targets, across different deposition systems entirely. This makes PLD an economical tool for research based environments, where it will be required to study many different and complex types of materials with fast turn-around times.
PLD is not without its drawbacks. The high-energy ablated material can leave the target with energies in the range of 0.1-10 eV as ionized species. This has proven useful in raising the surface temperature of the substrate and allowing crystallization at lower temperatures\textsuperscript{109}, however, these ions will also impinge on the substrate causing defects and can even sputter lighter elements out from the film and substrate\textsuperscript{103,110}. The plume can have compositional gradients, leading to nonuniform film composition, and lighter elements will tend to ablate preferentially, leading to a different film composition than the target. This problem is exacerbated from the different cross-sectional areas of each element leading to different scattering rates with any gas in the chamber and the lack of direct control over the material supplied to the substrate. Larger agglomerates of material can be ejected from the target as well and get incorporated into the film, appearing as boulders in the microstructure. Finally, the plume is relatively small and only on the order of a few cm, limiting the area over which a conformal film can be deposited. These effects can be mitigated by changing of the gas pressure, throw length, laser fluence and repetition rate, as well as using intentionally nonstoichiometric targets to compensate for differential ablation rates and increase scattering to lower the incident particle energy. Rastering of the laser over targets, use of multiple targets, and substrate rotation as well as movement of substrate in the surface plane can increase the size of usable film. However, these processes increase the complexity and cost of the deposition process.
2.5 **Sputtering**

![Image of sputter chamber in the Engel-Herbert group at Penn State](image)

*Figure 2-8: Sputter chamber in the Engel-Herbert group at Penn State.* The plasma plume from the sputter gun is visible in the bottom of the viewport. The heated substrate is visible at the top of the viewport.

Sputtering is another deposition technique that has been used to deposit a wide array of materials. In this technique, a plasma is generated over a target of the material to be deposited. The target is biased to cause ions from the plasma to accelerate into the target. This collision then ejects or “sputters” target material in all directions and deposit on the substrate held nearby.

There are two primary types of sputtering deposition, DC and AC, with different variants of each. In DC sputtering, the chamber is filled with an inert gas such as argon. A plasma is generating by applying a negative bias to the target in the range of -2kV to -5kV, and the positively charged argon atoms collide with the target and sputter material. A semi-toroidal magnetic field can be generated at the target surface using permanent magnets in a process called magnetron
sputtering. This field helps confine the ions to a circular region near the target surface, increasing the number of collisions with the target surface as well as lowering the pressure required to maintain a plasma. DC sputtering is the most simplistic but is limited to conducting target materials as positive charge will tend to build on the surface of dielectric materials and quench the deposition process. AC or radio-frequency (RF) sputtering mitigates this problem by alternating the target bias from negative to positive and is therefore applied in case electrically insulating target materials are being used. The negative cycle pulls Ar\(^+\) ions towards the substrate leading to sputtering, while the positive cycle repels the accumulated positive ions and “cleans” the surface for the following cycle.

Reactive sputtering has also been used with great success to synthesize certain oxides\(^\text{111-113}\), nitrides\(^\text{82,114,115}\), fluorides\(^\text{116,117}\), and carbides\(^\text{118,119}\) that are ordinarily difficult to stabilize using other deposition techniques. Typically the cation, such as Ti, is sputtered while a reactive gas such as oxygen, nitrogen, or methane is introduced into the chamber. The plasma excites these species creating highly reactive ions or free radicals, which then react with the sputtered material on its way to the substrate, creating the film of desired material.

A major advantage of sputtering is the flexibility of the target geometry, as total amount of sputtered materials scales with the surface area of the target and generated plasma. Targets can be made into a rectangular geometry, making them ideal for uniform deposition over rectangular substrates or roll-to-roll manufacturing, where substrate rotation is impractical. This, combined with the high deposition rates, deposition of nearly any material, and relatively low vacuum requirements has made sputtering a stable of thin film deposition in industry and research.
Like PLD, sputtering is a high-energy deposition technique, and the sputtered material impinges on the substrate with energies on the order of $0.1-10^4 \text{eV}^{120}$, which can both aid in film crystallization as well as cause defects and re-sputter lighter z-elements from the film or substrate. Boulders of target material that has sputtered from the target a few nm in size are common. These effects can be somewhat mitigated through the use of off-axis sputtering, in which the sputter gun is rotated 90° relative to the target ensuring that only sputtered material which has undergone multiple collisions with the background gas and lost much of its kinetic energy will deposit on the film$^{121}$. Numerous, high quality films and heterostructures have been grown in this way, at the expense of a greatly reduced deposition rate$^{121-125}$. As the source material is typically a single target, there is no direct stoichiometry control over the species supplied to the target, limiting the ability to achieve highly stoichiometric films. Further, the target surface may also change with time in multicomponent systems, as the lighter element typically will sputter fast than the heavier element. The target may also react with contaminants or the reactant gas in the chamber, leading to poisoning of the target surface and the sputtering process may be halted. The relatively high pressure required to maintain a plasma can introduce impurities into the chamber. *In-situ* monitoring techniques that require high vacuum are difficult to realize experimentally, and may require multiple differential pumping stages to use.
2.6 Growth windows and hybrid molecular beam epitaxy

The most reliable way to produce high quality multicomponent films is through the use of self-regulated growth. This method of growth was developed and used extensively in the deposition of GaAs thin films and other binary semiconductors\textsuperscript{126–128}. In this method, a nonvolatile element (Ga) is evaporated in conjunction with a more volatile element (As) and the molecular beams are co-supplied to the substrate. The formation of the film from these sources is then limited by two reactions. The lower bound is the vapor pressure of the volatile element above the growth front. If this vapor pressure cannot be maintained by the molecular beam, then the element will volatilize from the film. The upper bound is vapor pressure at which the volatile element will condense at the growth front and be incorporated in the film as 2\textsuperscript{nd} phase precipitates. The region in between these two bounds is known as the stoichiometric growth window, films grown in this

Figure 2-9: The hybrid molecular beam epitaxy system at Penn State

The most reliable way to produce high quality multicomponent films is through the use of self-regulated growth. This method of growth was developed and used extensively in the deposition of GaAs thin films and other binary semiconductors\textsuperscript{126–128}. In this method, a nonvolatile element (Ga) is evaporated in conjunction with a more volatile element (As) and the molecular beams are co-supplied to the substrate. The formation of the film from these sources is then limited by two reactions. The lower bound is the vapor pressure of the volatile element above the growth front. If this vapor pressure cannot be maintained by the molecular beam, then the element will volatilize from the film. The upper bound is vapor pressure at which the volatile element will condense at the growth front and be incorporated in the film as 2\textsuperscript{nd} phase precipitates. The region in between these two bounds is known as the stoichiometric growth window, films grown in this
region will be grow in stoichiometric fashion, while excess volatile phase will not condense or desorb from the growth front, leading to a film with high crystallinity and exceedingly low defect concentrations.

This type of growth is only possible if one of the elements constituting the film has a significantly higher vapor pressure than the other, and a substantial vapor pressure can develop at experimentally achievable conditions below the melting point of the compound material. For this reason, the growth window method has worked well for III-V and II-VI materials, as the elements forming this compound exhibit a significant vapor pressure difference, specifically pnictides, e.g. P, As, and Sb have high vapor pressures compared to Al, Ga and In, as well as the chalcogenides S, Se and Te compared to Be, Mg, Zn and Cd. It unfortunately has not been as well adapted to the field of oxide materials. This is primarily due to the low vapor pressure of most stable oxides. For example, growth of SrTiO$_3$ can be self-regulated, as the vapor pressure of SrO is greater than TiO$_2$. However, the desorption rate of SrO is negligible for temperatures below 750°C$^{129}$, and much greater temperatures than are ordinarily experimentally achievable would be required to develop a thermodynamic growth window at reasonable deposition rates$^{130}$.

Hybrid molecular beam epitaxy is a relatively new deposition technique in which one of the elemental sources is replaced with a high vapor pressure metalorganic source. This technique was first developed for the growth of SrTiO$_3$, in which the titanium elemental source was replaced by the metalorganic precursor titanium tetra-isopropoxide (TTIP). The motivation for this work was originally to find an alternative method to supply titanium, as it requires temperatures around 2000°C to develop a significant vapor pressure and reacts with almost all refractory crucible materials at these temperatures, leading to very short cell lifetimes. Further, oxidizing Ti to the
Ti$^{+4}$ state is difficult under the reducing conditions present in MBE’s, and oxygen plasmas or ozone are required. Even with this, SrTiO$_3$ films are still oxygen deficient when grown in this fashion, and require a post-growth anneal in oxygen for use as a dielectric. Both of these difficulties were immediately remedied by replacing the Ti source with TTIP. These metalorganics develop a significant vapor pressure at over an order of magnitude lower temperature than their elemental counterparts. The molecules themselves are already bonded to the metal putting it in a higher oxidation state, reducing the need to supply a reactive oxygen source. Carbon and hydrogen contamination from the metalorganic was found to only be a problem at low temperatures, and films grown about 750°C showed contamination levels on the order of bulk single crystals$^{131}$.

Perhaps the largest advantage of growth using $h$MBE is the development of an adsorption-controlled growth window. For growth of SrTiO$_3$ films, it was noted that at sufficient temperatures a range of TTIP fluxes could be adjusted and still produce a stoichiometric film with a constant out-of-plane lattice parameter$^{130}$. Further, the width of this growth window expanded with increasing temperature. These results were later repeated at Penn State for films of SrTiO$_3$ grown on LSAT, exhibiting an identical out-of-plane lattice constant as well as growth rate for films in the window (Figure 2-10)$^{97,132}$. RHEED reconstructions taken during growth for a sample revealed that the stoichiometry could be tuned during growth by changing TTIP pressure to find the limits of the growth window, confirmed by TEM of the microstructure of the film, which will be covered in depth in Chapter 4.

The driving mechanism behind these growth kinetics due to the different reactivities of the oxide surface with the TTIP molecule. Figure 2-11 a-c outlines the reaction kinetics of depositing TiO$_2$ from TTIP$^{133}$. Three distinct regimes arise from the growth rate of TiO$_2$. The first regime is
the reaction-limited regime and occurs at low temperatures. At this temperature the residence time of a TTIP molecule on the surface is ~4s, and both the reaction and desorption rate of TTIP are negligible and the surface becomes saturated with TTIP. The deposition rate is then limited by the rate of the reaction of the TTIP molecules. Increasing the temperature beyond 400°C leads to a substantial reaction rate, while the desorption rate is still negligible. In this regime, all TTIP molecules stick to the surface and react to form TiO₂, and so the growth rate is flux-limited by the number of TTIP molecules which can be supplied to the sample. Above 700°C, the residence time

Figure 2-10: Growth window of SrTiO₃. (a) XRD 2θ scans of a series of SrTiO₃ films grown on LSAT show the expected lattice expansion for nonstoichiometric films, and a constant lattice parameter for films grown within the window plotted in (b). (c) The growth rate also was seen to decrease for Sr-rich films and increase for Ti-rich films, due to an increase in the TTIP flux, while it was constant over the growth window. (d) Determination of the growth window was also found via RHEED images during growth by systematically altering the TTIP inlet pressure. (e) The changing stoichiometry and accurate determination of the window was confirmed by cross-sectional TEM, in which defects were visible in the Sr and Ti rich regions, but were absent within the growth window. Reproduced from references(97,132).
of a TTIP molecule is less than $10^{-2}$s, leading to a large number of TTIP molecules desorbing from the surface before they can react, and the growth is *desorption-limited*.

Comparing these results to those of SrTiO$_3$ reveals the growth window emerges at approximately the temperature of the desorption limited regime. Figure 2-11 d-e$^{97}$ shows x-ray reflectivity measurements for a film of TiO$_2$ and a stoichiometric SrTiO$_3$ grown under equivalent TTIP fluxes, and the effective rate of Ti incorporation was calculated for each film. It was found that the addition of SrO lead to a 20% increase in the relative Ti incorporation, illustrating the SrO surface. The growth window then simply emerges as a balance of the different reactivities of the two surfaces, and the percent coverage of either surface.

![Figure 2-11: Growth kinetics of metalorganic precursor.](image)

The growth rate of TiO$_2$ on a TiO$_2$ surface from TTIP is given in (a). The 3 different regimes for reaction limited, flux limited, and desorption limited can clearly be seen from the trends in growth rate. This information is used to approximate the % coverage of the surface by the TTIP molecule vs. the TiO$_2$ film (b) and the rate at which TTIP will desorb or react and deposit in the film (c). The approximate rate of Ti incorporation in a TiO$_2$ film (d) and a SrTiO$_3$ (e) grown at equivalent TTIP pressures and deposition time, showing the enhanced reaction rate from SrTiO$_3$. *Reproduced from references*($^{97, 133}$).
While the adsorption-controlled growth window is quite useful, it does exhibit a few constraints for its existence in perovskites. This is only possible for conditions where the metalorganic is deposited the desorption-limited regime, and that the surface of the metalorganic oxide (in this case TiO$_2$) has a less reactive surface than the oxide of the elemental source (SrO). As these two reactivities approach unity, the growth window will disappear.

Despite these restrictions, it appears as though hMBE is well suited to the growth of perovskites. To date, TTIP has been used in the growth of SrTiO$_3$, GdTiO$_3$, SmTiO$_3$, NdTiO$_3$, BaTiO$_3$, and CaTiO$_3$. Vanadium triisopropoxide (VTIP) has been used in the self-regulated growth of CaVO$_3$, SrVO$_3$, and LaVO$_3$. Hexamethylditin has been successful in depositing the tin based perovskites BaSnO$_3$ and SrSnO$_3$, and finally the ruthenium containing precursor TORUS has been used to grow films of SrRuO$_3$ and Sr$_2$RuO$_4$.

The benefits of a self-regulated growth window are profound for both the reproducibility, as well as the quality of films. The first success of hMBE was growth of La-doped SrTiO$_3$ with mobilities in excess of 30,000 cm$^2$ (Vs)$^{-1}$, which was only limited by the formation of twin domains below the cubic to tetragonal transition in SrTiO$_3$. This was later improved to 120,000 cm$^2$ (Vs)$^{-1}$ by suppression of these domains, greatly exceeding the record mobilities of not only thin films grown by other means, but of bulk single crystals as well. Films of SrVO$_3$ have exhibited similar success, with residual resistivity ratios in excess of 200, again exceeding the performance of bulk single crystals.
Chapter 3. Characterization Techniques

Observations are the driving force behind every scientific discovery. The ability to detect and see is prerequisite to understand the meaning behind the observation is therefore a fundamental element of the scientific method. The invention of the compound lenses led to the microscope and telescope starting two fields of studies: microscopy, the study of objects too small to see with the naked eye, and astronomy, the study of distant celestial objects. These two fields of study have diverged to the point where telescopes allow us to see distant galaxies, while microscopes are able to routinely visualize atoms, the basic building block of our universe. This Chapter describes the general principles, applications and equipment used in the characterization of thin films throughout this dissertation. First the in-situ characterization technique reflection of high energy electron diffraction is introduced, which provides detailed information about the film surface during the growth. Next post-growth analysis techniques to determine the structure of the grown films are introduced, namely x-ray diffraction (XRD) and transmission electron microscopy (TEM).

3.1 Reflection high-energy electron diffraction

One of the greatest benefits of materials science is the that the experiments we perform are typically on physical materials that are in a reasonable scale. However during thin film synthesis, the question becomes how to observe the deposition of a single monolayer of atoms while the sample is suspended in ultrahigh vacuum in a stainless-steel chamber mounted on a substrate heater keeping the sample at high temperature? One answer comes in the form of reflection high energy electron diffraction (RHEED).

Electrons, like x-rays, can be tuned to have a wavelength on the order of the atomic lattice spacing and can be readily generated in a lab environment from an electron gun, making them an
ideal probe for diffraction studies. Electrons interact much more strongly with matter than X-rays and as a result the diffraction pattern obtained from electrons with kinetic energies on the order of tens of keV are primarily from surface effects, while X-rays will probe the bulk of the material. Because electrons will strongly scatter if traveling at atmospheric pressures, a necessary prerequisite is a vacuum environment, making it an ideally suited technique to study the sample surface of films being deposited by physical vapor deposition methods such as MBE.

The electrons are generated from a heated tungsten filament, focused to a beam, and accelerated to 14 keV. In order maximize the surface sensitivity when diffracted by the film, the beam is incident at glancing angles to the substrate, approximately 1-2° relative to the substrate surface. The surface is effectively a 2D sheet in x-y plane, and probed only a few monolayers deep, so diffraction peaks are not a sharp point, but rather elongated rods in reciprocal space. The intersection of the Ewald sphere with these reciprocal rods gives rise to a diffraction spot, which is then projected onto a phosphor screen. The electron diffraction patterns can be collected real-time using a CCD camera, and be used to determine the atomic flux, growth rate, surface reconstructions, stoichiometry, surface morphology, and variety of other properties dependent on the surface.

As can be seen from Figure 3-1, there are numerous different features in each RHEED pattern, and each feature in reciprocal space can be traced back to a particular effect on the sample surface. The ideal case is for a flat, pristine single crystalline surface, in which the topmost layer is near identical to the bulk. This results in very thin, circular rods in reciprocal space, and small points in the diffraction screen, seen in Figure 3-1 (a). This only occurs for the highest quality thin films. What is more typical to observe, is if the topmost layer has laterally limited coherence,
potentially slightly different lattice parameter, possibly due to vacancies, defects, the formation of small lateral domains, different bonding configurations, terracing, or valence state modulation at the surface. This broadens the reciprocal lattice rods, giving rise to an increased, rod-like intersection with the Ewald sphere. The RHEED pattern appears as streaky rather than sharp spots, see Figure 3-1 (b). In certain cases, the surface formed a stepped structure, with two different out of plane lattice for each domain, such as in the case of tetragonal perovskite oxides arranging in a/c domains, leading to peak doublets Figure 3-1 (c). The last case specifically discussed is for films with increased surface roughness, in which 3D islands form on the surface that have height variations of a few monolayers, see Figure 3-1 (d). In this case, the electron beam will pass through the islands and forward scatter off the multiple different layers, breaking the surface diffraction condition. This causes the diffraction peaks to again appear as single spots, rather than long rods. This is similar to the first condition but now the diffraction spots are not confined to the Ewald sphere. A simple way to tell the different between the two conditions is by rotating the sample
(discussed more in the following section). The rods will intersect the sphere at different points, causing the diffraction spots to move as the sample is rotated. For the rough surfaces, moving the Ewald sphere will simply move the reciprocal points out of the diffraction pattern, and they will disappear when the sample is rotated out of the diffraction conditions.

A second feature of RHEED is the appearance of fractional diffraction peaks that appear between the primary peaks. These are shown in Figure 3-2\textsuperscript{148} for various reconstruction of SrTiO\textsubscript{3} thin films grown on silicon. These surface reconstructions are caused by a rearrangement of the atoms on the surface arranging in a periodic fashion on the surface to lower the surface energy giving rise to an ordered arrangement with periodicity larger than the unit cell of the underlying film. These reconstructions increase the size of the surface unit cell and can create some spectacular patterns. One useful feature of this, is that the reconstructions can change depending on both the termination layer, and percentage of adatom coverage of the topmost layer, which can then be used to determine the stoichiometry of the growth front. For instance, in SrTiO\textsubscript{3}, the c4x4 reconstruction is due to the formation of a stoichiometric film with a TiO\textsubscript{2} terminated surface\textsuperscript{149}, while no reconstructions are associated with a mixed-termination stoichiometric film surface\textsuperscript{64,150}. For simplicity, this dissertation uses an informal notation for the reconstructions in which the first, second and third positions refer to the 100, 210, and 110 pseudocubic azimuth, while where only 2 reconstruction positions are reported, these refer to the 100x110. For example, the c4x4 reconstruction is given as the 2x2x4, while for c2x2 reconstruction is indicated as 1x1x2. This shorthand notation is very useful for cases where data on the exact surface structure is not abundant as it is for SrTiO\textsubscript{3}, and must be inferred simply from RHEED.
RHEED intensity oscillations are also an essential feature for growth of heterostructures with atomic precision for films that grow in a layer-by-layer fashion. As each new layer is formed, the initial deposited atoms form small islands on the top of the preceding layer. These islands effectively roughen the surface, causing a drop in the diffracted RHEED intensity. This continues until approximately 50% coverage, when there is a minimum in the intensity. As deposition continues, the islands begin to coalesce and form a coherent layer, lowering the surface roughness and increasing the RHEED intensity until the next layer is completely. The time between each oscillation corresponds to the deposition time. The exception to this is for sequential growth, in which each individual sub-monolayer is deposited. This is the case for deposition of SrTiO$_3$ by depositing sequential layers of SrO and TiO$_2$. In this scenario, the intensity is typically at a maximum for the surface with the highest Z-number, while the 2$^{nd}$ surface has a minimum. This

![RHEED for 850°C SrTiO$_3$ on silicon](image)

*Figure 3-2: Reconstructions of SrTiO$_3$ on silicon grown by hMBE*. The effect of TTIP pressure on the growth surface is manifested by the different RHEED reconstructions observed along the different azimuths. Stoichiometric films showed either a 1x1x1 (no reconstructions), 2x2x1, or 2x2x4. While Sr and Ti-rich surfaces showed a 1x1x2 or 2x2x1 surface, respectively. *Reproduced from reference (148).*

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method has been successfully used to not only determine the time for each sub-monolayer deposition, but can also reveal changes in the stoichiometry\textsuperscript{100}.

3.2 X-ray diffraction

In contrast to RHEED, which provides excellent surface structure information, X-ray diffraction (XRD) techniques provide the most robust and accurate method to structurally characterize a thin film. The most basic of descriptions of XRD is Bragg’s Law, which dictates that X-rays will interfere constructively if the Bragg condition is met:

\[(\text{Eq. 9}) \quad n\lambda = 2d \sin \theta\]

where \(n\) is an integer of the wavelength of the incident X-ray (\(\lambda\)), \(d\) is the spacing of the lattice planes, and \(\theta\) is the angle of incidence between the X-rays and the atomic planes. As X-rays weakly interact with matter and travel through the material, they scatter elastically off the atomic lattice planes. Under certain scattering angles relative to the propagation direction of the incoming X-rays, X-rays diffracted at neighboring lattice planes will undergo a phase shifts that are a multiple integer of \(\lambda\), leading to the constructive interference and giving rise to a reflection spots in the diffraction pattern. While this condition relates the scattering angle \(2\theta\) to the lattice spacing, it does not give any information about the orientation of the sample. This is sufficient for polycrystalline or powder samples, where the large number of grains allow for all orientations to be represented. For single crystalline samples where there is only 1 orientation, the sample must be rotated to the diffraction condition. This is performed using a 4-circle diffractometer, where the sample can be rotated independently of the \(2\theta\) position. This allows for scans where the angle of incidence of x-rays on the sample surface is not equal to \(\theta\), as well as scans in off-axis scans, in
which the sample is rotate in \( \chi \). Rather than evaluating the Bragg condition, and Ewald sphere construction shown in Figure 3-3 is more elegant and allows a much simpler interpretation for determining diffraction peaks.

In this construction, each plane is represented by a reciprocal lattice point. The construction is best understood when drawn that the planes parallel to the sample surface (out-of-plane direction) is oriented along the y-axis, while the planes that are oriented in-plane are along the x-axis, as exemplified in Figure 3-3. For this example, the surface is oriented (00\( L \)), and the \((H00)\) is oriented in the plane of the source and detector. The incident wavevector \( K_i \) is drawn incident on the \( \Gamma \) point in the lattice at an angle of \( \omega \) relative to the x-axis. The Ewald sphere is constructed by drawing a circle of radius \( 1/\lambda \) centered around the tail of \( K_i \). Any reciprocal lattice spot that intersects with the circumference of the Ewald sphere will give rise to constructive interference. \( K_f \) is the diffracted wavevector, i.e. the direction under which constructive interference can be observer. It can be constructed by drawing a vector from the tail of \( K_i \) (center of the Ewald sphere) to the reciprocal lattice vector coinciding with the Ewald sphere. The \( G \) vector is the lattice vector for which diffraction occurs, and is given by

\[
G = K_f - K_i
\]

(Eq. 10)

and can be used to find the interplanar spacing as:

\[
G = \frac{2\pi}{d}
\]

(Eq. 11)

Because diffraction is an elastic scattering process in which energy and momentum are conserved, the magnitudes of \( K_f \) and \( K_i \) must be equal, and \( G \) must be equal to the difference in momentum and is known as the \textit{crystal momentum}. 

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The intensity of each peak in reciprocal space can be determined by the structure factor, $F_{hkl}$. This takes the form of

(Eq. 12) \[ F_{hkl} = \sum_{j=1}^{N} f_j e^{-2\pi i (hx_j + ky_j + lz_j)} \]

in which $h, k, l$ are the miller indices of the lattice plane, $x_j, y_j$ and $z_j$ are the atomic positions of the $j^{th}$ atom in the unit cell, and $f_j$ is the atomic form factor of the atom. The form factor dictates the scattering of the atom’s electron cloud with the x-ray. It is depended on the valence state of the atom and the wavevector of the incident x-rays, but in general scales with the atomic number $Z$. Given that each plane must consist of integer $h, k$ and $l$ values, and there are a finite number of atoms in the unit cell, solving this equation for the planes of interest begins to become trivial. From this equation, it can be seen that XRD is simply measuring the Fourier transform of the lattice.

Figure 3-3: Ewald Sphere construction (a) in a reciprocal lattice, showing the diffraction points for a cubic sample. A picture of a Panalytical Empyrean 4-circle diffractometer is given in (b), with the relevant angles and components given to show the relation between reciprocal and real-space. Courtesy Oak Ridge National Lab.
The relation between the real space 4 circle diffractometer and the Ewald sphere is as follows, assuming the sample is oriented as previously mentioned. The X-ray detector sits on the Ewald sphere, and a rotation of the 2θ motor will move the detector on an arc-like trajectory around the sample. Diffracted intensity is detected when the a $K_f$ vector is coincident with the detector position. The next angle, ω, is the given as the angle between the sample surface and the incident x-ray beam. Rotating this in reciprocal space rotates the angle of $K_i$. By setting ω equal to ½ 2θ, the detector will appear to move in a straight line propagating from the origin in reciprocal space. This is commonly called a 0-2θ scan for this reason, and probes the lattice spacing of all planes parallel to the sample surface. To access non-specular planes, an offset in ω must be added as $\omega_{\text{offset}}$. In this case the ω motor position is given by the following equation.

(Eq. 12) \[ \omega = \omega_{\text{offset}} + \theta \]

Rocking curves or ω scans are also useful for probing the crystallinity of the sample. In this case, 2θ is fixed, and the sample is rotated (ω). This rotates the reciprocal lattice point through the detector at a fixed condition of lattice spacing, effectively probing the relative misalignment of the plane of interest. This is a useful measure to quantify the crystalline quality, as defects will cause strain and tilting in the lattice plane, giving rise to a film peak broadening in ω-scans.

The last 2 angles, χ and φ, tilt the sample out of the diffraction plane (rotation around the in-plane direction that is in the diffraction plane) and rotate the sample around the out of plane direction, respectively. Up to this point, we have only considered the Ewald construction as 2D in the zeroth order Laue zone. However, there are reciprocal lattice points in planes above this lattice. Each plane of this zone is a higher order Laue zone. Rotating in φ will rotate the reciprocal lattice around the axis of the surface normal planes. By sitting at a non-specular diffraction spot and
rotating in $\varphi$ causes spots to effectively rotate into and out of the diffraction conditions. This is a useful technique for determining film symmetry within the film plane, as the number of identical peaks that appear for a full $360^\circ$ degrees will give rise to the rotational symmetry of the sample.

The last angle, $\chi$, rotates the lattice around the planes in the $y$-axis for the Ewald construction. This again can be used to move the higher order Laue zones into 2D construction, and is also necessary for alignment. Effectively, $\chi$ and $\omega$ are interchangeable, and just rotate in an orthogonal direction, which could be compensated for in $\varphi$. However, in most lab-based XRD systems, incident beam is a vertical line on the sample. Rotating $\chi$ away from zero causes the streak to distort the profile of the beam on the sample. The $\chi$ motor can be moved if the incident beam is focused to a spot on the sample rather than a line, as this only minimally will change the profile of the spot on the sample.

### 3.2.1 Thin film effects

X-ray diffraction works in the most simplistic case for perfect crystals, in which the elements can be described as an infinitely periodic arrangement. In thin films, this assumption is no longer valid, and small film dimensions as well as defects in the lattice contribute peak must be taken into consideration. The Scherrer equation\textsuperscript{151,152}, below, is way to see the effects finite particle effects. While it is typically used for power diffraction, the assumption holds true for thin films.

\begin{equation}
\tau = \frac{K\lambda}{2\theta \cdot \cos(\theta)}
\end{equation}

Here, $\tau$ is the finite size of the crystal or film giving rise to diffraction, $K$ is a dimensionless shape factor that is close to 1 and $\Delta2\theta$ is the broadening of the full width half max of the diffraction
peak. This sets the lower bound of the peak, as other effects such as defects as well as instrumentation beam broadening can lead to peak broadening. In case of single crystals the film peak appears broader and with lower intensity the thinner the film is. In addition, Kiessig fringes are a useful diffraction effect that can arise in the diffraction pattern. As mentioned earlier, diffraction is essentially a Fourier transform of the lattice. For an infinite lattice, the Fourier transform of an XRD peak is a delta function. For a finite film thickness, the Fourier transform is the sine function with the periodicity corresponding to the film thickness, which can be modeled to accurately determine the film thickness. This effect arises from a multi interference effect and is particularly pronounced for films with a sharp interface and surface, as surface roughness will give a nonuniform thickness and suppress the fringes.

3.3 Transmission electron microscopy

The transmission electron microscope (TEM) is arguably the most versatile tool available to scientists today. The first TEM was built by Knoll and Ruska in the early 1930’s, and by the end of the decade commercial TEM’s had already been manufactured. In retrospect this development from fundamental research to commercialization had taken place at an astonishingly fast pace considering that the wavelike behavior of electrons had only been demonstrated a few years prior.

While the driving force behind these early TEM’s was the desire to develop a microscope that could beat the optical diffraction limit, the microscopes continued to develop with improved lenses, detectors, and electron sources with each new scientific breakthrough. This rapid progress has led to the most current generation of electron microscopes, boasting sub-angstrom spatial resolution, energy resolutions on the order of a few meV\textsuperscript{153}, 3-dimensional mapping capabilities
(tomography), a suite of detectors for compositional mapping, and in-situ experimental capabilities.

The scientific theory behind TEM and all of the individual components cannot be accurately described within the scope of this thesis. Transmission electron microscopy itself is now considered too broad of a term and the specialization and advancements of this technique has led to a diversification of this field of research, as microscopists are now being specialized in the imaging of specific types of samples, such as biological or crystalline materials, or focus on a specific imaging methodology. The following section is a modest attempt to outline the general principle of transmission electron microscopy with emphasis placed on the components used in the experiments as well as analytical processing methods that has been applied in this thesis.

3.3.1 Conventional transmission electron microscopy

At the top of the TEM shown in Figure 3-4 is the electron gun. This was traditionally a heated tungsten filament that would radiate electrons via thermionic emission. These have largely been replaced by hexaboride crystals (LaB$_6$ or CeB$_6$), which has a low work function and thus a high electron emissivity, as well as longer operational lifetimes. However, the highest quality sources are field emission guns (FEG). These operate based on field emission, in which the gun is a tip of sharpened to a radius and placed in a high electric field (1 kV electrostatic potential). The sharp tip enhances the field to $10^{10}$ V/m, lowering the work function barrier and allowing electrons to tunnel from the tip. FEG’s are incredibly bright electron sources, able to supply high energy flux densities of 150 MW/mm$^2$ focused onto a small spot with typical diameter of 1 nm, having a high temporal coherence and excellent monochromaticity of the emitted electrons with
energy spread $\Delta E$ on the order of $\sim 1\text{eV}$. This high power density allows for excellent signal to noise ratio’s both in direct imaging, as well as spectral imaging using techniques like electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDXS), which will be discussed later.

A series of condenser lenses and apertures are located in the TEM column right below the gun. This stage “condenses” the beam from the gun on the sample and can be used in either a parallel beam or convergent beam configuration. The condenser apertures are a necessary component to remove electron beam artifacts and aberrations. The upper and lower objective lenses sit above and below specimen. These lenses focus the electron beam onto the sample and collimate the beam after transmitting through the sample. Below the objective lens sits the
projector system, which controls the magnification of the image, and changes whether the focal plane for diffraction or image plane is projected onto the screen.

The images formed in a TEM are due to diffraction of the electrons with the crystal, similar to X-ray diffraction. However, electrons have much higher energies, usually 80-300 keV, and thus wavelengths between 2-4 pm, much smaller than X-rays. This gives a very large $K_{in}$ in the Ewald sphere construction, so large that the sphere has negligible curvature compared to the reciprocal length scales of the crystal’s lattice. Therefore multiple $K_{out}$ vectors can be found for a single $K_{in}$. This is compounded by the fact that the samples are very thin, on the order of 20-50 nm, and the diffraction point in reciprocal space is spread out in one direction, forming relrods, leading to even more points intersecting the Ewald sphere.

The diffracted beams are scattered at different angles and are focused in the back focal plane. All beams with the same $K_{out}$ vectors are focused to the same point, giving rise to the diffraction pattern. Upon interacting with the thin specimen only a small percentage of the electrons are scattered, generating the dark field, while the unscattered electrons compose the bright field. An objective lens can be placed over the transmitted or diffracted beams in the back focal plane to generate a bright field or dark field image, respectively. While these images are easily interpretable, they do not contain precise information about the lattice. Images that contain both scattered and unscattered beams are contain the most information and for this reason are called high-resolution (HR)-TEM, but these are phase images. The contrast observed in these images is therefore not a true image and cannot be directly interpretable, but requires elaborate image simulations to quantitatively extract information from the image\textsuperscript{154,155}.

3.3.2 Scanning Transmission Electron Microscopy
Scanning transmission electron microscopy (STEM), is a complementary technique to TEM, and many of the electron microscopes used today are capable to image the specimen in both modes. In STEM, rather than illuminating the entire area with a parallel electron beam, the beam is focused down to a single point and rastered across the sample. Figuratively speaking STEM could be considered as imaging an object by raster-scanning it with a laser pointer, while conventional TEM is similar to illuminating it using a flashlight. At first, it seems as though high resolution TEM is the much more useful method, however STEM has numerous advantages that have made it in a staple tool in the characterization of materials at the atomic scale today.

STEM can often be thought of as a TEM in reverse. Rather than a single $K_{in}$ vector that is incident on the entire specimen, there are multiple $K_{in}$ vectors incident from focusing the beam down in a conical shape to a single point on the sample. The signal is obtained by using annular detectors, and measure the current generated from the incident electrons. Detectors set to collect electrons scattered to high angles, leading to the name high-angle annular dark field (HAADF) detectors, show the best contrast of high Z-number elements. Images obtained in this method are usually easy and straight forward to interpret, as there are very few artifacts from diffraction contrast. Bright field detectors (BF) collect the main beam and contrast arises from the loss of signal from scattered electrons as the beam is raster-scanned. While this signal gives excellent contrast for lighter Z-number elements, it contains a significant amount of diffraction contrast. Many of the images discussed in this thesis have been collected using annular bright field (ABF) detectors. These detect electrons scattered at lower angles, while allowing the main beam to pass through, greatly reducing the effect of diffraction contrast while still maintaining contrast from lower Z-number elements, such as oxygen. With the advent of aberration correction (discussed in
the following section), atomic resolution STEM imaging has become a routine task in transmission electron microscopy, and has allowed easy interpretation of atomic level displacements\textsuperscript{156,157}, composition mapping of single atom dopants\textsuperscript{157,158}, and measurement of valence changes across interfaces\textsuperscript{159,160}.

3.3.3 Astigmatism, aberrations, and resolution limits

Proper alignment of the microscope is a critical and difficult process; perhaps only second to preparation of the TEM specimen itself (see Appendix A.6). This is necessary to obtain the highest resolution images, and in a field that has advanced as quickly as electron microscopy obtaining the maximum amount of information possible from each image is always necessary. Assuming the beam and all apertures have been aligned on the optical axis, the theoretical resolution of the microscope is primarily determined by 3 factors; astigmatism, spherical aberrations, and chromatic aberrations. Astigmatism is caused by imperfections in the magnetic lenses and apertures, as well as slight misalignment of the apertures off the optical axis. This causes different parts of the beam to be in focus at different locations along the optical axis, which results in an image distortion. While astigmatism can occur in both the condenser and objective lenses, it can be corrected using magnetic octupole stigmators, which create a magnetic field to counteract the imperfections in the lenses\textsuperscript{161,162}. The equation for the resolution limit due to astigmatism is given by\textsuperscript{155},

(Eq. 14) \[ r_{ast} = \beta \Delta f \]

in which $\beta$ is the maximum angle of scattered rays collected by the objective lens given in radians, and $\Delta f$ is the maximum difference in focal length of the image plane. The resolution, $r_{ast}$,
is given as the minimum radius of an object in the image plane (i.e. no matter how small the object is in the actual sample, it always appear to have a radius of at least $r_{ast}$ in the image).

Up until the early 2000’s, spherical aberration was the main factor limiting the resolution in most microscopes. Spherical aberration arises because magnetic lenses focus electrons scattered at higher angles stronger than electrons near the optical axis. The resolution due to spherical aberrations ($C_s$) is given by the following equation.

(Eq. 15) \[ r_{sp} = C_s \beta^3 \]

$\beta$ is ordinarily between 10-100 milliradians, and $C_s$ is on the order of 0.1 mm. The typical resolution achievable is just over 1-2 Å. While this may seem very good at first, the reality is that magnetic lenses have incredibly poor $C_s$. The human eye has $C_s$ value of about 0.5 um$^{163}$, much lower than that of even the best electron microscopes. Fortunately, while it is difficult to make a better magnetic lens, it is possible to correct for through the use of aberration correctors. First realized experimentally in 1998$^{164}$, their development and widespread introduction into microscopes has been arguably the greatest boon to microscopists in the past two decades. Not only that it has made it possible to image atoms with picometer level precision, but a routine process in most research labs and universities, and the work presented in this thesis would not have been possible without it.

The third factor limiting the resolution are chromatic aberrations, $C_c$, arising from stronger interaction of magnetic lenses with electrons having a higher kinetic energy, quantified by$^{155}$

(Eq. 16) \[ r_{chr} = C_c \frac{\Delta E}{E} \beta \]

where $C_c$ is typically on the order of 1-3 mm, similar to $C_s$. However, since $\Delta E$ is usually about 1 eV for an FEG operating at 300 keV or even less for cold FEGs, $r_{chr}$ is less than an angstrom.
even without aberration correction. Chromatic aberrations become more pronounced when thicker specimens are imaged due to a much more pronounced inelastic scattering lead to an increased energy spread of 25-50 eV, greatly decreasing the resolution. While $C_c$ correction methods have been developed and may become more prominent as microscopes continue to advance, an inexpensive solution to minimize chromatic aberrations is to make thin sample specimens.

One option to try to improve the resolution is to use to lower $\beta$ by using a smaller collection angles. This is because the effect of aberrations are minimal near the optical axis, and thus the weakly scattered electron that remain near the optical axis are not as affected by aberrations as electrons scattered to higher angles. However, $\beta$ also sets information transfer limit, in which theoretical diffraction limited resolution is given by\textsuperscript{155} (Eq. 17)

\[ r_{th} = 1.22 \frac{\lambda}{\beta} \]

which, using the previous numbers for a typical electron microscope operating at 300 keV and 30 mrad convergence angle gives approximately 0.5-1 Å resolution. Again, like everything in microscopy, $\beta$ is also a tradeoff, reducing the effect of the residual aberrations even after they have been corrected by using a smaller collection angle comes at the expense of a lower theoretical resolution.

3.3.4 Spectrum imaging and mapping

One of the largest draws of STEM is the ability to collect spectroscopic information while simultaneously imaging with atomic resolution. The FEG gun is an incredibly bright source, capable of supplying a few nanoamps of current into an area less than 1 nm\textsuperscript{2} on the sample\textsuperscript{155}. When the electron probe interacts with an atom, it can suffer an inelastic loss and transfer energy ejecting a core-shell electron. The process of filling this hole with an outer-shell electron is
accompanied with the emission of a characteristic X-ray. Energy-dispersive X-ray spectroscopy (EDXS) takes advantage of this phenomena by measuring the emitted X-ray spectra from the sample. The signal is detected and correlated to the position of the focused electron beam. Fitting the position and intensity of the peaks of the characteristic X-ray spectrum against a library of standards allows to approximate the chemical composition with atomic resolution.

This process can be done in both TEM and STEM, as well as scanning electron microscopy (SEM), or in a dedicated source using either electrons or high energy X-rays as the probe. In TEM, the beam is typically focused down to a small probe approximately the size of the area of interest, and a single spectrum is collected. STEM offers the capability of spatial mapping composition, as the emitted spectra can be measured while scanning and correlated with the beam position. The advent of sub-angstrom probes has enabled mapping the composition of a single atomic column, allowing both chemical and structural information on the atomic scale to be extracted together.

The chemical accuracy of this technique depends largely on the standards used. Different crystal orientations and sample thicknesses can give different spectra, even for identical compositions, due to the various dynamical scattering events and different channeling effects along different crystal faces\textsuperscript{165–167}. The highest accuracy measurements require numerous standards of similar composition and sample geometry, and can give compositional information on the order of parts per thousandth. Synthesis of these standards is usually expensive and time consuming, so EDXS spectrum analysis is often done using the manufacturers supplied standards library, or semi-quantitative methods without using calibration standards. In the latter case the determination of sample composition is much less accurate, typically only about 1-10%. They are nevertheless quite useful for fast analysis, as well as measuring relative composition changes within a single sample.
Further, EDXS cannot detect elements lighter than lithium and X-ray yield for other, light elements is fairly low. For this reason, EDXS is not recommended for analysis of light elements.

The complementary technique to EDXS that is fairly unique to transmission electron microscopy techniques is electron energy loss spectroscopy (EELS). Every time an electron from the beam causes an atomic excitation, it also suffers an energy loss due to energy conservation. As the name states, EELS probes the energy of the electrons after passing through the sample using a magnetic prism spectrometer, and the resulting energy spectrum of the electrons can be used to determine they type and frequency of the various excitations. These energy dispersive prisms and accompanying components are almost exclusively manufactured by Gatan, and are referred as a Gatan image filter, or GIF).

While EDXS and EELS seem largely similar, EELS has a few distinct advantages over EDXS. Commercial semiconductor EDXS detectors have energy resolutions between 50-150 eV\(^{168}\). Superconducting microcalorimeter detectors may lower this number down to 1-5 eV, but these are still not widely commercially available\(^{169}\). The energy resolution of EELS is dictated primarily by the energy spread of the electron beam, ΔE. Resolutions of 1eV are regularly achievable in FEG systems, and monochromated systems can have ΔE of 100meV down to a record energy resolution as low as 5 meV\(^{170}\). This high energy resolution enables differentiation between different elemental species, as well as the oxidation state and even changes in the orbital energies due to crystal field splitting for the element in question\(^{171,172}\). As EELS does not rely on X-ray emission, it can be used to quantify chemical composition also for lighter elements, including lithium\(^{173}\). In addition to measuring core-loss spectra (50-2000eV, EELS also gives
access to the low-loss regime (0-50 eV), which reveals information about other characteristic excitation in materials, such as interband transitions, phonon excitations and plasmon peaks.

Energy filtered electron microscopy (EFTEM) can be thought of as the TEM analog of EELS mapping. Like EELS, EFTEM uses the GIF detector to convert the transmitted electron beam into a spectrum. Rather than measuring the spectrum, a slit aperture is used to select the electrons of a certain energy. The image is reformed in the GIF using the electrons from only that specific energy. The same information obtained from STEM-EELS can thus be obtained in EFTEM. The drawback of this method is that only one specific energy can be probed at a time. The smaller the energy resolution, the lower the signal, thus requiring long collection times for multiple images at different spectra.

While electron spectroscopy methods offer superior energy resolution, as well as access to energy levels not accessible in EDXS, it suffers from experimental difficulties. The high-tension tank that controls the energy of the electrons has a tendency to drift by 1-2 V\textsuperscript{174}, which causes the entire energy-spectrum to shift during imaging, which have to be considered to avoid or correct for this\textsuperscript{174–176}. Specimen must be thin, ideally 20-50 nm, to prevent multiple scattering events that convolute the recorded spectrum and raise the background intensity. While there is a wealth of information available in the fine structure of the energy-loss spectra, extracting and understanding that information can require complex modelling, particularly in the low energy loss regime where the tail of the zero-loss peak (ZLP) convolutes contributions from plasmons, interband transitions, phonons, and other low energy excitations\textsuperscript{177–179}. EDXS, while limited in capabilities, typically offers a more user-friendly approach, with less instrumental and sample restrictions.
Chapter 4. Industrially scalable growth of SrTiO₃ by hybrid MBE

*The following section is reproduced in part from: Lapano, et. Al. Scaling growth rates for perovskite oxide virtual substrates on silicon. Nature communications 10 (1), 2464

This chapter covers enhancing the growth rate of SrTiO₃ using the hMBE deposition technique. The research is focused on industrial applications of hMBE, with the ultimate goal of creating virtual single-crystalline SrTiO₃ thin films on silicon for virtual perovskite oxide substrates. The chapter explores (1) the most efficient method to quickly determine the bounds of the stoichiometric growth window and (2) the effects of scaling the growth rate to an excess of 500 nm/hr. (3) This technique is expanded to growing SrTiO₃ thin films on silicon and (5) how these films have been used as substrates for deposition of functional perovskite oxides.

4.1 Virtual substrates and enhanced deposition rates by hMBE

The availability of native substrates is a cornerstone in the development of microelectronic technologies relying on epitaxial films. Complex perovskite oxides are already established in industry as dielectrics, ferroelectrics, and piezoelectrics, and are potentially propagating into novel electronic device applications such as Mott transistors¹⁸⁰–¹⁸², spintronics¹⁸³,¹⁸⁴, and quantum computation¹⁸⁵–¹⁸⁷. Many of these applications rely on low defect concentration as well as epitaxial stabilization of structural phases near their electronic phase transitions to access their non-equilibrium states, requiring the use of single crystalline perovskite oxide substrates. Current single crystalline perovskite oxides with acceptable quality cost anywhere between $400 for 2” LSAT wafer, to $500 for a single 10 x 10 mm exotic substrate¹⁸⁸. If native substrates are not available virtual substrates - crystalline buffer layers epitaxially grown on a structurally dissimilar substrate - offer a solution.
In such cases robust and cost effective, while scalable, material integration schemes that suffice stringent economic requirements are in demand to realize new device generations with improved performance at lower cost, weight, and size. Such metamorphic epitaxial materials also represent a route to expand the application space of existing devices, and to realize completely new technologies by stabilizing material phases with otherwise unattainable properties. The technical challenges, such as scalability, high-throughput and compatibility of the individual fabrication steps to exploit such materials advancements and deploy them into the market impose stringent conditions for the entire materials integration process.

Metamorphic buffer layers have proven their usefulness at an industrial scale for SiGe, III-V compound semiconductors, and group III-nitrides, setting record performance in a wide application space from photovoltaics using a metamorphic multijunction solar cell with efficiencies up to 46%\textsuperscript{190–192}, III-V based lasers monolithically integrated on Si\textsuperscript{193,194}, high electron mobility transistors (HEMTs)\textsuperscript{195–197}, and heterojunction tunnel field effect transistors (TFETs) for high performance low power logic\textsuperscript{198}. Metamorphic epitaxial materials have allowed for more cost effective and larger non-native substrates for electronic devices\textsuperscript{199,200}, and are being considered key to realize and advance the existing quantum computing materials platform of Si/SiGe heterostructures towards all-electrical control of Si-based qubits\textsuperscript{201}.

A metamorphic buffer technology for complex perovskite oxides on Si is highly desirable given their wide range of properties, which can even be expanded utilizing epitaxial strain\textsuperscript{202}. Although epitaxial integration of SrTiO\textsubscript{3} on Si has been successfully demonstrated\textsuperscript{203} and has been scaled up to 200 mm Si wafers using an industry-scale molecular beam epitaxy (MBE) system\textsuperscript{204}, typical film growth rates of about 50 nm hr\textsuperscript{-1} or lower\textsuperscript{88,204–206} impede a sufficiently high
throughput required for profitability. MBE systems have been operated on an industrial scale since the 1980s primarily for the growth of high quality binary semiconductor structures with controlled stoichiometry and desired composition at growth rates in excess of 1000 nm hr$^{-1}$. Metamorphic buffers have been developed for non-oxide materials using this growth technology. The key feature permitting such high-quality material by MBE is the adsorption-controlled growth kinetics. The more volatile element is supplied in excess and desorbs in a self-regulated fashion if not incorporated into the film, which dramatically simplifies the flux calibration and enhances reproducibility of the growth process. Therefore, the roadblock to integrate perovskites oxide materials by MBE or any other thin film growth technique in a scalable, economic way is the lack of an adsorption-controlled growth mechanism at high film growth rate. Specifically in the case of SrTiO$_3$ deviations from ideal stoichiometry result in a lattice parameter expansion to accommodate defects formed in the film when grown under nonstoichiometric conditions.

Commonly employed thin film growth techniques can in principle be scaled up to achieve wafer size conformity for complex perovskite oxides and has been demonstrated for pulsed laser deposition (PLD), sputtering, metalorganic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), and MBE. However, scaling up growth rates have resulted in nonstoichiometric SrTiO$_3$ films. Figure 4-1 compiles the degree of stoichiometry control, quantified by the intrinsic SrTiO$_3$ film lattice parameter expansion, as a function of growth rate for different thin film growth methods, using the lattice parameters of the (non)stoichiometric SrTiO$_3$ series plotted in Figure 4-1 (These figures use a separate reference list for simplicity, listed in Appendix A.1.1). Sputtering and PLD utilize targets where the indirect control of deposition
parameters makes stoichiometry control more challenging with increasing film growth rate. Conventional solid-source MBE growth for perovskite oxides requires precise calibration of the Sr and Ti fluxes, however, the level of oxygen pressure needed for high growth rates adversely affect effusion cell flux stability due to unintentional oxidation of the source material in the crucible, thus limiting this technique to low growth rates and precluding it as a cost-effective production tool for virtual perovskite oxide substrates.

Figure 4-1: Growth rates and control of film stoichiometry. Intrinsic SrTiO₃ film lattice parameter reported for different growth rates using scalable oxide thin film growth techniques: pulsed laser deposition (PLD), sputtering, metal-organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), molecular beam epitaxy (MBE) and hybrid molecular beam epitaxy (hMBE). In all cases except hybrid MBE the degree of film nonstoichiometry increased with growth rate. The number close to data points shown refer to references detailed in Supplementary Figure 1. The defect concentration δ of Sr-rich (Sr₁₊δTiO₃) and Ti-rich (Sr₁₋δTiO₃) films due to non-stoichiometric growth condition was determined from the intrinsic film lattice parameter expansion using a calibration curve given in Supplementary Figure 2. A growth rate of 0.6 µm/hr for stoichiometric SrTiO₃ by hybrid MBE was achieved for the growth on LSAT substrates. The reference list for this figure can be found in the Appendix A.1.1.
4.2 Growth window determination using RHEED and STEM

The conditions to access the self-regulated growth of stoichiometric SrTiO$_3$ were determined for a range of growth rates by observing specific surface reconstructions in real time using \textit{in-situ} RHEED\textsuperscript{95,148}. This method avoids multiple film growths and time consuming lattice parameter measurements using \textit{ex-situ} XRD\textsuperscript{94,150} and makes accessing the self-regulated growth window a production-line compatible process. This accelerated mapping of growth conditions is key to ensure proper growth condition in a single calibration run in a timely manner, as shown in Figure 4-3. In this method, a SrTiO$_3$ film was grown on a (La$_{0.18}$Sr$_{0.82}$)(Al$_{0.59}$Ta$_{0.41}$)O$_3$ (LSAT) single crystal substrate. The Sr flux supplied from the effusion cell was held constant at 2.50$\times$10$^{13}$ cm$^{-2}$ s$^{-1}$ during the entire calibration run, measured using a quartz crystal monitor at the sample position prior to growth. The TTIP flux, given by the beam equivalent pressure (BEP) P$_{TTIP}$
measured at the sample position using an ion gauge, was altered throughout the growth by changing the gas inlet pressure (See Figure A-1). The color code in Figure 4-3 a indicates whether stoichiometric (green), Sr-rich (blue), or Ti-rich (purple) growth condition were present. Stoichiometric growth conditions were initially chosen and Sr and TTIP were co-supplied for 10 minutes, resulting in a 12-nm-thick template layer. The TTIP flux was then increased and growth was continued for 5 minutes. This procedure was repeated and RHEED images were taken in real time. Figure 4-3 a-b show the growth sequence along with atomic-resolution STEM micrographs of the calibration sample in cross-section, respectively. STEM imaging revealed that for layers grown under Ti-rich growth conditions small Ti excess was incorporated as point defects, which gave rise to a gradual increase in background intensity relative to the stoichiometric regions of the calibration sample. For growth conditions with larger Ti excess the formation of a Ti-rich second phase was observed. In the case of Sr-rich growth conditions STEM images revealed the local formation of SrO Ruddlesden-Popper stacking faults propagating throughout the film (Figure A-6). SrTiO$_3$ layers were grown within the self-regulated window subsequently on both types of nonstoichiometric layers to determine the minimum thickness required to outgrow the local nonstoichiometry. While stoichiometric SrTiO$_3$ could be repeatedly achieved on layers grown under Ti-rich conditions irrespective of its thickness and degree of Ti-excess, the thickness needed to recover a stoichiometric growth front on layers grown under Sr-rich conditions was about 15 nm. The STEM images further showed that defects from Ti-rich and Sr-rich regions propagated up to about 5 nm into the subsequently grown layer, shown by regions of higher intensity protruding from the 5th layer into the subsequently grown stoichiometric layer shown in Figure 4-3 b. This marks the minimum growth duration needed to ensure that growth conditions were
accurately assessed by surface sensitive RHEED and subsequent layers were not influenced by potential nonstoichiometries of the preceding layer. The RHEED pattern taken \textit{in-situ} during iterative deposition cycles are shown in Figure 4-3 c. In the Sr-rich regime, the RHEED pattern was diffuse with a 2-fold reconstruction along the \(\langle 110\rangle\) azimuth, which can be easily distinguished from the stoichiometric growth conditions, characterized by a sharp RHEED pattern and loss of the 2-fold reconstruction along \(\langle 110\rangle\) as well as the appearance of a 2-fold reconstruction along the \(\langle 100\rangle\). For Ti-rich conditions RHEED patterns were diffuse and exhibited a gradual loss of the 2-fold reconstruction along \(\langle 110\rangle\)\textsuperscript{148,150,216}. Therefore, the growth conditions correlated with the surface reconstruction seen in RHEED and can be used to map the self-regulated growth window on a single calibration sample. The entire growth calibration procedure contained ten different TTIP fluxes and a recovery growth (‘reset’ layer) after mapping the edge of the growth window towards the Ti-rich growth conditions. The growth of the calibration sample took about 70 minutes, which is considerably shortened with increasing growth rate.
4.3 Scaling of growth rates for SrTiO₃ on oxide substrates and silicon

Rapid growth condition mapping as shown in Figure 4-3 was applied to find the self-regulated growth window for Sr-fluxes ranging from 1.25×10¹³ cm⁻² s⁻¹ up to 2.50×10¹⁴ cm⁻² s⁻¹. The width and position of the growth window as a function of growth rate is shown in Figure 4-4. For a Sr flux of 1.25×10¹³ cm⁻² s⁻¹ (growth rate 25.6 nm hr⁻¹), the TTIP BEP at the growth position had to be kept between 4.28–7.10×10⁻⁷ Torr to maintain self-regulated growth, which shifted to 1.52–1.65×10⁻⁵ Torr as the Sr flux was increased to 2.50×10¹⁴ cm⁻² s⁻¹ (growth rate 600.5 nm hr⁻¹).
supplied from two Sr effusion cells operated in tandem. The actual position of the growth window changed linearly with growth rate, which was determined by the Sr flux supplied. The calibration curve of TTIP beam equivalent pressure \( p_{TTIP} \) and gas inlet pressure is shown Figure A-1, while the change in growth rate with supplied Sr flux is shown in Figure A-4. The absolute width of the growth window \( \Delta p_{TTIP} \) increased at higher growth rates (Figure 4-4), whereas the relative width \( \Delta p_{TTIP}/p_{TTIP} \) (Figure 4-4 b) decreased. The latter trend can be extrapolated to determine the growth rate at which unintentional drifts from the Sr effusion cell can still be compensated via the self-regulated adsorption mechanism. Assuming a Sr flux drift of about 1% the growth window would be sufficiently wide up to a growth rate of \( (9.1 \pm 1.6) \mu \text{m hr}^{-1} \) (Figure 4-4 c). This growth rate does not mark the highest possible growth rate that can be achieved using hybrid MBE, since the growth window width has been found to increase with growth temperature\(^{130}\).

To confirm stoichiometric growth conditions from film lattice parameter and surface morphology measurements using \textit{ex-situ} XRD and AFM, nominally 45-nm-thick SrTiO\(_3\) films were grown on LSAT(100) substrates. Films grown within the growth window showed a step-like terrace structure, a root mean square (RMS) surface roughness of less than 1 nm and absence of crystalline islands irrespective of growth rate (Figure A-3). Figure 4-5 a shows high-resolution \( 2\theta-\omega \) X-ray scans around the 002 SrTiO\(_3\) film and LSAT substrate peaks. The out-of-plane lattice parameter was found to be \( 3.930 \pm 0.003 \) Å irrespective of growth rate, which matches values previously reported for stoichiometric SrTiO\(_3\) films grown on LSAT\(^{83}\). While critical film thickness of SrTiO\(_3\) on LSAT substrates was only 180 nm,\(^{217}\) a ~500-nm-thick SrTiO\(_3\) film was grown homoepitaxially within the growth window for a growth rate of 600 nm hr\(^{-1}\). \( 2\theta-\omega \) X-ray scans of the 002 SrTiO\(_3\) film and substrate peak shown in Figure 4-5 b revealed that they are
indistinguishable, as expected for a homoepitaxially grown stoichiometric film\textsuperscript{218}. RHEED intensity oscillations are shown in Figure 4-5 c-d for SrTiO\textsubscript{3} films grown at 40 nm hr\textsuperscript{-1} and 600 nm hr\textsuperscript{-1} on LSAT, respectively. In both film growths RHEED intensity oscillations were visible which dampened out with time, indicating an initial layer-by-layer growth which transitioned into a step-flow growth mode. The growth of 10 monolayers of SrTiO\textsubscript{3} took only 23.8 seconds, in excellent agreement with the growth rate determined from film thickness measurements. Details of the X-ray fits to determine physical film thickness and intrinsic film lattice parameter are given in section A.1.5.

Figure 4-4: Scaling growth window. \textbf{a}, Titanium tetraisopropoxide (TTIP) beam equivalent pressures $p_{\text{TTIP}}$ as a function of film growth rate for which a growth window was accessed. The Sr flux was kept fixed while the TTIP flux was modulated. The black bars represent $p_{\text{TTIP}}$ values within the growth window, while the upper red and lower blue triangle indicate the edges of the growth window determined by reflection high-energy electron diffraction (RHEED). The red and blue bar above and below the respective triangles are the first $p_{\text{TTIP}}$ values for Ti-rich and Sr-rich growth conditions, respectively. \textbf{b}, Absolute growth window width $\Delta p_{\text{TTIP}}$ as a function of growth rate. The triangles mark the edges of the growth window, while the bars are the values at which a non-stoichiometric growth front was observed in RHEED. \textbf{c}, Relative growth window width $\Delta p_{\text{TTIP}}/p_{\text{TTIP}}$ as a function of growth rate, where $p_{\text{TTIP}}$ is the TTIP beam equivalent pressures at the growth window center. The line is extrapolated based on the existing data set, projecting that a growth rate of (9.1±1.6) $\mu$m hr\textsuperscript{-1} can be achieved at a given Sr flux stability of 1%.
Deposition of SrTiO₃ for virtual perovskite substrates on silicon

To directly prove the compatibility of high SrTiO₃ film growth rates with the integration on Si wafers 125-nm-thick SrTiO₃ thin films were grown and the results are shown in Figure 4-6. Two different Sr sources were used in tandem; a Sr effusion cell with low flux (2.50×10¹³ cm⁻² s⁻¹) to nucleate and initialize the growth on Si using a buffer layer⁹⁴, while a second Sr cell calibrated to a much higher flux (1.00×10¹⁴ cm⁻² s⁻¹) for the film growth at a high rate of 240 nm hr⁻¹. The film thickness was chosen to avoid film cracking due to the thermal mismatch between Si and SrTiO₃. Wide range X-ray diffraction scans confirmed single crystalline (001) oriented SrTiO₃.
films with an out-of-plane lattice parameter of 3.889 Å, consistent with stoichiometric SrTiO₃ films grown on Si at 850 °C, albeit at much lower growth rates of only 50 nm hr⁻¹. Figure 4-6 b and c show the rocking curve of the 002 SrTiO₃ film peak with a full width at half maximum of 0.28° along with the reciprocal space map of SrTiO₃ 103 in excellent agreement with those reports. Figure 4-6 d shows the film surface morphology of SrTiO₃ on Si grown at 240 nm hr⁻¹ which exhibited a stepped terrace morphology with a root mean square surface roughness value less than 1 nm, making it an ideal starting surface for subsequent epitaxial growth, thus fulfilling yet another requirement of a metamorphic buffer layer. Excellent film thickness uniformity across the entire 3-inch wafer was evident from optical inspection (Fig. 4-6e) and the SrTiO₃ film thickness variation was determined across the entire wafer using spectroscopic ellipsometry, see Figure 4-6 f. A less than 1% change in SrTiO₃ thickness was extracted detailed in Figure A-5. Cross-sectional STEM and energy dispersive spectroscopy (EDXS) in Figure 4-7 shows a single crystalline SrTiO₃ film on the silicon substrate, separated by a 2-4 nm amorphous SiOₓ interfacial layer. Secondary ion mass spectrometry (SIMS) of SrTiO₃ on silicon is given in Figure A-7, revealing carbon incorporation from the metalorganic precursor is limited primarily to the interface due to the decreased cracking efficiency of the metalorganic precursor at low temperatures. Carbon contamination is minimized for the bulk of the deposition at higher temperatures, in agreement with previous studies.
Figure 4-6: Virtual perovskite oxide substrate on Si. a, Wide range 2θ-ω X-ray scan of a ~126-nm-thick SrTiO$_3$ film grown on 3 inch Si wafer at a growth rate of 240 nm hr$^{-1}$. b, Rocking curve (ω-scan) of the 002 SrTiO$_3$ peak with a full width at half maximum (FWHM) of 0.28°. c, Reciprocal space map of the 103 SrTiO$_3$ film peak in reciprocal lattice units of stoichiometric SrTiO$_3$. d, Atomic force microscopy image of the SrTiO$_3$ on Si with ‘epi-ready’ step terrace morphology and a surface roughness (RMS) of ~1 nm. A line profile of the film is shown above. Scale bar on AFM image is 200 nm. e, Photograph of the perovskite oxide virtual substrate, a SrTiO$_3$ metamorphic buffer layer on a 3” Si wafer. The SrTiO$_3$ film is transparent, the yellow coloration is from interference due to its finite thickness ($\lambda/4$). f, Wafer scale map of SrTiO$_3$ film thickness on Si obtained from spectroscopic ellipsometry with a smaller than 1% film thickness variation across the wafer.
4.5 **Bottom electrodes and functional perovskite oxides on silicon**

Highly conductive bottom electrodes are a critical component for capacitors, field-effect transistors, giant magnetoresistive sensors, solar cells, and a host of other electronic devices. The most well-known conducting bulk single crystal substrate for perovskites is Nb:SrTiO$_3$, as it offers lattice parameter similar to many perovskites. Similar to undoped SrTiO$_3$ these crystals are not

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Figure 4-7: **Microscopy of SrTiO$_3$ on silicon**  
**a**, HAADF-STEM imaging of an un-annealed SrTiO$_3$ film grown on 3” silicon at 240 nm hr$^{-1}$. Low defect, single crystalline film was found at all observed areas, in agreement with x-ray results. Defects were found more closely concentrated near the interfacial region, and disappeared in the bulk of the film. The surface roughening is due to ion beam damage induced during sample preparation process.  
**b-g**, HAADF and energy dispersive x-ray spectroscopy (EDSX) imaging taken at the interface of the sample. All scale bars are 4 nm.
scalable to large area wafers. Platinum (111) films grown on various substrates, such as Al$_2$O$_3$ (0001)$^{220-223}$ or TiO$_2$/SiO$_2$/Si$^{224,225}$ stacks is a common bottom electrode for industrial applications but is not suitable for epitaxial growth of 001 perovskites. A common alternative is to simply deposit an epitaxial conducting film, such as (Ca,Sr,Ba)RuO$_3$$^{226-228}$, La$_{1-x}$Sr$_x$MnO$_3$$^{229}$, LaNiO$_3$$^{230}$, and (Ca,Sr)VO$_3$$^{138,231}$, however the same restrictions to small sample geometry still apply.

The previously described method has been used to grow a series of epitaxial SrTiO$_3$ films on silicon. Conducting films of SrVO$_3$, SrNbO$_3$, as well as multiferroic BiFeO$_3$ have been deposited on these films in varying degrees of development for use as epitaxial bottom electrodes.

### 4.5.1 SrVO$_3$

SrVO$_3$ is a highly conducting, complex oxide exhibiting strong electron correlations offering an optically transparent window in the visible regime, making it a potential replacement for indium tin oxide (ITO)$^{10}$, and potentially interesting for applications such as perovskite solar cells and energy conversion materials$^{232,233}$. Films of SrVO$_3$ were deposited on SrTiO$_3$/Si wafers using at a variety of temperatures and thickness with varying levels of success in conjunction with Lei Zhang. Cracking of the SrVO$_3$ of films at thickness beyond 20 nm from the large epitaxial mismatch (3.93 SrTiO$_3$/Si vs 3.84 SrVO$_3$) imposing a large tensile strain on SrVO$_3$ forced the bottom electrode to remain fairly thin. Attempts to decrease the deposition temperature to prevent expansion of the lattice upon cooling due to thermal mismatch led to a shrinking of the SrVO$_3$ growth window, and precipitation of 2$^{nd}$ phases during SrVO$_3$ film growth if the stringent conditions for stoichiometric growth were not met. Despite these difficulties, conducting, single-phase SrVO$_3$ thin films were deposited with sheet resistances of about 10 $\Omega/\sqmu$m.
Attempts to nucleate SrVO$_3$ directly on Si were unsuccessful, and a SrTiO$_3$ buffer layer of at least 10 nm was required obtain a coherent SrVO$_3$ film. Thicker SrTiO$_3$ films typically let to more improved subsequent growth of SrVO$_3$. The primary hurdle in this investigation is the large thermal expansion mismatch between Si and perovskite oxides, leading to a large buildup of tensile strain in the films upon cooling. Future work could focus on lowering of the growth temperature to minimizes the strain buildup. Previous studies have shown that CaTiO$_3$ is better lattice matched to Si and can be deposited via thermal MBE$^{234}$.

4.5.2 SrNbO$_3$

Much like SrVO$_3$, SrNbO$_3$ is an optically transparent, conducting oxide. In SrNbO$_3$ the absorption edge occurs at higher energies, making it transparent in both the optical as well as ultraviolet regime, with potential applications in UV photo-diodes and LEDs. Further, as SrNbO$_3$ exhibits a much larger lattice constant of 4.024Å, it would be more closely lattice matched bottom electrode to common ferroelectrics such as Pb(Zr, Ti)O$_3$ and BaTiO$_3$ (see Figure 7-1). Furthermore since the epitaxial strain imposed on SrNbO$_3$ would be compressive the films would not crack but rather develop structural defects to mitigate the stress.

SrNbO$_3$ films of ~40 nm thickness were grown by Joseph Roth at Penn state using RF-plasma sputtering from a Sr$_2$Nb$_2$O$_7$ target on 50-nm-thick virtual SrTiO$_3$ substrate on silicon at a growth temperature of 730°C. Spotty RHEED (Figure 4-8) as well as well as small polycrystalline rings were observed post growth. AFM scans showed films were crack-free with ~ 1 nm surface roughness. Films exhibited a lattice constant of 3.983 Å and no change in the underlying SrTiO$_3$ lattice constant. Room temperature resistivity of SrNbO$_3$ films of about 8x10$^{-4}$ Ω·cm were determined, approximately an order of magnitude higher than the best SrVO$_3$ thin films. The sheet
resistance of 200 Ω/sq., is promising and can further be lowered by increasing the film thickness. The close lattice match of relaxed SrNbO$_3$ compared to piezoelectric PZT and multiferroic BiFeO$_3$ make this bottom electrode material superior to the vanadates with smaller lattice parameter.

Figure 4-8: SrNbO$_3$ sputtered on SrTiO$_3$. RHEED images of SrNbO$_3$ is shown in (a). AFM images of the film in (b) exhibit surface roughness on the order of 1 nm. XRD (c) shows both the SrTiO$_3$ and SrNbO$_3$ peaks with the magnified insert exhibiting Keissig fringes.
4.5.3 BiFeO$_3$

Multiferroic materials have the potential to lower power consumption of current spintronics$^{235}$ and potential for a new low power computing paradigm$^{236,237}$. BiFeO$_3$ is the current front runner and the most heavily studied multiferroic, exhibiting both ferroelectric and antiferromagnetic behavior at room temperature, as well as a slight canting of the AFM moment leading to weak ferromagnetic behavior. One of the challenges for the adoption of BiFeO$_3$ in industry is low temperature (<500°C) integration on silicon to ensure back-end-of-the-line compatibility$^{238}$. Atomic layer deposition (ALD) is a common deposition technique in industry, as it deposits highly conformal films over large areas and over high aspect ratio structures, and can be deposited at low temperatures, however BiFeO$_3$ films deposited at such low temperatures are amorphous and must be post-growth crystallized. Virtual perovskite substrates on Si can be used to help lower the BiFeO$_3$ crystallization temperature.

Collaborators at Drexel University have developed an ALD based approach to deposit amorphous Bi$_2$O$_3$ and Fe$_2$O$_3$ on SrTiO$_3$-buffered Si. Subsequent annealing at 500°C led to crystallization BiFeO$_3$ nucleated from the SrTiO$_3$ layer. XRD and HAADF-STEM in Figure 4-9 a revealed a relaxed-epitaxial arrangement between the BiFeO$_3$ film and SrTiO$_3$ buffer layer. XRD θ-2θ scans give a lattice parameter of 3.94 Å for BiFeO$_3$, slightly smaller than the bulk lattice constant, indicating that the BiFeO$_3$ film may be in tensile strain from the thermal mismatch between the film and the Si substrate. XRD ϕ-scans reveal the same BiFeO$_3$(100)//Si(110) orientation as SrTiO$_3$, with 4 distinct peaks indicating the film is epitaxial oriented. This process outlines a new route to integrate BiFeO$_3$ on silicon, and has potential to expand to other oxides deposited via ALD.
4.6 Concluding remarks

These growth experiments demonstrate that it is possible to integrate functional oxides in a scalable and economic way on Si, addressing a long-standing challenge to synthesize high-quality perovskite materials on an industrial scale. The accessibility of the self-regulated growth window at high growth rates afforded by hybrid MBE and the compatibility of this growth process with Si enables functional diversification of electronic devices in the current More than Moore era. The wide-ranging properties of perovskite oxides will open up routes to augment additional functions to existing devices. The scalability of growth rates enables the development of a metamorphic buffer technology for virtual perovskite oxide substrates. Rather than being limited...
to single crystal substrates with sizes of up to only two inches using bulk crystal growth techniques such as Czochralski or Bridgman-Stockbarger methods, perovskite oxides on Si wafers with excellent crystalline quality and epi-ready surface morphologies provide more cost effective substrates and thus will enable more growth experiments. The availability of virtual substrates will drive innovation at the fundamental level and speed up the process development from basic scientific discoveries to system level maturity, thus boosting research productivity and technological significance of functional epitaxial oxide thin films. While accessing a self-regulated growth window at high growth rates was demonstrated for SrTiO₃ as a prototypical perovskite oxide, many ABO₃ perovskites (ABO₃, A = Ca¹³⁷, Sr²¹⁷, Ba¹³⁶, Gd¹³⁴, Nd²³⁹, Sm¹³⁵ with B = Ti; A = Sr⁹⁶, Ca²⁴⁰, La¹⁸⁹ with B = V; as well as LaAlO₃⁹⁷, BaSnO₃¹⁴⁰, and SrRuO₃¹⁴³) have already been successfully grown by hybrid MBE. This suggests that scaling growth rates is a general feature of this growth approach rather than being limited to SrTiO₃, indicating that the development of virtual substrates for perovskite oxides can be expanded to other perovskite oxides in an economic, scalable way as well.
Chapter 5. Polar phenomenon in incipient ferroelectric films and superlattices

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This chapter covers the growth and characterization of the (1) incipient ferroelectric CaTiO$_3$. Second harmonic generation (SHG), STEM, and theoretical calculations are employed to understand the relation between strain, structure, and ferroic order. (2) The ferroelectric properties of $(CaTiO_3)_n(SrTiO_3)_n$ superlattices are again explored using SHG and STEM, with the additional synchrotron XRD. It is found that both interfacial roughness, as well as film symmetry, can either induce or suppress the ferroic order.

5.1 Ferroelectricity in strained SrTiO$_3$ and CaTiO$_3$

Non-centrosymmetric materials that are capable of sustaining a permanent, switchable electric dipole moment remain a continued area of interest for numerous industrial applications. It is the discovery of this unique property in BaTiO$_3^{241,242}$ and similar materials in the 1980’s that drove the research field of perovskite thin films. Pyroelectric materials, which couple electric polarization to a change in temperature, are currently used in thermal imaging cameras$^{243}$, heat sensors$^{244}$, and show potential use in power generation$^{245}$. Piezoelectric and ferroelectric materials are widely used in transducers$^{246,247}$, sonar systems$^{248}$, sonograms$^{249}$, non-volatile memory$^{250}$, nonlinear optics$^{251}$ and fuel injectors$^{252,253}$, and potential applications in computing$^{254,255}$ and optical lens correction$^{256,257}$. These materials are unfortunately hamstrung in two main different
ways. Firstly, the polar phase is inherently unstable at elevated temperatures as the vast majority of bulk perovskites are centrosymmetric above 1000°C, preventing their use in high temperature applications such as monitoring fatigue in critical engine components$^{258,259}$. Secondly, many of the most common piezoelectric materials contain Pb due to the lone pair formation when it is in the 2+ valence state, which makes it easy to polarize and gives a greater piezoelectric and ferroelectric response. However, Pb poses health concerns and also suffers from volatilization at elevated temperatures, leading to premature failure of components and inherent incompatibility with high temperature environments. The abundance of perovskite structured materials does not accurately reflected the small percentage perovskites that exhibit non-polar symmetry, and searching for new non-polar structures remains a topic of interest$^{27}$.

The discovery of room temperature ferroelectricity in films of the strained dielectric SrTiO$_3$ led to a fervor of research activity in the field of strain-enabled functionality in thin films$^{40}$. Enhancements in ferroelectric transition temperatures of BaTiO$_3$$^{41}$ and PbTiO$_3$$^{43}$ spurred on this research in conjunction with the ferroelectricity predicted and experimentally confirmed in tensile-strained CaTiO$_3$ films on LSAT and NdGaO$_3$$^{49}$. Comprehensive theoretical predictions of the strain-phase diagram for various ferroelectric and dielectric phases show that these materials are highly sensitive to magnitude, sign of the strain, direction, as well as oxygen octahedral rotation angles and symmetry$^{260-263}$.

Pure epitaxial strain is limited by the critical thickness of films up to which they remain coherently strained. Higher strains often yield an enhancement of the ferroelectric properties, but impose limits to the film thickness. For instance, SrTiO$_3$ grown on LSAT can reach 180 nm at a compressive strain of -0.95%, while for films on DyScO$_3$ at 1.02% tensile strain began to relax.
Effects between the substrate and film was shown to greatly influence sample properties, in some cases more than the strain itself, such as the case of CaTiO$_3$ thin films$^{49}$. This enhancement was attributed to a suppression of oxygen octahedral tilting within the unit cell, allowing the A-site Ca cation to displace off the centrosymmetric position, rather than the B-site which is traditionally observed in proper ferroelectrics. However, this effect was only seen for the first few monolayers in close proximity to the interface when the film was grown on a cubic substrate, lacking any rotations. When CaTiO$_3$ was grown on NdGaO$_3$, which does exhibit rotations, only a small enhancement of the ferroelectric properties was observed. Thus, it was concluded that interfacial region with suppressed rotations was primarily responsible for the enhanced ferroelectric properties, rather than strain, with the natural progression then turning to layered superlattices with multiple interfaces between these materials in a single film.

Improper ferroelectrics are a novel class of materials that use layering techniques to break inversion symmetry and build in a net polar moment$^{30,264,265}$. In the simplest case, numerous perovskites exhibit unusual tilt symmetries and cation off-centering that appears to break inversion symmetry on the pseudocubic unit cell, but the neighboring unit cells have the opposite apparent polarization, and so the net polarization of the bulk unit cell remains zero. By layering two materials together that contain certain rotational symmetry elements, the inversion symmetry can be broken potentially allowing for a net polarization to develop$^{29}$. This strategy presumes that the individual components will retain their bulk-like symmetry in the superlattice. This is not necessarily the case, as the previous Figure 1-8 demonstrates that many perovskites exhibit numerous nearly generate symmetries, and different layering and strain effects could force another symmetry to become the stable state.
SrTiO₃ and CaTiO₃ are two ideal materials to study the effects of structure and symmetry in strain enable ferroelectricity, as they are chemically similar, but differ structurally: SrTiO₃ is cubic while CaTiO₃ is orthorhombic \textit{Pbnm} at room temperature\textsuperscript{261,266}. Further, both of these materials have been thoroughly studied in thin film and the separate effects of strain, symmetry, and layering can be deconvoluted from the ferroelectric properties.

5.2 Growth and Microscopy of Compressively Strained CaTiO₃

5.2.1 Growth window and structure of thin films

Films of CaTiO₃ were grown using the hybrid molecular beam epitaxy system at Penn State in collaboration with Dr. Ryan Haislmaier. Calcium was supplied via a thermal effusion cell calibrated to 2.0x10\textsuperscript{13} atoms/cm\textsuperscript{2}s, while Ti was introduced to the system in the form of a TTIP. Oxygen was supplied during growth to a chamber pressure of 5x10\textsuperscript{-7} Torr. The growth window for CaTiO₃ was first found for 25-nm-thick films on LSAT due to the favorable lattice match as and similar to previous work\textsuperscript{137}. Films in the growth window showed sharp, crisp RHEED diffraction patterns, while nonstoichiometric films grown under conditions outside the growth window exhibited diffuse RHEED pattern. Initially, no correlations between surface reconstructions and film stoichiometry was noted. Later work by Roth et. al. showed that reconstructions where similar to SrTiO₃, but were more difficult to determine due to the lower symmetry of the \textit{Pbnm} and a resulting doubling of the CaTiO₃ unit cell, as well as the decreased intensity of the 10 diffraction rod attributed to structure factor considerations\textsuperscript{267}. X-ray diffraction confirmed the presence of a growth window with a constant out of plane lattice parameter for coherently strained CaTiO₃ films grown at TTIP gas inlet pressures between 57 and 69 mTorr.
(Figure 5-1), while CaTiO$_3$ films grown outside this TTIP gas inlet pressure regions showed a lattice parameter expansion.

**Figure 5-1: CaTiO$_3$ growth window.** (a) The out-of-plane lattice constant for a series of CaTiO$_3$ films grown on LSAT is shown, with the stoichiometric window outlined in green, with accompanying RHEED images (b) taken along the <110> zone at Ca-rich, stoichiometric, and Ti-rich conditions. The $\frac{1}{2}$ order peak, highlighted by the white arrows, is visible in all zones due to the inherent unit cell doubling of the lattice.

After the growth window had been determined, a series of 14-nm-thick CaTiO$_3$ films were grown on DyScO$_3$ 001 (+3.23%), LSAT (1.26%), LaAlO$_3$ (-0.76%), LaSrAlO$_4$ (-1.68%), and YAlO$_3$ (-2.73%) substrates using the methods described above. The thickness was selected to minimize strain relaxation in the films and to enable the growth of coherent CaTiO3 on substrates with larger lattice parameter mismatch, while providing a uniform thickness across all films that could be accurately characterized.
X-ray diffraction measurements shows that the out of plane lattice constant decreased in a linear fashion from films on LaSrAlO₃ to LSAT, while there was an abrupt change in the lattice constant for films on DyScO₃ and YAlO₃. Atomic force images of these films exhibited cracking, confirming that these were in fact relaxed (Figure 5-2).

Second harmonic generation was used to probe the polar nature of the films and confirmed a polar to nonpolar transitions of the strained films. Tilt-scans and polarimetry plots taken at 77K, shown in Figure 5-3 revealed films on DyScO₃ and LSAT exhibited an in-plane polarization with monoclinic symmetry, consistent with density function theory (DFT) predictions. 

Figure 5-2: Strained CaTiO₃ films: Strain series of CaTiO₃ films were grown on DyScO₃, LSAT, LaAlO₃, LSAO, and YAlO₃. 2θ-θ scans are given in (a), with the extracted lattice constant shown in (b). Films exhibited crisp RHEED diffraction patterns, suggesting all were grown within the window (c). AFM images of films on DyScO₃ and YAlO₃ showed relaxation faults and cracking, respectively, as films were relaxed (d) in agreement with the extracted lattice constant. Reproduced from reference (44).
Compressively strained films exhibited an out of plane polarization, with a slight monoclinic distortion for CaTiO$_3$ films on YAlO$_3$ and LaAlO$_3$, while the polarization on LaSrAlO$_4$ was purely tetragonal.

Temperature dependent SHG scans were carried out to determine critical transition temperatures between 77K to 1100K (Figure 5-3 a). Films on LSAT and DyScO$_3$ showed a relaxor ferroelectric-like transition at ~180 K and 225 K, respectively. These values were slightly higher than theoretical predictions and experimental results from previous work$^{49}$, but confirmed the trend of increased $T_c$ with increasing tensile strain. These films exhibited a broad transition over a few hundred degrees, with SHG intensity disappearing for CaTiO$_3$ on LaAlO$_3$ at 813K, and an apparent transition at approximately the same temperature for the film on LaSrAlO$_4$, although some remnant polarization remained up to the temperature limitations of the experimental setup (1100K). A transition was observed at 420K for the film on YAlO$_3$, disappeared entirely at 700K, and then began to increase at 820K up to 1100K. This unusual transition may be due to the relaxation faults within the film causing spurious SHG intensity.
5.2.2 Scanning Electron Microscopy of CaTiO₃

High resolution (HR)-STEM microscopy was employed to unravel the SHG on LaSrAlO₄ and LaAlO₃ and obtain a more complete view of the microstructure. The samples were prepared using a manually thinning technique on an Allied Multiprep polishing system. Wedge polishing proved more difficult than expected due to the layered nature of LaSrAlO₄. Striations began to appear parallel to the interface when the sample approached 50 μm thickness and led to the sample breaking apart as the sample was polished further. This was partly remedied by reinforcing the sample between silicon pieces enough to obtain a thin region containing the interface, though some
fracturing of the sample still occurred. The sample was thinned using a PIPS2 ion thinner to electron transparency (See Appendix A.6 for more information on sample preparation).

Electron microscopy was carried out using an aberration corrected FEI Titan operating at 200 kV in STEM mode, HAADF-images are shown in Figure 5-4. Images revealed numerous domains that were not previously reported for films grown on LSAT\textsuperscript{49}. This can be explained through structural considerations. CaTiO\textsubscript{3} is orthorhombic with a\textasciitilde a\textasciicircum c\textasciitilde Glazer notation, with the shortest axis being the pseudocubic axis of in phase (+) rotations (3.819 Å) as compared to the longer (-) rotational axis (3.826 Å). Strain would then dictate that this (+) axis is oriented out-of-plane for films grown on LSAT, and so although antiphase domains are still possible, the rotational symmetry should still remain a\textasciitilde a\textasciicircum c\textasciitilde. On LaAlO\textsubscript{3}, strain would suggest that this axis remains in the plane, giving equal rotational domains of a\textasciitilde a\textasciicircum c\textasciitilde and a\textasciitilde a\textasciicircum c\textasciitilde. To confirm this, atomic displacement mapping was carried out, with particular focus on the directionality of the Ca atomic displacements. Two structurally distinct domains were found, the first corresponding to the a\textasciitilde a\textasciicircum c\textasciitilde domain, in which the Ca atoms displace vertically in an antiferrodistortive manner, while a second domain in which the Ca atoms showed now displacements, but appeared elliptical in cross section, due a 90° rotation of the film. This corresponds to the a\textasciitilde a\textasciicircum c\textasciitilde domain, as the Ca atoms displace along the viewing direction and overlap when viewed in projection. This was further confirmed by selected area fast Fourier transforms (FFT), in which \(\frac{1}{2}\) order peaks can be used to precisely determine the orientation.
Films on LaSrAlO$_4$ showed similar $a^*b^*c^-$ and $a^*b^*c^*$ rotational domains, again due to the compressive strain imposed by the substrate. Additional structural defects were observed propagating from the substrate, causing the large mismatch in step-edge height between the film and the substrate. The perovskite structure is composed of alternating layers of AO and BO$_2$, while the RP phase is comprised of repeat unit cells of (AO-BO$_2$-AO)$_n$, due to the addition of a second rock salt layer. For the majority of the film this is irrelevant as it is only the in-plane lattice constant that dictates the strain behavior. At step-edges this symmetry is broken, as the step edge height of LaSrAlO$_4$ is approximately 1.5x the height of CaTiO$_3$. For films in which excess A-site is supplied, vertical or diagonal RP faults can develop to accommodate the $\frac{1}{2}$ unit cell offset between the two terraces. For purely stoichiometric films, a large strain gradient originating at the step-edge typically develops as there is no excess A-site cations for the RP fault. STEM analysis reveals that these films are most similar to the latter case.

Figure 5-4: Scanning transmission electron microscopy high angle annular dark field of CaTiO$_3$ (STEM HAADF) on (a) LaSrAlO$_4$, and (b) LaAlO$_3$ sample. A fast Fourier transform (FFT) of the film region is shown on the top right with the 100 and 001 peaks circled. The pseudo-cubic film axes are shown on the bottom left. The crystal structures of the strained CaTiO$_3$ films and the substrates are shown on the right of each STEM image.
Atomic displacements mapping was used to measure any polarization in the films at room temperature and is shown in Figure 5-5. Cation imaging using HAADF images was used first to measure any off-centering of the Ti-cation relative to the Ca-sublattice (Figure 5-5 c). This method has been used to measure polarization direction in numerous other ferroelectrics\(^{268-272}\). In both films the Ti atom remained centrosymmetric within the cation sublattice, and no polar off-centering was measurable within the resolution limit of the microscope. The oxygen sublattice when observed using ABF imaging revealed that the polarization may arise from oxygen displacements, rather than Ti as is usually observed for other ferroelectrics. For selected areas on LaSrAlO\(_4\), there was an apparent displacement of the oxygen relative to the Ti atoms in the out-of-plane direction, consistent with the SHG polarimetry measurements. Unfortunately, oxygen imaging is more sensitive to aberrations and sample tilt, this imaging alone is not enough to confirm the presence of a ferroelectric moment\(^{273}\). A large amount of charging occurred for film on LaAlO\(_3\), and prevented high quality oxygen images from being captured.

In both cases, the large number of structural defects arising from substrate constraints led to a large amount of non-uniform strain in the film. Studies of nanoparticles and bulk CaTiO\(_3\) crystals have shown that SHG signal can arise from the interfaces of these domains as well as surface effects breaking inversion symmetry\(^{274-275}\). Any type of anisotropic strain will by definition break inversion symmetry, and it is very probable that defect dipoles from vacancies or other defects present at the step edges on LaSrAlO\(_4\), may also give rise to SHG signal. This nonlinear strain causes the transition temperatures to be spread over a large temperature range, as seen for the tensile strained films. Further, the high temperature remnant SHG signal can be attributed to the defects and rotational domains, which will persist irrespective of temperature, or
until CaTiO$_3$ undergoes a transition to a higher symmetry structure at 1512K, beyond the range of the experimental setup$^{276}$.

![Diagram](image)

**Figure 5-5: Annular bright field imaging and polarization measurements.** (a) ABF-STEM images of CaTiO$_3$ on LaSrAlO$_4$ were used to plot the atomic structure. Polarization direction is plotted in (b). (c) It was found that the net polarization was due to a displacement of both the Ca and Ti positions relative to the oxygen sublattice, with the approximate displacement vectors given in by the blue arrows in the CaTiO$_3$ lattice. Polar displacement plots show a net charge displacements primarily in the out of plane direction (d), although a slight in plane component is found at the interface (e).

### 5.2.3 Theoretical calculations of epitaxy-induced polarization

Density functional theory was used to further elucidate these results as due the limitations of STEM in imaging these highly strained films on LaAlO$_3$ and LaSrAlO$_4$. Calculations were
carried out by Kelvin Lu of the Sinnott Group at Penn State using the plane-wave basis and projector augments wave (PAW)\textsuperscript{277} and gradient function of Perdew-Burke-Ernzerhoff (PBE)\textsuperscript{278} in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{279}. Crucially, these calculations captured thin film effects by using a repeat unit cell containing 1 substrate perovskite block, and 6 CaTiO\textsubscript{3} blocks that were fixed to the in-plane dimensions of the substrate. Relaxed structures revealed the $a'b^+c^-$ rotational pattern, in agreement with STEM imaging. Further, calculations predicted that CaTiO\textsubscript{3} thin films on LaSrAlO\textsubscript{4} exhibit entirely out of plane polarization and estimated the magnitude to $P_{[001]} = 9 \ \mu\text{C/cm}^2$. CaTiO\textsubscript{3} on LaAlO\textsubscript{3} is largely out-of-plane polar, with a somewhat lower total polarization of $P_{[001]} = 4 \ \mu\text{C/cm}^2$ due to the lower epitaxial strain. Additionally, a slight in plane polarization of $P_{[100]} = 0.6 \ \mu\text{C/cm}^2$ and $P_{[010]} = 1.3 \ \mu\text{C/cm}^2$ was calculated as well, which was reflected in the SHG polarimetry plots. In both cases, the magnitude of the polarization alternated at each unit cell due to the antiferrodistortive Ca displacements and oxygen rotations coupling with the displacement of the Ti atom within the oxygen octahedral cage.
5.2.4 Concluding remarks

The polar phases of strained CaTiO$_3$ are explored using SHG, HR-STEM, and DFT calculations. Films under tensile strain behave as expected from phase-field calculations, with an increasing $T_c$ of in-plane polarization with increasing strain. Compressively strained films revealed much more potential for further exploration, with polar phases being stable up to 800 K at experimentally achievable strains, well beyond what is predicted by bulk phase-field calculations. HR-STEM clearly revealed numerous domain walls and strain gradients within the film that could not be measured from the XRD scans which may enhance this transition beyond the expected values, and is most likely responsible for the elongated polar-nonpolar transition at high temperatures. DFT of thin film structures revealed that the polar phase is enhanced from the boundary conditions imposed by the substrates, and a coupling of the polar mode to the octahedral
rotations and antiferrodistortive displacements. While further study is needed to truly deconvolute this phenomenon, it opens the door for further studies of compressively strained perovskites and the potential of high temperature ferroelectricity and other novel phenomena.

5.3 Phenomena in complex oxide superlattices

5.3.1 Synthesis, synchrotron diffraction, and polarization measurements of superlattices

The requirement for flux-closure at a polar-nonpolar interfaces leads to the development of novel new microstructures\(^{268,269}\) and the influence of octahedral rotation coupling across interfaces can dramatically alter the ferroelectric and other functional properties in perovskites\(^{49,280}\). At room temperature, SrTiO\(_3\) and CaTiO\(_3\) are both paraelectric, but when strained on LSAT they undergo a ferroelectric transition at low temperatures with an out of plane polarization for SrTiO\(_3\) and an in-plane polarization for CaTiO\(_3\). Understanding how these two polar modes interact in confined films, as well how rotations can influence these properties will be critical in developing new functional superlattices, making these an ideal materials system for study.

To further elucidate proximity effects that can emerge in the SrTiO\(_3\)//CaTiO\(_3\) system superlattices were grown by Dr. Ryan Haislmaier at Penn State using an \(h\)MBE approach on LSAT substrates. Sr and Ca were supplied via thermal effusion cells, and Ti was supplied by TTIP. The background oxygen pressure was kept at approximately 1x10\(^{-7}\) Torr. The growth windows for both determined using XRD from the methods described previously. Superlattices were deposited using a shuttered-codeposition approach, in which A-site and TTIP shutters were both open for the deposition of a superlattice layer. Both shutters were closed after depositing the individual superlattice layer and growth was paused to allow the surface atoms to diffuse to the step edges.
and form an atomically smooth surface, after which the A’ cation and TTIP were opened to co-deposit the following A’TiO₃ layer. This process was continued in stepwise fashion until the superlattice structure reached a thickness of about 100 nm. RHEED intensity oscillations were observed during growth to determine both the monolayer formation time, as well as to ensure that the growth front recovered after the deposition of each layer to ensure atomically abrupt interfaces. A more detailed analysis of the growth process is given in ref (281).

Synchrotron source XRD performed on all superlattices were conducted to characterize the structure, and temperature dependent SHG measurements and polarimetry were used to determine their polar properties (Figure 5-7). Diffraction experiments were carried out at Advanced Photon Source, Argonne National Laboratory using an X-ray energy of 16 keV, wavelength of $\lambda = 0.775$ Å, and a beam size of $50 \mu$m (vertical) $\times 80 \mu$m (horizontal), on a Dectric PILATUS 100K pixel array area detector. LSAT ($a = 3.868$ Å) was chosen as a substrate as its lattice constant sits directly between the pseudocubic lattice constants of CaTiO₃ ($a_p = 3.822$ Å) and SrTiO₃ ($a = 3.905$ Å). While this allowed the superlattice to be grown to relatively large thicknesses without relaxing, the primary superlattice reflection was obscured by the substrate peaks, requiring the higher order superlattice reflections to precisely determine periodicity and structure to compare to the in-situ RHEED oscillations.
The superlattice diffraction does not give discrete peaks for the SrTiO$_3$ and CaTiO$_3$ individual layers, but rather diffraction from the supercell repeat unit formed by each (SrTiO$_3$)$_n$(CaTiO$_3$)$_n$ layer. The strongest diffraction occurs for specular (00$L$) peaks that follow the form $L = (2 \times I \times n)$, where $I$ is any even integer. In the case of the $n = 10$, this would be for peaks such as $n = 10, 20, 30$, etc. The LSAT (00$L$) series of peaks sit directly on top of these peaks and unfortunately obscures these primary diffraction peaks. Satellite peaks are weaker in intensity, and occur when $n$ is not a factor of $L$ such as for $n = 18, 19, 21, 22$, etc.

This leads to one of the most interesting features, the splitting of the satellite peaks in between the primary substrate peaks. This effect has been observed previously in superlattices of

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**Figure 5-7: Properties of incipient ferroelectric superlattices.** Synchrotron X-ray diffraction of the $n = 1$-$10$ (CaTiO$_3$)$_n$(SrTiO$_3$)$_n$ series of superlattices (a). Significant splitting of the $L = 0.5$ and 1.5 peaks is observed for the $n = 1, 3, 7, 8, 9$ and 10. SHG temperature scans (b) show only films that exhibit split peaks have a transition. Reproduced from reference (281).
GaAs/AlGaAs$^{282}$ and YBa$_2$Cu$_3$O$_{7-x}$/PrBa$_2$Cu$_3$O$_7$\textsuperscript{283} and is attributed to a non-integer periodicity of the superlattice caused by slight deviation of the monolayer formation time from the ideal time, presumably due to effusion cell drifts. The effect is more pronounced for higher $n$ superlattices, as a 1\% overestimation of the monolayer time leads to an extra $n \times 0.01$ excess unit cell growth per superlattice layer. The width between the split peak intensities can be used to estimate additional non-integer periodicity, $\Delta$. For $n = 2$, $\Delta_2 = +0.05 \pm 0.01$; for $n = 5$, $\Delta_5 = 0.05 \pm 0.01$; for $n = 8$, $\Delta_8 = 0.25 \pm 0.01$; and for $n = 10$, $\Delta_{10} = -0.17 \pm 0.01$\textsuperscript{281}.

SHG measurements of the superlattices revealed unexpected behavior. All samples exhibited some degree of polar behavior, with varying degrees of out-of-plane and in-plane components, but films with a large degree of L=1.5 peak splitting ($n = 3, 7, 8, 9, 10$)\textsuperscript{281} exhibited a transition from a polar to non-polar phase. These findings suggest that layering of ferroelectric parent material can suppress, rather than enhance, the ferroelectric moments in the superlattice (Figure 5-7 b).

5.3.2 Analysis of CaTiO$_3$/SrTiO$_3$ superlattice structure using HAADF and ABF-STEM

HR-STEM imaging was performed to confirm the cause of the peak splitting in XRD, as well to determine the role of structural distortions in the superlattice structure and their relation to a spontaneous polarization. Electron microscopy samples the of $n = 2, 3, 4, 5$ and 10 superlattices were made using manual sample preparation. Both wedge polishing and dimpling was used to make these samples, with similar results in sample quality. Samples were imaged in the aberration corrected FEI Titan running at 200 keV in STEM mode. HAADF images (Figure 5-8) revealed samples were of high quality with little to no stacking faults visible in the films. Interfacial intermixing due to a deviation from ideal shutter times was roughly determined by measuring A-
site cation intensities shown in Figure 5-8 c-f. As Sr has a higher Z number, it appears brighter in the HAADF image, Ca will be darker, while A-site row constituting the interface potentially having mixed cations have an intensity between the two. The $n = 2 \& 3$ samples showed signs of intermixing, while the $n = 4 \& 5$ sample exhibited much sharper interfaces, confirming that the layer mismatch $\Delta$ observed by splitting of the XRD peaks led to interface mixing. Figure 5-9 reveals atomic resolution EDXS imaging was performed for the $n = 3$ sample exhibiting a large degree of intermixing.
Figure 5-8: HAADF STEM of CaTiO₃/SrTiO₃ superlattices. Cross-sectional STEM of the $n = 2$ and $5$ superlattices is shown in (a, b). The highest intensity spots correspond to Sr atoms. Ca and Ti are similar in brightness. Intensity profiles over the A-site cation columns are taken on magnified images of the $n = 2-5$, indicated by the dashed red line. While the $n=2$ and $n=3$ superlattices revealed pronounced mixing of the A-site layers at the interfaces, the profile across the interface was much more abrupt for $n=4$ and $n=5$ superlattices. Reproduced from reference (281).
Structural mapping of atomic displacements and distortions were carried out to determine how the structure of the constituent materials in the superlattices differed from their bulk counterparts, and how distortions coupled between the two materials across the CaTiO$_3$/SrTiO$_3$ interface. The HAADF images for the $n = 3$, 5 and 10 superlattices are shown in Figure 5-10. As expected, there was no net displacement of the Ti atoms in the oxygen octahedra, supporting that the films were indeed nonpolar. The most notable feature in these superlattices was a coherent antiferrodistortive displacement of the Ca atoms perpendicular to the growth direction. For the $n = 10$ and $n = 5$ superlattice structure, these displacements were determined to be approximately 18 pm relative to the cubic positions. A proximity effect was observed near the interfaces where the two materials were in contact, in which, in which the Ca displacements were slightly suppressed, while they were induced in Sr. For the case of $n = 3$, the A-site displacements approached the bulk value in CaTiO$_3$ only for the central monolayer. Additionally, they were never entirely suppressed in the SrTiO$_3$ and the CaTiO$_3$ antiferrodistortive moment remained coupled through the SrTiO$_3$.

Figure 5-9: Interfacial mixing of $n = 3$ CaTiO$_3$/SrTiO$_3$ superlattice. Atomic resolution EDXS of (a) Ti, (b) Ca, (c) Sr revealed the layered structure of the superlattices. Purple arrows in the compiled map (d) shows a sizeable interfacial mixing of the CaO and SrO layers. Reproduced from reference (281).
layer, forcing the A-displacement pattern to remain continuous throughout the observed area of the film.

Oxygen octahedral rotations were extracted using annular bright field microscopy. Oxygen resolution imaging was only obtained for $n = 3$ and $n = 10$ superlattice, shown in Figure 5-11, as noise from the ABF detector prevented further imaging for the $n = 5$ superlattice. As seen for the cation distortions, the oxygen octahedral rotations were suppressed in CaTiO$_3$ and induced into

**Figure 5-10: Cation antiferrodistortive measurements across interfaces.** (a) Atomic structure of CaTiO$_3$ and SrTiO$_3$ overlayed on $n = 10$ HAADF image. (b) Schematic of an enlarged unit cell shows coherent displacement of the A-sites (yellow). These displacements are extracted from the HAADF-STEM images and plotted as a function of layer position for the (c) $n=10$, (d) $n=5$, an (e) $n=3$ CaTiO$_3$/SrTiO$_3$ superlattice.

Oxygen octahedral rotations were extracted using annular bright field microscopy. Oxygen resolution imaging was only obtained for $n = 3$ and $n = 10$ superlattice, shown in Figure 5-11, as noise from the ABF detector prevented further imaging for the $n = 5$ superlattice. As seen for the cation distortions, the oxygen octahedral rotations were suppressed in CaTiO$_3$ and induced into
SrTiO$_3$ near the interface. The rotational displacements of the CaTiO$_3$ layers were decoupled in the $n = 10$ superlattice, the SrTiO$_3$ thickness was too large. In contrast, for the $n = 3$ superlattice the octahedral rotation pattern propagated throughout the entire superlattice structure and was also present in the SrTiO$_3$ layers. Interestingly, the rotations are much smaller compared to the value seen in CaTiO$_3$ films grown on LSAT, reaching only 2° compared to 10° that was seen for films grown on LSAT and NdGaO$_3$. One possibility for this is that the rotations have been suppressed due to the superlattice layering scheme, although suppressed rotations are predicted to enhance the ferroelectric moment$^{49}$, rather than remove it as it was seen experimentally in the CaTiO$_3$/SrTiO$_3$ superlattices.

A more likely scenario is that the phase of CaTiO$_3$ stabilized in the superlattices is different from the phase observed when grown as film on LSAT and NdGaO$_3$ substrates, in which an $I4/mmm$ phase was stabilized at room temperature. The structure of bulk CaTiO$_3$ exhibits antiferrodistortive motion of the A-site perpendicular to the direction of the in-phase rotation, i.e. the (+)-axis. In this case, the (+) axis must be oriented out of plane and therefore cannot be viewed in cross-section. It is likely that the superlattice film is therefore $a^-a^+c^+$ or if the rotations are indeed suppressed in the plane of the film, $a^-d^+c^+$, and small measured tilting of the oxygen octahedra could be an artifact due to the overlap of the Ca atom in the HAADF image, leading to the $Pbnm$ phase. The calculated strain-phase diagrams from Biegalski et. al.$^{49}$ suggests that these polar phase cannot be stabilized in $Pbnm$ CaTiO$_3$ for tensile strains below 1.5%, beyond the 1.1% achieved in this experiment, and may explain the absence of ferroelectricity in some of the superlattices. However, the inconsistency in the interfacial mixing of the superlattices and the experimental results prevents drawing any definitive conclusions.
The discrepancy in the symmetry between CaTiO$_3$ observed in this work and observed previously on LSAT$^{49}$ can be explained through steric arguments in order to minimize the free energy of the film. In the $I4/mmm$ phase for CaTiO$_3$ on LSAT, the antiferrodistortive mode will be perpendicular to the interface, forcing the Ca atoms into the high symmetry position of the cubic substrate, creating a large interfacial energy and requiring large relaxation lengths to compensate. This is seen as distortions propagating 3 unit cells into both the film and the substrate$^{49}$.
Conversely, in the superlattices the AFD mode is parallel to the interface in more energetically favorable configuration, and the relaxation occurs over a single monolayer. This lowering of the interfacial energy is critical in superlattices, and stabilizes the \textit{Pbnm} phase over the \textit{I4/mmm}, explaining the lack of ferroelectricity in some of the superlattices.

The polarization that was observe in some of the superlattices could be attributed to intermixing of the CaTiO$_3$ and SrTiO$_3$ layers. Previous reports have shown doping of SrTiO$_3$ with CaTiO$_3$ leads to the formation of a polar nanoregions$^{284-286}$. SHG intensity is seen primarily in samples that have non-integer periodicities, seen from the split XRD peaks. This would lead to incomplete layer formation after each block of the superlattice, causing substantial interfacial mixing and a polar Sr$_{1-x}$Ca$_x$TiO$_3$ phase, while films with sharp interface exhibit no polarization.

5.4 Concluding remarks

Compressively strained CaTiO$_3$ exhibited ferroelectric behavior well exceeding what was predicted through DFT calculations, while superlattices of strained ferroelectric SrTiO$_3$ and CaTiO$_3$ exhibited a greatly reduced ferroelectric moment. In each of these cases the symmetry of the film, and how it can be manipulated through strain and layering techniques was critically important in understanding the measured ferroelectric properties. Further study on these materials is required for fully understand the behavior of ferroelectric responses of strained films, and how they are affected by strain and interface effects, such as octahedral rotations. The effect of interfacial mixing of the superlattices must be decoupled from the measured polarization, and ideally CaTiO$_3$ should be stabilized in the \textit{I4/mmm} state, perhaps through synthesis of the superlattices on different substrates and strain states, or by replacing the SrTiO$_3$ with an orthorhombically distorted material. Despite the advancements in electron microscopy and
synchrotron diffraction, these measurements are experimentally nontrivial, and cooperating between theory and experiments is crucial to advance this field.
Chapter 6. Growth and characterization of the rare-earth vanadates

This chapter describes the growth and characterization of LaVO$_3$, YVO$_3$ and (LaVO$_3$)$_n$(YVO$_3$)$_n$ superlattices. A brief introduction leads into (1) growth and room temperature characterization of LaVO$_3$, followed by (2) low temperature characterization of unusual phase ordering of these films using synchrotron diffraction and HR-STEM. The next section covers (3) growth of YVO$_3$ thin films, and (4) coupling of these two materials into a series of superlattices, and the preliminary structural results.

6.1 Introduction to the rare earth vanadates and film structure

The materials by design strategy has generally taken root in many fields of materials research, but has been in particular powerful in the class of transition metal oxide (TMO) ABO$_3$ perovskites$^{8,265,287,288}$. The complex coupling present in these materials links charge, spin, and orbital degrees of freedom with the crystalline framework surrounding the transition metal ion$^{289,290}$. Small perturbations to their atomic structure can lead to drastic changes in the macroscopic material properties and has been used to drive or suppress electronic phase transitions between a metallic and insulating ground state$^{291}$, to induce ferroelectricity$^{49}$, and to manipulate magnetic transitions$^{292}$ in perovskite thin films.

Perhaps the most common and most well developed method to alter the structure is by subjecting the material to mechanical stress by growing them epitaxially on a lattice mismatch substrate. This type of biaxial strain inherently drives a tetragonal distortion into the material, and
has been shown not only to enhance\textsuperscript{41}, but even induce a polar moment in the materials\textsuperscript{40,49}. However, the magnetic and electronic properties of these materials are closely tied to the hybridization of the oxygen 2\textit{p} and the \textit{d}-orbitals of transition metal elements occupying the B-site, thus the degree of oxygen octahedral rotations and with it the tilting pattern of the BO\textsubscript{6} octahedra must be considered. Determining how strain affects octahedral rotations is still not fully understood for all chemistries present in perovskite films, primarily as these distortions are difficult to quantify requiring sophisticated synchrotron diffraction\textsuperscript{293,294} or aberration corrected electron microscopy methods\textsuperscript{295}. Even in perovskite systems with simple electronic configuration, such as CaTiO\textsubscript{3} where \textit{d}-orbitals are not occupied, further complexities such as continuation of oxygen octahedral pattern across interfaces of layers with different tilt systems need to be considered as well as the substrate can drive or suppress octahedral rotations in close proximity to the interface.

One of the most often overlooked factors in thin films growth is the orientation of the oxygen octahedral rotational pattern of the film relative to the substrate. In the general case epitaxial strain will impose a biaxial strain in the in-plane direction, which couples to a uniaxial out-of-plane response of opposite sign, informed by the Poisson ratio. In cubic perovskites, which lack octahedral rotations it can be safely assumed the film will orient in such a manner to minimize epitaxial strain energy, though even these simple systems can lead to novel phase formations\textsuperscript{268}. In contrast perovskite systems with lower symmetry due to the presence of octahedral rotations, predicting the film’s epitaxial relationship with the substrate can become quite difficult, as it is energetically preferred to maintain oxygen octahedral connectivity across interfaces. Disrupting oxygen connectivity gives rise to a large energy penalty from breaking of the oxygen bonds across
the interface, and it is for this reason generally assumed the film will follow the substrate’s symmetry. However, in numerous $Pbnm$ perovskites there is a non-negligible discrepancy in the pseudocubic lattice parameters and minimization of strain energy in the film requires that the axis with the largest lattice parameter mismatch to the in-plane lattice parameter of the substrate is oriented out of the plane. The balance between the two energy contributions, namely strain energy and interface energy from (dis)continuity of the oxygen octahedra is still in its infancy.

To study these effects in more detail we have chosen the rare-earth perovskite LaVO$_3$ and YVO$_3$ (Figure 6-1). Both materials exhibit the GdFeO$_3$ $Pbnm$ structure, with the $a\,a\,c^+$ Glazer oxygen octahedral rotation pattern at room temperature. Crystal field splitting separates the vanadium $3d$ band into the empty $e_g$ and doubly occupied $t_{2g}$ bands, which is further split by the orthorhombic distortion to the lower lying $t_{2g}$ $d_{xy}$ level and two energetically degenerate $d_{xz}$ and $d_{yz}$ levels$^{32}$. The strong on-site Coulomb repulsion of the B-site leads to the formation of a Mott gap, separating the fully occupied lower Hubbard band (LHB) from the unoccupied upper Hubbard band (UHB). Despite the fact that vanadium assumes the $3+$ valence state, leaving two electrons in the $3d$ orbitals, an insulating state with an optical band gap of 1.1 eV is found at room temperature$^{291}$. Upon cooling below 140K, LaVO$_3$ undergoes an orthorhombic to monoclinic transition due to a tilting of the orthorhombic ($+$) axis, coupled with a Jahn-Teller distortion leading to an elongation of VO$_6$ octahedra$^{296}$. This distortion slightly lifts the degeneracy of the higher lying $t_{2g}$ orbitals, energetically preferring an alternating occupation of the $d_{xz}$ $t_{2g}$ and $d_{yz}$ $t_{2g}$ orbitals in a G-type orbitally ordered fashion. At approximately the same temperature, it undergoes a magnetic phase transition from the high temperature paramagnetic state to a C-type antiferromagnetically ordered state, which is explained by the Goodenough-Kanamori rules.$^{296,297}$
In YVO₃, these two transitions are further apart in temperature. Here, the structural phase transition and concomitant orbital ordering occurs at $T_{oo} = 200$K, while the paramagnetic to C-type antiferromagnetic order transition takes places at $T_{N} = 118$K. In addition a low-temperature orbital and magnetic transition occurs at $\sim 70$ K$^{298,299}$ in which the orbital and spin order switch types. Below this temperature C-type orbital order coexists with a G-type Antiferromagnetic order, indicating a strong coupling between the spin and orbital degree of freedom. The strength and type of these spin and orbital orders are closely tied to the degree of the oxygen octahedral rotations and is much stronger in YVO₃ due to the larger rotation angles compared to LaVO₃ being nearly cubic. Recent theoretical studies on LaVO₃ have predicted that a large enough compressive strain will drive the $d_{xy}$ orbital above the $d_{xz}$ and $d_{yz}$ and stabilize an A type spin ordered state$^{32,206}$. 
6.2 Effect of strain, octahedral rotations, and temperature on LaVO$_3$ thin films

In this section, the effects of substrate symmetry on films of orthorhombic LaVO$_3$ on substrates of NdGaO$_3$(001), NdGaO$_3$(110), and LSAT is discussed, as well as on SrTiO$_3$, DyScO$_3$ and GdScO$_3$ to study how strain can influence these transitions. In particular, we observed that the (+) axis of LaVO$_3$ remains in the plane of the film irrespective of the octahedral rotation pattern.
of the NdGaO$_3$ substrate. We employed synchrotron XRD diffraction to determine the precise symmetry of the films on the substrate, as well as high resolution STEM images to comprehensively probe the atomic crystal structure on a unit cell level across the substrate film interface. Density function theory is used to develop a general method to determine a mechanism for the reconstruction.

6.2.1 Growth of LaVO$_3$ thin films by hMBE

Films of LaVO$_3$ were grown using the hMBE technique. The La was supplied via a high temperature effusion cell in elemental form, while vanadium was supplied via a metalorganic precursor vanadium triisopropoxide (VTIP). The chamber was kept at base pressures below 5x10$^{-8}$ Torr to suppress the formation of the unwanted LaVO$_4$ phase. Therefore, oxygen was supplied entirely by the metalorganic precursor or scavenged from the substrate to avoid formation of secondary LaVO$_4$ phase and to ensure a single phase LaVO$_3$ film$^{300}$. A series of films on LSAT was grown to determine the growth window bounds, shown in Figure 6-2. Stoichiometric films showed either sharp RHEED diffraction patterns or crisp streaks. La-rich films exhibited streaky RHEED images that transitioned to a more 3D-like diffraction pattern along with increased intensity in the background from diffuse scattering, while for films grown under V-rich conditions films 2$^{nd}$ phases could be identified in RHEED. Contrary to previous results$^{139}$, films grown outside of the window exhibited a small lattice expansion from the stoichiometric value of 3.988 Å $\pm$ 0.001 Å$^{301}$. This is in contrast to previous thin film studies of LaVO$_3$ grown on SrTiO$_3$ and LSAT in which the lattice parameter expanded with nonstoichiometry$^{232,302}$, but is in agreement with some bulk studies$^{303}$, as well as similar to the lattice expansion observed in SrVO$_3$$^{95}$, SrTiO$_3$$^{130}$, and CaTiO$_3$$^{267}$ thin films grown by hMBE. This may be due to different defect
formation depending on the oxygen partial pressure in the chamber affecting the lattice parameter differently. The synthesis of phase pure perovskite films was extremely sensitive to the film surface, and required epitaxial stabilization to prevent over-oxidation, similar to other oxygen sensitive perovskite films grown via hMBE\textsuperscript{304}. Any surface defects such as scratches or contaminates was found to favor the nucleation of LaVO\textsubscript{4}, which then grew laterally through the film with growth time, leading to micron scale LaVO\textsubscript{4} intergrowths, identified as either circular spots or long, scratch-like features on the surface\textsuperscript{300}. Films grown under V-rich condition also exhibited these features, as the oxygen was supplied primarily through VTIP. Interestingly, LaVO\textsubscript{3} films grown on SrTiO\textsubscript{3} substrate never exhibited these intergrowth phenomena. Previous reports have shown that SrTiO\textsubscript{3} behaves as an “oxygen-sink”, scavenging oxygen from the growing film and thus aiding in the reduction of thin films that are sensitive to over-oxygen pressures such as in the case of Brownmillerite phases\textsuperscript{305,306}. Annealing at the growth temperature in forming gas allowed to convert these intergrowths back to the perovskite structure, although the epitaxial relationship between the film and substrate in this area has not been explored.

Films were grown on the previously mentioned substrates (Figure 6-3). XRD patterns exhibited an approximately linear trend of the out of plane film lattice parameter with strain. While for increasing tensile strain the out of plane lattice parameter decreased it increased with increasing compressive strain. Kiessig fringes were observed for all films with sharp RHEED patterns.
Figure 6-2: Growth of LaVO$_3$ on LSAT. (a) The out-of-plane lattice parameter of LaVO$_3$ films as a function of VTIP pressure used for the growth. The stoichiometric growth window was found to be smaller than that of SrTiO$_3$, in agreement with previous literature, and difficult to determine purely from XRD measurements. (b) Compiled XRD plots of the LaVO$_3$ films reveal only a small change in lattice constant between stoichiometric and nonstoichiometric films. (c) RHEED images taken after LaVO$_3$ were used to confirm the growth window, and appear to be a more sensitive probe of stoichiometry in this case.
6.2.2 Structural analysis of substrate symmetry effects on compressively strained LaVO₃

LaVO₃ films grown on NdGaO₃ (001), NdGaO₃(110), and LSAT substrates were characterized using synchrotron radiation at the Cornell High Energy Synchrotron Source (CHESS) to determine the film symmetry, in conjunction with electron microscopy and lab source X-ray diffraction (Figure 6-4). Samples grown on SrTiO₃ had been characterized in a previous

Figure 6-3: Strain series of LaVO₃. Films of LaVO₃ were grown on various perovskite oxide substrates with varying lattice parameter and octahedral orientations. (a) ON-axis XRD scans revealing pronounced Kiessig fringes for all films as well as streaky RHEED with no second phase, indicating an excellent film quality. (c) The substrate in-plane lattice parameter lattice determined from XRD with respect to the psuedocubic in-plane lattice constant. The linear relation indicates no relaxation of the films occurred.
Both bulk LaVO₃ and NdGaO₃ exhibit the a–c⁺ oxygen octahedral rotation pattern in Glazer notation. Critically, the presence of peaks in ½ (e o o), ½ (o e o), or ½ (e o o) family would indicate that the (+) axis was in the even (e) direction. All films regardless of substrate symmetry revealed that the (+) axis was in the film plane. This is remarkable, because for LaVO₃ grown on NdGaO₃ (001) the orientation of the (+)-axis must rotate from out-of-plane (substrate) to in-plane.

![LaVO₃ film orientation on varying substrate symmetry](image)

**Figure 6-4: LaVO₃ film orientation on varying substrate symmetry.** (a) The synchrotron diffraction patterns of the half order peaks of LaVO₃ on NdGaO₃ (001) indicate that despite the substrate mismatch, LaVO₃ will orient (110) in compressive strain. (b) Cross-sectional STEM microscopy as well as (c) RSM maps are given for both LaVO₃ films on NdGaO₃ (001) and (110). Both films are coherently strained with few visible stacking faults.

Electron microscopy was used to further understand this phenomenon. The images were acquired using an FEI Titan³ G2 double-aberration corrected microscope operating at 200kV. The extracted lattice distortion along each zone axis, and how these distortions are unique to a specific symmetry are summarized in Figure 6-5. While previous studies have shown that it is possible to determine the symmetry of a material based solely on imaging along a single zone axis, this
required multiple STEM simulations, as well as high-resolution images in which overlapping oxygen atomic columns can be fit with a high level of accuracy\textsuperscript{295,309}. In order to circumvent the complexity of such an approach, LaVO\textsubscript{3} films on NdGaO\textsubscript{3}(001) samples were imaged in HAADF-STEM along the 100\textsubscript{p}, 210\textsubscript{p}, and 110\textsubscript{p} zone axes. Small structural distortions were extracted from the atomic positions and compiled to determine the orientation of the (+)-axis with atomic resolution. For the 100\textsubscript{p} zone axis, an antiferrodistortive displacement of the A-sites was extracted from HAADF-STEM from both the substrate and the film. In the substrate, a horizontal displacement, i.e. within the film plane was found to alternate in opposite in-plane direction perpendicular to the zone axis for adjacent AO planes. This indicated that the (+)-axis is oriented perpendicular to the film plane, i.e. aligned along the 001\textsubscript{p} orientation, as expected for the substrate. Within the LaVO\textsubscript{3} film however the antiferrodistortive displacement of the A-site showed vertical displacements that alternated for AO planes adjacent along an in-plane direction, suggesting a 90° rotation of the (+) axis for the film with respect to the substrate. A similar observation is found when analyzing ABF-STEM images taken along the <110>\textsubscript{p} zone axis. A pronounced rotation of the oxygen octahedra is found in for NdGaO\textsubscript{3} substrate, which is absent in the film due to the overlap of the projected oxygen. The most obvious example of the change in orientation between the film and substrate however is when viewed along the <210>\textsubscript{p} zone. The NdGaO\textsubscript{3} substrate has evenly spaced A-site atoms within the plane which is expected for the case of the (+) axis remaining out of the plane of the film. In the bulk of the LaVO\textsubscript{3} film, due to the projection of the A-sites they appear to form dimer pairs that are clearly visible by eye in the HAADF image. This configuration is only possible for the case where the + axis of oxygen octahedral rotates from the out of plane direction in the substrate, to the in-plane direction in the film. It should be noted that
these are not true dimer pairs, but only appear to be so as they are projected onto a 2 dimensional image, and their spacing is not directly relevant to any electronic properties, but is rather a very convenient and simple way to identify the in-phase axis from the HAADF image. A full map of the different views of the atomic structure along the 3 different zone axes, for the different orientations of the in-phase axis is given in Figure A-11.

It is along this zone axis that allows to identify a transition region of up to about 4 unit cells away (indicated by a yellow line) from the LaVO₃/NdGaO₃ interface (indicated by a green line) where the projected La atoms have not yet formed the dimer pairs. In fact, this transition layer can be seen in the plotted atomic displacements along all zones. The significance is that oxygen octahedral rotational pattern is disrupted between the film and substrate, suggesting that this region must have a metastable transitional state that is inherently different from both the parent materials. This transitional region is not seen for films grown on NdGaO₃ (110), and are therefore attributed to the different orientation of the (+)-axis in LaVO₃ film and NdGaO₃ (001) substrate. The combination of imaging the cross-section along the tree zone (axes) acquires a comprehensive picture of the film’s microstructure and epitaxial relationship, and shows the film transitions to an orientation other than that of the substrate.
It is assumed that the driving force behind the formation of this metastable state arises from Figure 6-5: Atomic distortions in LaVO₃ thin films. The green area indicates the substrate, while the blue is the film. The antiferrodistortive moment along the (100) zone is plotted in (a), the oxygen octahedral rotations tilt angle on the (110) zone in (b), and a La-La projected interplanar spacing is plotted in (c). The left of image series contains a small diagram of the measured atomic distortion, as well as the direction of the in phase (+) and out-of-phase (-) octahedral tilting in the substrate (bottom) and film (top). In all plots, there is an approximately 4-unit cell thick transient region in which the film rotates from (001) to (110).
the competition between strain energy and maintaining oxygen octahedral connectivity. In LaVO₃, the shortest pseudocubic axis is along the (+)-axis, i.e. the direction along with the rotation of neighboring oxygen octahedra are in phase. When grown epitaxially on NdGaO₃ which imposes a compressive strain the shortest axis is energetically favored to be in the film plane. However, if the (+) axis is in the film plane and therefore perpendicular to the (+) axis direction in the substrate the octahedral connectivity is discontinued, which either requires to elongate bond lengths or even break bonds, both increasing the total energy. To gain further insight into this nontrivial configuration at the NdGaO₃(001)/LaVO₃(110) epitaxial system, we collaborated with Prof. James Rondinelli’s group. Density functional theory calculations performed in his group revealed that the (+)-axis can be reoriented from the out-of-plane direction of the substrate to the in-plane direction in the film and maintaining corner connectivity of the oxygen octahedron simply by displacing two out of the four oxygens per unit cell along the [210] direction.

These theoretical predictions were confirmed experimentally from plan view STEM images, as well as further imaging along the [210]p zone, shown in Figure 6-6. Stripes oriented along the [210]p with an average stripe separation of ~2 nm were observed in the plan view samples. Cross sectional imaging of these stripes revealed that they formed at the layer at the interface between the film and substrate and propagating into the film. These stripes arise from the strain gradients arising from octahedral displacements across the interface to accommodate the two different strain gradients. Unfortunately, the atoms along the <210>ₚ appear closely spaced in projection, making imaging of oxygens impossible along this zone, and the distortion must be inferred from the DFT calculations.
The analysis of the epitaxial relationship identifies a new strategy to stabilize an otherwise energetically unfavorable structural configuration. While previous studies have shown that it is possible to suppress or induce specific symmetry elements in a thin film by use of a substrate with specific orientation to impart a specific oxygen octahedral rotation pattern, this work demonstrates that new configuration can be stabilized in the proximity of interface and potentially new properties can emerge and can be spatially confined even between two materials with the exact same symmetry. The driving mechanism is a competition between strain energy through epitaxial mismatch and reorientation of the octahedral rotation pattern without disrupting the corner connectivity. The rotation forces the oxygen octahedra at the interface to adopt a transient symmetry element and distorts to maintain connectivity. This route offers a new and generally

**Figure 6-6: Striped phases on LaVO$_3$ thin films** (a) Plan view STEM images of the LaVO$_3$ film on NdGaO$_3$ revealing the striped structure along the [210] zone highlighted by the black arrows with an average stripe separation of $1.85\pm0.15$nm. The direction and spacing is confirmed from the FFT image shown in (b). Cross-sectional HAADF (a) and ABF (b) STEM images taken along $<210>$, reveal periodic distortions at the interface and into the first 4 monolayers.
applicable method for manipulation the atomic structure of epitaxial complex oxide thin films and thereby tuning of properties in a widely applicable manner, offering new materials design opportunities for complex oxides exhibiting ferroelectric, magnetic, or multiferroic order or to refine electronic properties in strongly correlated electron systems.

6.3 Low temperature phenomena in strained LaVO₃ thin films

The electron-electron and electron-phonon interactions present in perovskite oxides are responsible for a great many of their desirable properties. Further, the relatively simplistic structure of the perovskites allows for straightforward manipulation of the structure to tune these properties. While small changes in the structure give rise to dramatic changes in the physical properties it is critical to deduce such structural distortions with very high precisions. This becomes even more challenging if the slight distortions are further modulated by epitaxial strain. In order to ensure that the film is coherently strained film thicknesses have to be kept to below the critical film thickness. The volume of the single crystalline thin film available to be probed by XRD is therefore very limited requiring sophisticated XRD apparatus with brilliant light sources and the ability to monitor a large reciprocal space to be able to access all relevant film XRD film reflections. These measurements become all the more crucial as many of these phase transitions are accompanied by a structural transition as well. Characterization of low temperature phases with a high degree of precision will be crucial in advancing the understanding of structure-property relationship for these phases and to develop a more comprehensive understanding.

The two most common ways to probe structure in thin films is through XRD and TEM/STEM. High temperature characterization can be achieved with relative simplicity using ohmic heating, which is compatible both at atmospheric pressure and in vacuum using heaters that
can be made compact to work with almost any sample size and experimental setup\textsuperscript{310,311}. Combining cryogenic cooling is technically more complicated and typically achieved via helium compression or directly cooling the sample being in thermal contact with a cryogenic liquid such as helium or nitrogen. In both cases, excess noise is introduced to the experiment through compressors or boiling of the cryogenic liquid, and samples must be thermally insulated against the rest of the experimental setup to prevent condensation of water from the atmosphere on the cold surfaces and minimize thermal load experienced by the coolers. The following section describes the low temperature structural behavior of films of LaVO\textsubscript{3} on NdGaO\textsubscript{3} (001) and LSAT (001) substrates, recorded using synchrotron diffraction and STEM microscopy.

While determining basic structural parameters such as lattice constants, epitaxial orientation, and strain can routinely be characterized via XRD, quantitative determination of the symmetry and atomic positions within the unit cell is a nontrivial process for perovskite oxide thin films. This is because these small distortions give rise to so-called half order peaks, or peaks that are symmetry forbidden in a cubic system, but appear in pseudocubic systems due to small distortions of the a-site cation or octahedral rotations\textsuperscript{12}. The intensity of the scattered x-rays from these peaks can then be used to determine the structural distortions\textsuperscript{13}. These peaks can be measured in a straightforward manner in powder or bulk crystal systems. However, in thin films, many of these peaks are not accessible due the substrate restricting both the incident and exit x-ray paths, as well as the small scattering volume of the film prevents many of the peaks from being viewed on a conventional lab source diffractometer.

Recent work in this area has shown that it is possible to refine these films for the rhombohedral\textsuperscript{312} and orthorhombic\textsuperscript{308} class of perovskite oxides, and in theory can be expanded
other perovskite symmetries. In this method, a high-brightness synchrotron source is used to compensate for the low scattering intensity of the half-order thin film diffraction peaks. In addition, rather than measuring all peaks, only a select few are measured which are most sensitive to changes of both a-site displacements and rotations. In ideal cases, as few as 7 half-order peaks are required to accurately determine these structural distortions. This process was applied to study films of LaVO$_3$ across the structural transition at 140 K.

Synchrotron diffraction experiments were performed at Cornell High Energy Synchrotron Source (CHESS). An energy of 19.37 keV (0.64 Å) was used to avoid absorption edges from either the LaVO$_3$ film, or NdGaO$_3$ and LSAT substrates. The film was mounted to a 4-circle goniometer, with a cryostat capable of operating reliably from room temperature to 10 K. Temperature was monitored via a silicon diode mounted in the copper sample stage. The sample was kept under vacuum using an aluminum tube with kapton tape windows, as well as an inner cryo-shroud to prevent ambient radiation from heating the sample. Later experiments used a polycarbonate dome that allowed for full 180° access to the film, but was not compatible with the inner shroud, making temperature measurements unreliable, and also led to a slightly higher background signal. Films were cooled from room temperature down to approximately 25 K and a series of scans was taken at each temperature to determine both changes in lattice constant octahedral rotations, particularly in the vicinity of orbital and magnetic ordering transition at 140 K. This was performed by fitting of $\frac{1}{2}$ order peaks intensities in the method described in Ref. (294).

The rotation angles alpha and gamma as well as the displacement of the A-site cations $d1$ and $d2$ as a function of temperature are summarized for LaVO$_3$ films on NdGaO$_3$ (001) in Table 6-1. Notably, there was a small decrease in the alpha rotation, while the beta rotation increased ($\alpha_{\text{film}} = \ldots$)
7.4° and \( \beta_{\text{film}} = 11.8° \) due to epitaxial strain when compared with the bulk values obtained from \textit{Bordet et. Al.} (\( \alpha_{\text{bulk}} = 8.7° \) and \( \beta_{\text{bulk}} = 7.9° \))\textsuperscript{296}. Further details of this experimental analysis can be found in Appendix A.5.

\textbf{Table 6-1: Structural changes of LaVO\textsubscript{3} as a function of temperature.} \textit{Alpha} and \textit{gamma} refer to the in-plane and out-of-plane rotations, respectively, while \( d1 \) and \( d2 \) are La displacements in the unit cell.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Alpha (°)</th>
<th>Gamma (°)</th>
<th>d1 (pm)</th>
<th>d2 (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>5.3</td>
<td>-</td>
<td>2.1</td>
<td>7.0</td>
</tr>
<tr>
<td>150</td>
<td>4.2</td>
<td>6.6</td>
<td>3.2</td>
<td>5.0</td>
</tr>
<tr>
<td>175</td>
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<td>7.1</td>
<td>3.1</td>
<td>4.6</td>
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<tr>
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<td>6.4</td>
<td>10.1</td>
<td>2.8</td>
<td>4.6</td>
</tr>
<tr>
<td>225</td>
<td>7.4</td>
<td>11.8</td>
<td>2.4</td>
<td>4.4</td>
</tr>
</tbody>
</table>

In this experiment, the alpha peak was fit using the \((0.5 -1 -1.5)p\), gamma was fit using the \((2.5 -0.5 2.5)p\) and \((0.5 -2.5 2.5)p\), \( d1 \) was fit using (-1 0.5 3)p, and \( d2 \) was fit using the 0.5 0.5 0.5 peak. Cooling the samples from room temperature was accompanied by a continuous decrease of the oxygen octahedral rotation angles until the phase transition temperature of ~145K. Over this transitional region, the thermal expansion coefficient of LaVO\textsubscript{3} and NdGaO\textsubscript{3} are similar (\( \alpha_{\text{LVO}} = 1.4\times10^{-5}\text{K}^{-1} \) and \( \alpha_{\text{NGO}} = 8.7\times10^{-6}\text{K}^{-1} \)) and only a negligible amount of strain is accumulated from thermal mismatch. Upon further reducing the temperature the octahedral rotations slightly increased. It should be noted that the unusual orientation of the film on the substrate, as well as the twin domains formed in the film made the peak fitting below the phase transition somewhat unreliable. While a peak may decrease in intensity for one domain type, it may not be affected or even increase in another domain type. This convolutes the fitted peak intensities. The fitting methodology can become more robust to domain by measuring multiple different peaks to fit a
single distortion type. However, many of these additional peaks are inaccessible in x-ray with the + axis of the film in the plane of the substrate. Further study on single-domain films, preferably with the c-axis oriented out-of-plane, is required for a more precise fitting.

In addition to the change in octahedral rotation an unexpected feature occurred upon cooling, namely the appearance of satellite peaks off the primary diffraction spot, as shown in Figure 6-8. or LaVO$_3$ on NdGaO$_3$ (001) a single pair of satellite peaks appeared indicating the formation a stripe pattern elongated along the pseudocubic (110) zone axis in the film plane with an average stripe width of about 22 nm, approximately equal to the film thickness, all propagating along the $\langle 1\ 1\ 0 \rangle$ direction. Higher order satellite peaks could be seen on the (004) RSM, which indicate that the striped domains have sharp boundaries corresponding to a more square, rather than a sinusoidal modulation pattern in the LaVO$_3$ film$^{313}$. LaVO$_3$ films on LSAT showed similar satellite peaks in the RSM in a 4-fold pattern along both the $\langle 1\ 1\ 0 \rangle$ and $\langle 1\ 1\ \bar{1}\ 0 \rangle$, as well as diffuse peaks with lower intensity. This pattern is expected for either 2 sets of striped domains, or a checkerboard pattern. As LSAT is cubic, it is expected that there would be no preferential

![Figure 6-7: Structural distortions in LaVO$_3$ characterized by synchrotron diffraction](image)

(a) The pseudocubic unit cell of LaVO$_3$ is shown, with the octahedral rotation angles alpha ($\alpha$), beta ($\beta$), and gamma ($\gamma$). (b) Distortions of the La cite of the centrosymmetric position, represented by the black dot, are shown as a combination of $d1$ and $d2$ displacements. Reproduced from Ref. (294).
orientation of the domains, while the orthorhombic NdGaO$_3$ structure breaks the 4-fold symmetry and stables a single orientation of stripe domains.

Cryogenic HAADF-STEM (CryoSTEM) images were taken in plan-view to analyze these domain structures for LaVO$_3$ on LSAT. Imaging was performed at the FEI Titan at Cornell through their PARADIM initiative, operating at 300 kV. Room temperature imaging of the sample

Figure 6-8: Reciprocal space maps of the LaVO$_3$ L=4 peak for films on NdGaO$_3$(001) and LSAT. At room temperature, a single peak is seen for both films on LSAT (a) and NdGaO$_3$. Upon cooling through the transition temperature satellite peaks appear with a 2-fold and four-fold symmetry for NdGaO$_3$ (001) (c), LSAT (001) (d), respectively.

Cryogenic HAADF-STEM (CryoSTEM) images were taken in plan-view to analyze these domain structures for LaVO$_3$ on LSAT. Imaging was performed at the FEI Titan at Cornell through their PARADIM initiative, operating at 300 kV. Room temperature imaging of the sample
revealed no stripe structure, although orthorhombic 90° rotational domains were prevalent throughout the film, one of which is highlighted in Figure 6-10 c. The sample was then cooled to liquid nitrogen temperatures using a Gatan double tilt cryo holder. Although a precise temperature measurement was not possible, it is expected the sample was in the vicinity of 80K, but definitely below the phase transition temperature. A faint striped structure emerged at these low temperatures that were barely visible in the HAADF, see Fig 6-8 a. The local stripe structure observed in HAADF-STEM confirmed a spatial separation between the areas with different orientation of the stripes, rather than a checkerboard like arrangement. FFT’s of the image revealed elongation of the peaks along the \(\langle 1\,1\,0\rangle\) direction, similar to the satellite peaks seen in the RSMs taken by XRD. These satellite peaks in the FFT taken from the microscopy images could not be resolved. To provide further evidence that the microscopy images contained stripes of only one orientation FFT was masked except for the masks of the \((110)\) and \((\overline{1}\overline{1}0)\) and their inverted images are shown in Figure 6-9 c to enhance the contrast of the stripes from the HAADF.

Atomic resolution strain maps were taken on a higher magnification images in Figure 6-10. These reveal that the same stripe formation is due to a phase coexistence of two monoclinic domains of apparent opposite in-plane lattice parameters. The bulk of the film appears to have lattice constants of \(a = 3.9\ \text{Å}\) and \(b = 4.0\ \text{Å}\). These are broken up into a striped arranged by 3-4 nm boundaries of \(\text{LaVO}_3\) where \(a = 4.0\ \text{Å}\) and \(b = 3.\ \text{Å}\). This two-phase coexistence is attributed to the overall minimization of strain energy to accommodate the different lattice parameters from the orthorhombic to monoclinic phase transition.
While the images shown in Figure 6-9 confirm the presence of a stripe structure the orientation of the (+) axis is not clear. This can, however, be extracted from HAADF-STEM image captured with a higher magnification by determining the angle formed between neighboring La atoms. Figure 6-10 shows a map of the La angle, where the antiferrodistortive pattern is tracked. Two clear domains are shown, indicated by the change in the direction of the antiferrodistortive direction by 90° from near-horizontal (left) to near vertical (right). Interestingly, in bulk, the transition from the orthorhombic to monoclinic phase is accompanied by a reduction of the (+) axis length. It was therefore expected that the orientation of the (+) axis is coupled to the in-plane lattice parameter of the film. Specifically if the length of the in-plane film lattice parameter is modulated it would affect the (+) axis orientation. Instead, the octahedral rotation pattern is decoupled from the strain. The stripes are oriented in the same direction from lower left to upper right corner irrespective of the (+) axis orientation. This means that large regions of the sample
exhibit a metastable phase solely stabilized by the interplay of octahedral rotation and strain, which has not been reported before in LaVO$_3$ where the (+) axis is longer than the in-plane (-) axis. This phase is predicted to potentially exhibit an A-type antiferromagnetic order$^{263}$, rather than the C or G type which is ordinarily seen in LaVO$_3$. While this non-equilibrium configuration is may affect the spin and orbital order, the type of order for both degrees of freedom as well as the spatial arrangement requires further study to fully comprehend how the magnetic and orbital coexist in this unusual state.

Figure 6-10: Strain and rotational domains in monoclinic LaVO$_3$. (a) Atomic resolution HAADF-STEM imaging of the LaVO$_3$ sample at 80 K, containing 90° rotational domain with the (+) axis in the plane, evidenced by the 2 different sets of $\frac{1}{2}$ order diffraction spots seen in (b,c) the selected area FFT taken from the red and blue area in (a), respectively. (d) Map of the La bond angle extracted from (a) giving rise to a blue red lines along the in-plane (-) axis, arising from the antiferrodistortive displacement of the La and the slight deviation from 90°. The (+) axis is along the ‘wiggle’, i.e. perpendicular to the blue-red stripes. The boundary between the two different orientation domains is shown by the black line. (e,f) Unit cell maps of the two in-plane lattice constants $a$ and $b$. Two distinct area with different lattice parameter in the same crystallographic direction emerge irrespective of the orientation domains.
YVO₃ and antiferromagnetic superlattices

In the family of rare earth vanadate perovskites, YVO₃ has the rare earth element Y³⁺ with almost the smallest ionic radius, in contrast to LaVO₃ where the largest rare earth ion La³⁺ occupies the A-site. Therefore, LaVO₃ has the largest lattice parameter and the lowest degree of octahedral rotations. The pseudocubic lattice constants are \( a_p = 3.927 \, \text{Å} \) and \( c_p = 3.925 \, \text{Å} \) \( (c_p/a_p \sim 1.00) \) making it nearly cubic⁵. YVO₃ on the other hand has a Goldschmidt factor much smaller than unity and is a highly distorted orthorhombic perovskite with much smaller lattice parameters of \( a_p = 3.844 \, \text{Å} \) and \( c_p = 3.775 \, \text{Å} \) \( (c_p/a_p = .982) \). In light of the rich phenomena found in strained LaVO₃ films, the solid solution of (La,Y)VO₃ will provide samples in which complex spin and orbital order formation is expected. Specifically, the large difference of the A-site cation can potentially favor a regular arrangement of La and Y ions, while the heterostructure growth of superlattice structures is possible as well. In both cases it is important to establish the condition under which high quality YVO₃ can be grown. It would be ideal if a self-regulated growth window would be accessible for YVO₃ as well which would allow to grow these vanadate superlattices with superior stoichiometric control.

6.4.1 Growth study of YVO₃ films by hybrid MBE

YVO₃ thin films were grown using a hMBE approach similar to LaVO₃, in which the Y cation was supplied using a high temperature effusion cell, and vanadium and oxygen was supplied through VTIP. The oxygen background pressure was kept as low as possible to prevent the formation of YVO₄ or other unintentional phases prone to form because V tries to assume the valence state 5+. Unlike LaVO₃, the growth of YVO₃ was particularly sensitive to the substrate. Films grown directly on LSAT exhibited 3D island growth, as observed by a spotty RHEED
pattern, which resulted in films with broad XRD peaks the absence of Kiessig fringes due to the surface roughness. The nucleation of YVO₃ growth on LaAlO₃ proved somewhat more successful, but substrate twins led to XRD scans that were not straight forward to interpret, impeding this as strategy to develop the lattice parameter as a measure of stoichiometry in the films. The highest quality YVO₃ films were found for growth on NdGaO₃ substrates. It is still unclear why the nucleation behavior of YVO₃ was inferior for LSAT, and somewhat acceptable on LaAlO₃ and NdGaO₃ substrates. It is however noticeable a non-polar interface is formed when grown on the ladder two substrates, preventing a high surface energy and thus a polar catastrophe in the ultrathin limit upon nucleation, which may play a decisive role.

A stoichiometric series of samples was grown on NdGaO₃(110) to determine the presence of a growth window, and how the YAlO₃ film would accommodate defects (Figure 6-11). Growing under vanadium rich conditions did not significantly affect the lattice parameter, as determined by XRD, but led to the formation of 2nd phase in the growth front, which were observed in RHEED and were also visible by AFM. Y-rich films showed more diffuse RHEED and a double-peak along the <100> and <110> zones, associated with 3D growth. XRD showed a broad peak occurring a larger scattering angles indicating a reduced film lattice parameter in the out-of-plane direction. The broad peak appeared like a convolution of two different lattice parameter, indicating the formation of twins in the film. The complexity of the strain relaxation mechanism present in the film made it hard to unambiguously determine the growth window for YVO₃. Relying on the rather qualitative measure of RHEED image quality a growth window was determined that was approximately 3-6 mTorr wide, ranging from gas inlet pressure pVTIP of 63 mTorr to 66 mTorr. For these growth conditions films show sharp, crisp electron diffraction...
patterns. XRD scans revealed two different peaks at $2\theta = 47.6^\circ$ and $2\theta = 48.2^\circ$ indicating the formation of twins with different out of plane lattice parameter. Kiessig fringes appeared for both sets of films, indicating each twin domain surface was atomically flat.

![Figure 6-11: YVO$_3$ Growth window. A stoichiometric series was grown for YVO$_3$ on NdGaO$_3$ (110) using a hMBE approach. Accompanying RHEED and XRD results are given. Nominally stoichiometric samples, as determined from RHEED, are indicated in green, while films grown under nominally Y-rich and V-rich conditions are shown in blue and red, respectively. The splitting of the YVO$_3$ film peak in XRD is apparent for films grown at VTIP pressures of less than 69 mTorr.]

AFM images shown in Figure 6-12 revealed striped domains on the surface of these films, with approximately 2 nm step heights and 20 nm between each domain. This could in part be due do a rotation of (+) axis of the film from in-plane to out-of-plane, as there is a 1.5% difference in pseudocubic lattice constant between these two orientations. However, the 2 nm corrugation on an ~25 nm thick film correlates to an 8% difference in height, and therefore there must be some as of yet unidentified complex frustration between epitaxial strain, lattice expansion, and octahedral orientation. The reciprocal space map on the 103 again reveals two different peaks, due to the two different domains on the film.
While the formation of the twin domains lead to some striking images and interesting spatial modulation of strain and octahedral rotation pattern, they impede a simple and straightforward characterization of the film’s stoichiometry using the lattice parameter expansion. While YVO$_3$ films nucleate well on a LaVO$_3$ buffer layer, this further leads to an increasing complexity of the XRD data, as well as limit the film thickness studied as the substrate must be compatible with both LaVO$_3$ and YVO$_3$ lattice parameters. Fitting the two different peaks in XRD is nontrivial, as the peaks overlap and are further convoluted by fringes. The insulating nature of YVO$_3$ preclude the use of transport measurements. Further studies of the exact nature of these films is required, including analysis via synchrotron diffraction and STEM to characterization rotational tilt patterns, as well as finding a substrate that stabilizes YVO$_3$ in a single domain.

6.4.2 The growth of LaVO$_3$ and YVO$_3$ superlattices

Given the complex spatial arrangement of strain and orientation of the octahedral orientation pattern it is expected that metastable configuration are formed in which frustration between these two structural degrees of freedom impose boundary conditions that can give rise to non-equilibrium magnetic and orbital texture unattainable in bulk of thin films, making this an intriguing field of research. The (+) axis in the both orthorhombically distorted crystals is the axis that dictates the direction of the orbital and spin order. By growing these films on NdGaO$_3$ (001) that has a lattice parameter larger than YVO$_3$ and smaller than LaVO$_3$, epitaxial strain would favor that the LaVO$_3$ (+) axis is lying in the film plane, as was previously studied, and out-of-plane for the tensile strained YVO$_3$. This configuration, if assumed in the superlattice structure, can give rise to unusual orbital and spin order phenomena to ‘cope’ when transitioning between these two materials. Similar to recent results on the formation of superlattice. Further, as they both exhibit
disparate transition temperatures for spin, orbital, and structural order, it is of interest to determine if the lattice will exhibit two disparate transitions pertaining to each constituent material, or a single transition. In fact, counterpoising the different order in such a structure may give rise to long-range three-dimensionally ordered supercrystal configuration that can be activated by ultrafast optical excitation similar to previously reported for PbTiO$_3$/SrTiO$_3$ superlattice structures$^{315}$.

Figure 6-12: Surface morphology of YVO$_3$ films. AFM scans of the YVO$_3$ film stoichiometric series are shown above. Twin domains of approximately 20 nm are seen propagating in the (110) with height variations of 1-2 nm. The two separate twins can be seen in the RSM of the (103) split peak. This splitting may be due to two different orientations of YVO$_3$, or a stabilization of the monoclinic phase.

Growth of the vanadate superlattices was achieved using the standard $\hbar$MBE approach. Numerous challenges were faced in the growth of these superlattices, including calibration and maintaining sufficient flux stability of two high temperature cells. Relatively small growth
windows, lack of RHEED intensity oscillations during growth, and the complex XRD pattern of YVO₃ films making it hard to determine the physical film thickness to precisely calculate shuttering times. Further, the formation of the undesired overoxidized phase appeared more often for growth experiments for vanadate superlattices than previous growths of the constituent films, perhaps due to the increased thermal load on the cryopanel from the additional high temperature cell, which raised the oxygen background pressure in the chamber by a factor of 4-5. Because of these difficulties, and no foreseeable short terms solutions, the YVO₃ monolayer formation time was estimated by assuming it is equal to that of LaVO₃ calculated from XRD, namely 28.7 s for a rare earth ion flux of 2.5x10¹³ atoms/cm²/s supplied from the high temperature effusion cells. Recent upgrades of the hMBE computer control software allowed to adjust the VTIP foreline pressure in real-time during growth when switching between LaVO₃ and YVO₃ layers, precluding the need to find an overlapping growth window as it was necessary for the CaTiO₃/SrTiO₃ superlattices²⁸¹.

Superlattices of (LaVO₃)ₙ(YVO₃)ₙ, n = 3, 5 &10, were synthesized as described above. Fluxes of both La and Y were calibrated to 2.5x10¹³ atoms/cm²/s by QCM. The background pressure in the chamber was 2x10⁻⁷ Torr during growth. Each layer was deposited effectively using codeposition, with the respective rare-earth cation shutter and VTIP inlet open together during the layer deposition. The VTIP inlet pressure was set to 51 mTorr during LaVO₃ deposition and 60 mTorr during YVO₃. There was a 15 second pause between each monolayer where the mainshutter was closed to allow the VTIP inlet pressure and effusion cell flux to stabilize. The LaVO₃ was always deposited first to aid the nucleation of the superlattice on the substrate. It was observed that the Yttrium cell flux decreased by about 20% over the course of an entire growth
day, which was corrected for the $n = 3 \& 10$ superlattices by periodic adjustment of the yttrium effusion cell temperature. RHEED for the $n = 5$ (Figure 6-13 b) showed slightly diffuse RHEED, as well as the vertical double peaks and chevron like Kikuchi lines in the diffraction pattern, which could be due to excess vanadium from the decrease in the Y flux. The $n = 3 \& 10$ exhibited higher quality, more crisp RHEED pattern with elongated rods and peaks arranged in a circular fashion. After growth no 2nd phases were observed in RHEED. XRD scans (Figure 6-13 a) revealed the appearance of superlattice peaks for all samples. Kiessig fringes were present for the $n = 3 \& n=10$ superlattice samples. A slight shift in the primary superlattice peaks was noted for the $n = 5$, sample, attributed to nonstoichiometric growth conditions either due to an error in the shuttering times or drift of one or both rare earth fluxes. A large area reciprocal space map was taken for the

**Figure 6-13: Rare-earth vanadate superlattices.** XRD 2θ scans reveal superlattice peaks for the $n = 3, 5$ and 10 superlattices, as well as Kiessig fringes for the $n=3$ and 10 (a). RHEED patterns show streaks for the $n=3$ and 10, while the $n = 5$ is spotty (b). A large area RSM of the $n = 3$ sample is given in (c).
$n = 3$ sample, revealing the superlattice peaks are slightly offset from the substrate peaks, potentially from the presence of a slight monoclinic distortion in the superlattice at room temperature.

Figure 6-14 shows AFM scans on the $n = 3$ revealed unusual topology, with long stripes separating flat regions with atomic steps, and meandering depressions that appear to terminate with no particular relation to a crystallographic axis. The $n = 10$ exhibited 2 disparate terminations, in certain regions showing a corrugate surface, with atomic steps visible on the corrugations, and other areas with a crystalline 2nd phase similar to vanadium rich films. The $n = 5$ film revealed a

![Figure 6-14: Surface morphology of vanadate superlattices.](image)

Atomic force microscopy scans of the (a,b) $n = 3$ superlattice with different scan sizes, showing atomically smooth terraced surface, as well as larger area twin structure. The $n = 5$ sample (c) shows a much rougher surface, while the $n = 10$ surface exhibited 2 different morphologies (d, e).
rough surface, similar to what has been observed before for the growth of vanadate films under V-rich conditions.

While it was demonstrated that the growth of vanadate superlattices is indeed possible using hybrid MBE, the most interesting questions, namely how the magnetic and orbital order couple across the interfaces, will have to be answered in the future. Given that the type of order is originated from the Jahn-teller distortion on the V-site, it remains to be seen how the superlattice will impose a structural alteration. X-ray magnetic circular dichroism (XMCD) measurements performed at a synchrotron using photon energies tuned to the vanadium edge can provide this information and may shed new light on the spin and orbital order in vanadate materials and their responses on ultrafast time scales if excited into non-equilibrium states.

6.5 Concluding remarks

With the ability to grow strained rare earth vanadate thin films and superlattices they continue to be an interesting topic of correlated complex oxide materials being in a Mott insulating ground state. This current research has unlocked numerous new structural phenomena in vanadate thin films, both at high-temperatures and at cryogenic temperatures in which the spin-orbit coupling phenomenon is active opening the path to study new and exciting, while nontrivial phenomena. Further, the structural modes seen in these films can be utilized to tune order in a variety of other $Pbnm$ perovskites, useful in either interfacial effects between substrates and a film or in superlattices. Growth by $h$MBE, coupled with careful considerations to prevent the formation of undesirable overoxidized phases during growth has greatly simplified the growth process to obtain stoichiometric, single phase thin films. However, obtaining single domain films with control of the crystal orientation, which will be necessary to fully understand the complex physics
seen in these materials remains an elusive challenge. Low-temperature structural refinement of the films has proven to be a challenge, however the combined application of X-ray diffraction using brilliant light sources complemented by an in-depth structural analysis using HAADF-STEM to determine A-site displacements and rotation angles of the oxygen octahedra is a viable way to elucidate the complex arrangement and spatial modulation of (+) axis orientation and strain. This work has shown that while difficult, measurement of these angles using synchrotron diffraction, as well as direct imaging of oxygen octahedra is possible, and opens the door for future experiments in this area.

Superlattices of these two materials have been synthesized and characterized using standard methods, but as of now the associated spin and orbital order remains largely unexplored. The biggest unanswered questions remain how the structure couples between these layers, and how the orbital and magnetic order is altered due to this layering. As the layer thickness of YVO₃ and LaVO₃ is varied it would be interesting to explore whether there exist a transition regime above which the superlattice behave like a spin and orbital order coupled crystal in which both LaVO₃ and YVO₃ responses can be clearly distinguished from one another, while for layer thicknesses below the transition regime the responses resemble that of an single crystal with unique properties of its own. The characterization methods employed previously for these two materials will need to be utilized to fully understand the structure both at room and low temperatures.
Chapter 7. Continuation and Future Works

The following section discusses avenues for future research based on the findings uncovered during this thesis. The first section proposes development of tailored substrates made with a specific lattice constant, symmetry, and conductivity, suited for applications of epitaxial perovskite oxide thin films on silicon. The second section discusses the previous work on strontium vanadate Ruddlesden-Popper phase thin films, including applications and expected properties, difficulties faced during growth, and potential routes to overcome these difficulties.

7.1 Epitaxially tailored and flexible virtual substrates for perovskites

One of the biggest roadblocks in the field of complex oxides is the lack of available substrates with suitable lattice parameters that are scalable to commercially interesting scale. This is exemplified in Figure 7-1, showing the various commercially available single crystal substrates and their lattice parameter (bottom). Perovskite gallates, scandates, and tantalates can easily exceed 500 USD for a single 10 x 10 mm substrate, and are not always readily available as the supply of these crystals are limited. The real potential of the hMBE growth technique may be in the growth of virtual oxides substrates on silicon in which tailored lattice parameters on Si, ideally with an integrated bottom electrode that can serve as epitaxial template for subsequent growth of other functional oxides.

The field of oxides on silicon sprouted from the need to grow high-\(k\) dielectric for MOSFET devices. While amorphous HfO\(_2\) was chosen over ternary complex oxides, this still created a wealth of information available of oxide stability on silicon, both computationally and experimentally\(^{316-318}\). The most obvious starting point for virtual substrates with tailored lattice parameter would be the deposition of a titanate solid solutions CaTiO\(_3\)-SrTiO\(_3\)-BaTiO\(_3\). In bulk
form, all three of these materials have been synthesized on silicon\textsuperscript{203,234,319}, and can be grown using $h$MBE\textsuperscript{136,216,267}. Simply adjusting the composition ratios of the A-site cation can create a gradual transition from a lattice parameter as low as 3.83 Å for CaTiO$_3$, up to 4.05 Å for BaTiO$_3$, before accounting for built in strain from the thermal expansion mismatch of the film and silicon. The elements Ta and Sc are also available as metalorganic precursors with alkoxide ligands, and could in principle be grown by $h$MBE on silicon as well.

Lattice matched metallic substrates are also highly sought after for their use as back electrodes. Transparent oxides are in particularly useful as contacts in LED’s, as well as electrodes in solar cells. SrRuO$_3$ has already been integrated on silicon through a variety of techniques\textsuperscript{320–322}, and is capable of being grown by $h$MBE\textsuperscript{143}, although the current precursor has proven problematic due to the large amount of solvent required to stabilize the RuO$_4$ in solution\textsuperscript{142}. SrVO$_3$

![Potential perovskite substrates on silicon](image)

**Figure 7-1: Perovskite oxides on silicon for virtual substrates.** The above plot represents the potential for perovskite oxide alloys on silicon. The range of lattice constants currently created with commercial substrates can be continuously spanned via oxide substrates with a variety of symmetries possible. Metallic substrates (denoted by the e$^-$) can be integrated on silicon as well.
has been grown on SrTiO$_3$ with some success, but films had to be kept to a relatively small thickness of below 20 nm to prevent cracking. Ideally, films could be grown on a more closely lattice match virtual substrate to alleviate this limitation.

In all cases, the most crucial step in the process is the deposition of the template layer directly on silicon. During this process, it is critical to prevent carbon contamination as well as oxidation of the silicon substrate before the template layer is completed$^{216}$, as this leads to second phases which will drastically degrade structural quality of the film. This is where the $h$MBE process has shortcomings, as the thermal decomposition of the MO precursor causes both oxygen and carbon exposure to the film growth front. Increasing temperature will lower the amount of carbon incorporation, but also increase the oxidation rate, which currently prevents the optimization of film nucleation which would result in a much reduced formation of structural defects, specifically threading dislocations and stacking faults, which would dramatically improve the rocking curve width. From these considerations it seems that the ideal method would be to nucleate the initial layer using traditional MBE techniques with the metals all supplied through an effusion cell$^{203,323,324}$, or Ti-ball$^{325}$, and the bulk of the film later deposited with $h$MBE, ideally in a different chamber to prevent any carbon contamination of the initial layer.

Another hurdle that stands in the way to unlock the full potential of metamorphic perovskite buffers on Si as virtual substrate is the thermal expansion mismatch between the silicon substrate and perovskite films. This can be as high as a factor of 10x, leading to internal stresses that will very quickly cause cracking upon cooling. The critical thickness appears to be in the 100 nm range for SrTiO$_3$ on Si, and will be even thinner if films with larger lattice parameter mismatch are deposited on top up the virtual perovskite substrate, limiting their application for oxides. Yet
in this research, it was found that Sr-rich films rarely, if ever, exhibited cracking. There might be two reasons for that. Excess Sr during SrTiO_3 film nucleation may modify the formation of the amorphous SiO_x layer, lowering the T_g and allowing the film to essentially float on the underlying glass layer. Since excess Sr will be incorporated into the buffer layer as Ruddlesden-Popper stacking faults they might offer an additional relaxation pathway to mitigate stress building up in the film. Silicon on insulator (SOI) wafers offer a possible solution to this problem. Instead of using thermal SiO_2 oxide, a low T_g glass such as soda lime silicate could be used instead. Annealing at temperatures as low as 500°C could be used to remove all internal stress from the deposition process and produce thick, stress free films in the micron range, ideal for optical applications.

Much of the groundwork has already been done to further advance in this direction. The combination of MBE with hMBE seems to be the best path forward that can lead to large area wafers of single crystalline oxides. With proper funding and manpower, this can be a highly productive area of research and industrial growth in a few years to come.

7.2 SrVO_3 Ruddlesden Popper series

The majority of this work has thus far focused on films and superlattices of the perovskite. However, layered perovskites present even more opportunities to drive unusual and novel phenomena. Improper ferroelectricity^{28}, polar metals^{326,327}, MITs^{328}, and high temperature and unconventional superconductivity^{329,330} all exist in a layered Ruddlesden-Popper (RP) series of perovskites. The characteristic of these films is the addition of rock salt layer every n number of perovskite block layer. This additional layer can break inversion symmetry, split 3d bands, and
reduce the dimensionality of the Fermi surface. Further, many of the RP structures are bulk stable for periodicities of \( n = 1 \) up to around \( n = 4 \), and higher periodicities can be synthesized using thin film deposition methods\(^{326}\).

Vanadate and titanate RP’s have huge potential to explore structurally coupled electronic, magnetic, and polar properties in the field of perovskite oxides that so far has been untapped. Sr\(_2\)VO\(_4\) is a bulk stable Mott-insulating RP predicted to be a \( d^1 \) superconductor, while the higher order RP’s such as Sr\(_3\)V\(_2\)O\(_7\) or Sr\(_4\)V\(_3\)O\(_{10}\) could exhibit unusual intermediate metal to insulating properties between the Mott insulating and transparent metal end members. Ca\(_3\)V\(_2\)O\(_7\) is most likely a polar metal, with a similar mechanism to Ca\(_3\)Ru\(_2\)O\(_7\)\(^{327}\). RP’s of the rare-earth titanates such as La\(_{2-x}\)Sr\(_x\)TiO\(_4\) could be the electron analog to the AFM hole conducting cuprate superconductors. As films of Sr\(_5\)Ti\(_4\)O\(_{13}\)\(^{331}\), Sr\(_2\)RuO\(_4\)\(^{143}\), and Sr\(_3\)Ru\(_2\)O\(_7\)\(^{143}\) have all been synthesized by \( h \)MBE, it should be possible to expand to the growth of Ruddlesden-Popper phases with different chemistry.

Initial growth experiments of Sr\(_{n+1}\)V\(_n\)O\(_{3n+1}\) have been shown to be possible, but overall quality of the films were not yet satisfactory. Three different growth methods were tested: shuttered growth, co-deposition, and shuttered-codeposition. In all cases, Sr was supplied by a thermal effusion cell and vanadium via VTIP. For shuttered deposition, the Sr and VTIP shutters were opened sequentially for each SrO and VO\(_2\) monolayer. Shutter times were calculated by looking at RHEED intensity oscillations, similar to the growth of the Sr\(_5\)Ti\(_4\)O\(_{13}\) RP by Haislmaier et. Al\(^{331}\). Films grown in this manner appeared to have the primary film peak, but no higher order peaks, indicating the lack of a long range ordered layering scheme.

The second method used was a shuttered-codeposition technique, in which the perovskite layer was deposited using codeposition, while VTIP was closed for during the deposition of the
rocksalt double layer. This method has two advantages. First, the growth window could be used to self-regulate stoichiometry during the growth of perovskite layer. Second, the Sr shutter remained open throughout the entire growth, eliminating problems with thermal transients caused from heat reflection off the effusion cell shutter. Unfortunately, this method did not allow for control over the surface termination. Additionally, VTIP reactivity seemed to be enhanced at after depositing the SrO double layer, requiring the VTIP pressure to be lower during the deposition of the perovskite layer than what was used to grow the bulk perovskite counterpart, leading to a mixed phase of Sr$_2$VO$_4$ and Sr$_3$V$_2$O$_7$. Films grown in this method showed additional satellite peaks, and therefore more long range order, but still not of acceptable quality to probe electronic structure (Figure 7-2 a). HAADF-STEM of one of the films showed an unusual microstructure. Previous reports state nonstoichiometries were accommodated by the formation of additional rock salt or perovskite layers, for excess A-site or B-site cations, respectively$^{326}$. Instead, the RP layers appear to bend and distort drastically, which accounts for the wide peaks seen in XRD.

The last method for the growth of Ruddlesden Popper phases is pure codeposition, which was used to deposit the ruthenate containing RP’s by both $h$MBE$^{143}$ and traditional MBE$^{332}$. One enabling trait in the growth of the ruthenates is the high volatility of Ru at high oxygen pressures, thus it is unclear if the growth is adsorption controlled in $h$MBE from the volatile precursor or from the volatility of Ru itself. Films of Sr$_2$VO$_4$ were grown in this method, which appeared largely similar to the optimized films grown using the shuttered codeposition method. The inhibiting factor of these growths appeared to be the instability of the VTIP precursor. Further
experiments will be required to refine the growth process, as well as determine if there is a self-regulated growth window for RPs grown in this fashion, and if it can be adapted to other systems.

![Sr\(_2\)VO\(_4\) XRD Peaks](image)

**Figure 7-2: Strontium Vanadate RP growth series.** XRD diffraction of the series of Sr\(_2\)VO\(_4\) RP films grown using shuttered co-deposition (a). The stoichiometric RP peak positions are indicated by the solid lines. Nonstoichiometries in the film caused by instabilities in the VTIP precursor, as well as differential reaction rates let layering defects, visible by extra peaks in the XRD scans, as well as faults visible in STEM (b, c).

The biggest difficulty in the growth of these films is determining how to control the orientation of the incorporated RP layers, as well as the different reactivity of the VTIP precursor depending on the surface chemistry present. A potential work around is to instead grow vertical RP structures on a substrate that has been cut with vertical RPs, such as LaSrAlO\(_4\) (100) substrates.
In theory, the surface should remain at a constant 2:1 Sr:V ratio and allow for self-regulated growth. Current experiments in synthesizing these films are underway, and hold potential for the synthesis of quasi 1-dimensional metals.
References


46. Obradors, X. et al. Pressure dependence of the metal-insulator transition in the charge-transfer oxides RNi03 (R =Pr,Nd, Nd0 7Lao 3). 47,

47. Canfield, P. C., Thompson, J. D., Cheong, S.-W. & Rupp, L. W. Extraordinary pressure dependence of the metal-to-insulator transition in the charge-transfer compounds NdNi03 and PrNi03. 47,


60. Maeder, M., Ramírez, A. & Zehe, A. A RHEED study of as-received and atomically clean Silicon surfaces in UHV-environment. (1200).


71. Andersen, J. E. T. & Møller, P. J. Impurity-induced 900 °C (2×2) surface reconstruction of


128. Depuydt, J. M., Cheng, H., Haase, M. A. & Potts, J. E. Growth and Doping of Zinc Selenide


176. Kimoto, K. & Matsui, Y. Software techniques for EELS to realize about 0.3 eV energy resolution using 300 kV FEG-TEM. *J. Microsc.* **208**, 224–228 (2002).


186. Gulian, A. M. & Wood, K. S. Triplet superconductors as the basis for solid-state quantum


200. Weiss, B. *et al.* Monolithically-Integrated Multilevel Inverter on Lateral GaN-on-Si Technology for High-Voltage Applications. in *2015 IEEE Compound Semiconductor*


244. Tsai, C. F. & Young, M. S. Pyroelectric infrared sensor-based thermometer for monitoring indoor objects. (2003). doi:10.1626005


300. Fitting Kourkoutis, L., Hotta, Y., Susaki, T., Hwang, H. Y. & Muller, D. A. Nanometer


317. Coh, S. et al. Si-compatible candidates for high-dielectrics with the Pb$_{1-x}$Sr$_x$TiO$_3$ perovskite structure. doi: 10.1103/PhysRevB.82.064101


329. Bednorz, J. G. & Muller, K. A. Possible high Tc superconductivity in the BaLaCuO system.


Appendix

A.1. Industrially scalable growth of SrTiO₃ by hybrid MBE

A.1.1. List of References for Figure 4-1


9. Ambwani, P. Transport and Magnetism in Bulk and Thin Film Strontium Titanate. (University of Minnesota, 2015).


A.1.2.  *TTIP beam equivalent pressure vs Baratron inlet pressure*

![Graph showing the calibration curve of titanium tetraisopropoxide (TTIP) beam equivalent pressure $p_{\text{TTIP}}$ and gas inlet pressure. The data set was fit using a second order polynomial expression. A good agreement was achieved with an $R^2$ value of 0.99.]

**Figure A-1**: The calibration curve of titanium tetraisopropoxide (TTIP) beam equivalent pressure $p_{\text{TTIP}}$ and gas inlet pressure. The data set was fit using a second order polynomial expression. A good agreement was achieved with an $R^2$ value of 0.99.
A.1.3. **Effusion cell stability**

**Figure A-2: Growth rate extracted from GenX fit of the X-ray data shown in** Figure A-4 for SrTiO$_3$ films grown on LSAT as a function of Sr flux measured by the quartz crystal monitor at sample position in units of $10^{13}$ cm$^{-2}$ s$^{-1}$ of Sr atoms. The relation can be approximated by a linear function, the fit has an $R^2$ value of 0.94. For Sr flux values exceeding $2.00 \times 10^{14}$ cm$^{-2}$ s$^{-1}$ the effusion cell has been found to become rather unstable with sizeable flux drifts of about 4% per hour resulting in a much smaller growth rate than expected from Sr flux calibrations using the quartz crystal monitor prior to the growth. The high Sr flux rates needed to demonstrate a growth rate of 600 nm hr$^{-1}$ were generated from two Sr effusion cells operated in tandem.
A.1.4. **AFM of films vs growth rate**

Figure A-3: AFM images of nominally 45-nm-thick SrTiO₃ films grown on LSAT at varying growth rates (top). All samples exhibit surface roughness of less than 1 nm. Samples grown at fluxes above $2.5 \times 10^{13}$ Sr atoms cm$^{-2}$ s$^{-1}$ show step and terrace morphology. AFM images of nonstoichiometric films are shown (bottom). Defects of ~0.2 μm in size are seen on the Sr-rich sample, while the Ti-rich sample exhibited a smooth, featureless surface. All scale bars are 250 nm.
A.1.5. Genx fits of SrTiO₃ films on LSAT

Figure A-4: X-ray diffraction scans and fits obtained from GenX³⁹ for the growth rate scaling of SrTiO₃ films grown on LSAT. Excellent comparison of experimental data and fits were obtained. The film growth rate was obtained from the film thickness determined from the von Laue thickness fringes and the growth time. Sizeable deviation from the expected out-of-plane lattice parameter was observed for the film grown at a growth rate of 413.7 nm hr⁻¹, attributed to the drift of a single Sr effusion cell operated at fluxes higher than 2.00×10¹⁴ cm⁻² s⁻¹.
A.1.6. **Wafer Metrology**

![Diagram of wafer metrology](image)

**Figure A-5:** Wafer scale metrology of the metamorphic buffer layer SrTiO$_3$ on Si obtained from spectroscopic ellipsometry. Phase difference $\Delta$ and amplitude ratio $\Psi$ were collected in the spectral range of 0.75 eV to 3.0 eV collected at 25 locations across the wafer. The thickness values of the individual layers, namely amorphous silicon oxide ($a$-SiO$_x$) interlayer thickness, SrTiO$_3$ film and SrTiO$_3$ surface layer thickness were extracted employing a least squares Levenberg-Marquardt regression algorithm using optical models of the Si substrate, $a$-SiO$_x$, SrTiO$_3$ and a SrTiO$_3$ surface layer to account for the film surface roughness using the Bruggeman effective medium approximation.
Figure A-6: **a**, Cropped HAADF-STEM image of the Sr-rich region of the calibration sample shown in Figure 4-3. The linear strain maps of the image are shown in **b, c**. Areas of high strain highlight the location of the horizontal and vertical Ruddeslden-Popper (RP). Scale bars are 3 nm. **d**, A composite of the strain components overlaying the original image, highlights the exact location of each RP fault.

Figure A-7: Secondary ion mass spectrometry (SIMS) of SrTiO$_3$ on silicon is obtained using a PHI nano TOF. A primary 30 keV Bi$^{3+}$ ion beam was rastered over a 100 x 100 µm area. The etch rate is approximately 3 nm cycle$^{-1}$. Profile covers approximately 85 nm, and begins after the first 75 nm of film has been etched away. The small increase in the carbon signal at the start of the profile is due to adsorption of background gas species in the analytical chamber. A small carbon signal slightly above the detection limit is present throughout the film. The carbon concentration is estimate this to be in the mid-$10^{17}$ atoms cm$^{-3}$ based on previous studies into carbon incorporation of films growth by $h$MBE$^{219}$. Carbon concentration increases at the interface due to lower cracking efficiency of the carbon-containing precursor at lower temperatures during deposition of the buffer layer.
A.2. Atomic fitting of lattice

Fitting of atomic columns was performed using a series of matlab packages developed primarily by Dr. Colin Ophus at the National Center for Electron Microscopy (NCEM) with contributions from Dr. Gregory Stone and Dr. Debanghu Mukherjee during their time at Penn State. Alterations and additional script were written by the author for specific applications for this thesis.

A.2.1. Drift Correction

Drift correction for this work was carried out using orthogonal scanning image pairs (with the exception of CryoSTEM which will be covered later). The process is coarsely outlined in Figure A-8 a. Two orthogonal images are taken with both the HAADF and ABF detectors. By assuming that there is no drift in the fast-scan direction, the two images can be shifted to correct for both linear and non-linear drift artifacts. This is performed by iterative shifts of each scanline, followed by correlations to the reference image to determine the true, non-drifted image. A full in-depth report is published by Ophus et. al in reference. The HAADF detector offers higher signal to noise ratio, and is used to determine the shifts of each scanline. The drift corrected ABF image is created by substituting the ABF images into the drift matrix from the HAADF. ABF images reveal the position of the anion sublattice, however this is convoluted with the much heavier cations and can prevent accurate fitting. To minimize this effect, the ABF image can be inverted to have the same contrast as the HAADF. The HAADF image is then scaled and subtracted from the ABF, removing the cations from the
image making the anion sublattice stand out, and with the oxygen atoms can be fit accurately, shown in Figure A-8 b.

Figure A-8: Images of the $n = 10$ superlattices taken using simultaneous HAADF and ABF detectors. Drift correction is employed by taken orthogonal images, with the assumption that there is no drift in the fast-scan direction (a). The drift matrix for each row is created using the HAADF images. The ABF images are then corrected using the same drift matrix. Oxygen contrast is enhanced by subtracting the HAADF multiplied by a scaling factor from the inverted ABF image. For ranges of scaling factors between 1.0 and 1.5, the cations begin to disappear and only the oxygens are visible (b).
A.2.2. Gaussian Fitting Atomic Columns

Atomic columns were fit from either the raw or drift corrected images. The HAADF image is loaded into “RealspaceLattice01” GUI in matlab (Figure A-9 a)(created by Ophus and Stone). Atom peaks are determined roughly using a simple maximum nearest-neighbor 2D peakfinding approach. Extraneous peaks are filtered out through smoothing, minimum peak intensities, and minimum peak separation distances. These peaks are then used to generate the lattice and assign each cation peaks a distinct $u$ and $v$ position, as well as an atomic basis vector. A second can be used to add in additional peaks from light $z$-elements, such as oxygen, that are no present in the HAADF image. The approximate peak positions are determined using a linear interpolation between the 4 nearest neighbor cations. Each atom position is refined using a Gaussian fit to the atomic columns, again using the HAADF image for the cations (Figure A-9 b) and the HAADF-ABF composite image for the anions, with the total atomic positions plotted over the ABF image (Figure A-9c ). These atomic positions are used to calculate structural distortions and symmetries such as linear and shear strains, octahedral rotations, ferroelectric polarizations, etc. In theory, the atomic positions can be determined with sub-pixel precision due to the Gaussian fitting. However, because scan line distortions, drift, and charging effects, cations can typically only be fit to $\sim \pm 2$ pm precision, while oxygen positions are closer to $\pm 10$ pm precision.
Figure A-9: Fitting of atomic columns. The GUI for determining the rough peak positions as well as the lattice vectors and basis vectors is given in (a). Gaussian fitting is used to further refine these peak positions in HAADF image (b). The A and A' sites are given in green, while the B sites are in blue. Oxygen sites are interpolated and fit using the composite ABF-HAADF image, with the total atomic positions plotted in (c) over the ABF image.
A.2.3. Fast-Scan image correction

*The image acquisition method described below uses freely available python package from Savitzky et. Al. on the github repository. The following is an abbreviated description of the process developed by Savitzky et. Al. in Ref. 334.

The primary difficulty in CryoSTEM is the drift of the sample in the microscope during image. Many current cryogenic microscopy holders are nothing more than cooled traditional side-entry holder. The long rod can have fairly large temperature gradients from the liquid nitrogen reservoir at the end of the holder to sample, causing significant linear drift during image. Boiling of the LN will also cause small vibrations in the rod, which gives rise to smaller, nonlinear drift during imaging. The orthogonal drift correction method is well suited to removing all drift artifacts when only a small amount of drift is present to begin with. However, with larger drifts it becomes difficult to align the rotated images back to the reference due to the long time between each acquisition, as well as the assumption that there is no drift in the fast-scan axis may not be valid.

A second method to remove drift is the use of fast-scanning image acquisitions. The distortion from drift simply a matrix transformation of the true image positions with the drift velocity vector, multiplied by the total acquisition time. By reducing the image acquisition time, either by a reduction of the pixel resolution or pixel dwell time, the total drift in each image can be greatly reduced. For instance, by lowering the pixel size by a factor of 4 (from a 4096x4096 to 1024x1024), and the dwell time by a factor of 2.5 (from 1 µs to 0.25 µs), the total drift is reduced by a factor of 16 per image.

This process is outlined in Figure A-10 for an image of an LaVO\textsubscript{3} thin film. Using a traditional scan image (2048x2048, 1 us dwell time, 4.2 second capture time), scan distortions as well as drift are present in the image. A stack of 50 images are taken at a lower resolution (512x512 pixels), but using the same dwell time to maintain a high signal-noise ratio per pixel, reducing the
capture time of each image to 0.26 seconds. The drift matrix is comprised of the pixel shifts of each image relative to all other images in the stack using cross-correlation. Unit-cell phase shifts, can be easily picked out as discontinuities in the drift matrix, and these correlation pair values are ignored. Further, the first and last 5 images are thrown out as these have drifted too much between the acquisition time. The image is then reconstructed by applying the average shifts of each image from all relevant correlation pairs, and averaging over the shifted image stack. The fast scan times reduce the total drift, while averaging over a large number of images removes linescan and random noise from the detector.

Unfortunately, this image technique will only reduce, not remove drift entirely as the orthogonal drift correction theoretically does. However, the drift velocity during imaging can be approximated from the average shifts between image and the collection time per image, and a shear transformation could give the true image. However, for most cases this is not necessary, as the small amount of drift is below the noise limit.
Figure A-10: Fast-Scan imaging of LaVO₃ thin film. The original scanned image, taking using a single image is shown in (a). Scan distortions and small amounts of drift are visible. A fast-scanning image series of 50 was taken (right), in which the reduced pixel count decreased the scan time by a factor of 16. Selected images from the stack are shown (b). Cross-correlations between each image in the stack are taken, and the relative shifts between each image are given (c). Only images 5-45 were selected for use. Discontinuities in the images are related to unit-cell shifts and these image pairs are ignored, showed in the clipped shift matrix. The corrected shift matrix is reconstructed from the clipped matrix, to approximate the relative shift of each image. This is then used to create the reconstructed images (d) in which all line distortions are remove, and the total drift is reduced significantly.
### A.3. Atomic distortions of orthorhombic unit cells

<table>
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<th></th>
<th>100</th>
<th>210</th>
<th>110</th>
</tr>
</thead>
<tbody>
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<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td><img src="image3.png" alt="Diagram" /></td>
</tr>
<tr>
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<td><img src="image4.png" alt="Diagram" /></td>
<td><img src="image5.png" alt="Diagram" /></td>
<td><img src="image6.png" alt="Diagram" /></td>
</tr>
<tr>
<td><strong>Axis in plane, perpendicular to zone axis (a\textasteriskcentered b\textasteriskcentered c\textasteriskcentered)</strong></td>
<td><img src="image7.png" alt="Diagram" /></td>
<td><img src="image8.png" alt="Diagram" /></td>
<td><img src="image9.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

**Figure A-11: Zone axis of the Phnm unit cell.** The figure represents all the possible atomic positions for the 3 different zones (<100>\textsubscript{p}, <210>\textsubscript{p}, and <110>\textsubscript{p}) observed in this study, for the 3 different scenarios of the (+) axis in the plane and parallel to the zone (a\textasteriskcentered b\textasteriskcentered c\textasteriskcentered), the (+) in the plane perpendicular to the zone (a\textasteriskcentered b\textasteriskcentered c\textasteriskcentered) or the (+) axis out of the plane (a\textasteriskcentered b\textasteriskcentered c\textasteriskcentered).
A.4. CryoSTEM of LaVO\textsubscript{3} in cross-section

Cross sectional images of LaVO\textsubscript{3} on LSAT (110) zone, as well as the NdGaO\textsubscript{3} (110) and (1\overline{1}0) zones we taken at cryogenic temperatures. No domains were visible in any of the samples. This could be an artifact of the sample preparation process, as the TEM sample thickness is on the order of the periodicity and has been known to prevent formation of long range order\textsuperscript{335}. HAADF and ABF images again revealed the 4 monolayer transitional region in films of LaVO\textsubscript{3} on NdGaO\textsubscript{3} (001) due to the rotation of orientation between film and substrate. This region did not occur on the LSAT sample, but rather a continuous change in the octahedral rotations from the cubic substrate to the orthorhombic film took place.
Figure A-12: Low-temperature atomic imaging of LaVO$_3$. Images taken on the pseudocubic (110) axis of LaVO$_3$ on LSAT (a-c) and NdGaO$_3$(001) (d-f). Films show few stacking faults. The HAADF (b) and ABF (c) reveal a gradual transition between the LSAT substrate across the interface indicated by the green arrows to the film. On NdGaO$_3$, the transition is again apparent in the ABF image (f) from a canting of the V-O-V bond angle. This transitional is indicated by the orange arrows.
A.5. Fitting of synchrotron diffraction data

The high intensity of the synchrotron diffractometer and the ability to automate movement and alignment of the diffractometer to a series of peaks allows for hundreds of scans to be captured over the course of a week at a beamline. Coupled with the areal detector capabilities of the Pilatus Dectris x-ray detector leads to hundreds of gigabytes of data to parse, requiring the use of batch processing.

First, all rocking curve ($\omega$) scans were converted to a 3D matrix reciprocal space map, showing intensity as a function of $H$, $K$, and $L$ in pseudocubic units of the film using a python script from the synchrotron. A MATLAB graphical user interfaced (GUI) was built to be able to view different slices of this matrix in reciprocal space (Figure A-13). Once the peak was aligned using the GUI, a mask was created to remove excess background signal from the unnecessary pixels in the detector in $h$ and $k$, and the scanned compiled in $l$ to create a typical $l$ vs. intensity scan shown in Figure A-14 (a) for all the temperature scans. Each of these scans is fit using a series of Gaussians to determine the peak from the background intensity (Figure A-14 (b)). In most cases, a single Gaussian curve for the peak and one for the background is sufficient. However, additional peaks could be added to account for substrate effects to obtain a better fit. While a lorentzian, or Gaussian-Lorentzian fit may give more information, a simple Gaussian fit using MATLAB’s built-in fitting functions proved much faster, and was still able to reliably extract the integrated intensity. This process had to be repeated for each scan at each temperature. Therefore, batch processing was utilized to fit each peak. In this method, the proper fitting parameters were found for the low temperature scan, and then these were applied to each subsequent scan at the peak at all temperatures.
The integrated intensity of the fit to the peak, with the background subtracted out, was then obtained simply by integrating the result of the Gaussian fits that corresponding to the film peak. This data, given in (Figure A-14 (c)), is used to determine the rotational angles and displacements using a mathematica fitting code developed by Dr. Matthew Brahlek, and described in Ref. (294).

![Figure A-13: Matlab GUI for viewing reciprocal space maps.](image)

The above screenshot shows the scan of the (1 0.5 3) peak at 25 K. Sliders could be adjusted to show the 2D slice through the 3D matrix, to manually find the peak in $h$, $k$, and $l$. For instance, in the top left box, different slices in $h$ are taken and plotted in $k$ and $l$. This was then done in $k$ and $l$. A 3D view of the peak is created in the bottom middle image. Once centered, a mask is created around the peak in the bottom left to remove the background to create the lines can.
Figure A-14: Extracted data and Fit (103.5) peak. (a) The extracted peaks from the dataset of the (1 0 3.5) peak as a function of temperature. Each peak must then be fit to determine the integrated intensity from the background. (b) The raw data is of the scan taken at 20 K is plotted as black dots. This is then fit using a 2 Gaussians in this case, one for the peak and one for the background, the result of which is plotted in the dashed red line. The fit of the peak is given as the blue line, while the background is a green dashed line. (c) The integrated intensity of the peak is plotted as a function of temperature, with a drastic change in intensity observed between 100 -120 K.

The majority of the TEM samples discussed in this thesis were manually prepared, cross section wedge samples, and so a brief writeup is included in this section. The method is based off of notes from Greg Stone, taken during his training at the National Center for Electron Microscopy (NCEM) from Marissa Libbee.

(Beginning from a 10x10 single-crystal thin film sample) The 10x10mm thin film is first diced to achieve 2 x 1-2mm squares. Sample should ideally be cleaved to prevent contamination from getting on the sample surface, but if this is not possible, samples can be mounted to a glass slide face-down using Crystalbond™ and diced to the desired size using diamond saw. If samples are diced, they need to be cleaned properly in acetone and isopropyl alcohol (IPA) to remove any traces of organic contamination.

After dicing and cleaning, the samples need to be made into a stack. A small amount of epoxy such as EPO-TECH™ should be applied to the film on one of the diced pieces. The next piece is placed on top, film side down, with the edges aligning as well as possible. For clarity, this can be thought of as making a “film sandwich” with the substrate as the bread and the film and epoxy in the middle. Use as little epoxy as possible while still creating a conformal coating over the film when the pieces are sandwiched together. The stack is then placed in a small vice with sufficient pressure to force the excess epoxy out, but not crack the sample. It should stay in this vice for 10-15 minutes before being placed on a hot plat to cure for at least 1 hour, although it can be left overnight if desired. It is sometimes useful to attached polished silicon sample on the top and bottom side of the stack as well. This adds an additional layer of protection to the sample, and
prevents cracks from forming on these sides and propagating to the middle. Additionally, silicon becomes translucent when thinned below 10 um, and serves as a good thickness indicator.

One the epoxy has cured, the sample is mounted to a pyrex stub using crystalbond for polishing. All polishing in this thesis was done with the aid of the Allied Multiprep polishing system. This is achieved by mounting the sample such that the film is normal to both the plane of the pyrex stub, as well as the front of the stub. Care should be taken to make sure the back of sample is directly on the stub, and the film is sticking up and the sample does not tilt. This can happen if the 2 faces of the sample twisted or shifted in the clamp, leading to edges that aren’t square. In wedge polishing, 3 sides need to be polished to optical smoothness. Both the top and bottom of the sample, as well as the wedge edge. If the edge is not polished, cracks will begin to form from the scratches at the edge and the sample will break before getting thin. It is therefore useful to mount it such that the most oblong edge of the sample is polished first. If it is difficult to get the sample to sit flat, it may be useful to polish one side flat using a course grit, then flipping over top mount flush with the stub for a better mechanical bond.

The stub and sample are placed in the Multiprep for polishing (Figure A-15). Diamond lapping films are used rather than a standard polishing pad. This is because a standard pad is soft and will deform which rounds out the edges, causing the edges to become thin before the film does and again leads to cracking. Beginning with a 30 um grit, the sample should be polished until it is entirely flat, and all rough edges from cleaving the sample are removed. From here, polishing should continue using smaller and smaller grits using approximate guidelines from Dr. Stone’s notes in Table A-1. Ensure that all marks and scratches have been removed from the sample before moving on to the smaller grit. Polishing should follow the rule of 3’s. First, never take of more
than 3x the current grit size before checking the sample (i.e. If using 3 um grit lapping film, check the sample in the microscope every 9 um). Second, always take off 3x the previous grits before moving to the next (i.e. If the previously used grit was 6 um, at least 18 um of sample must be removed using the 3 um grit before moving on). This ensures that any cracks or scratched on the surface are caught early, and defects from the larger grit size are not carried over when switching to smaller grit. The glue line of the sample should run parallel to the direction of the polishing pad. This minimizes stress on the glue line, and prevents larger chunks that have broken off from the sample from coming in contact with the interface.

**Figure A-15: Polishing Equipment.** (a) The stub for the sample. The sample is mounted on this using Crystalbond. The sample should sit on edge, with the film normal to both the flat of the pyrex stub, as well as the front plane of the stub. (b) The Allied Multiprep with a sample stub mounted, so the sample is facing down on the polishing pad.
Table A-1: Standard polishing distances for flattening wedge and backside. This table describes how much material to take off at each grit, at what rotation (RPM) to run the multiprep, what force should be applied during polishing (load), and to run the multiprep clockwise (CW) or counter-clockwise (CCW).

<table>
<thead>
<tr>
<th>Lapping Film (dia. in µm)</th>
<th>RPM</th>
<th>Polish Distance (µm)</th>
<th>Load</th>
<th>Direction</th>
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</thead>
<tbody>
<tr>
<td>30</td>
<td>100</td>
<td>150</td>
<td>3</td>
<td>CCW</td>
</tr>
<tr>
<td>15</td>
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<td>3</td>
<td>CCW</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>30</td>
<td>0</td>
<td>CCW</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>20</td>
<td>0</td>
<td>CCW</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>10</td>
<td>0</td>
<td>CW</td>
</tr>
<tr>
<td>0.5</td>
<td>50</td>
<td>3-5</td>
<td>0</td>
<td>CW</td>
</tr>
<tr>
<td>0.1</td>
<td>50</td>
<td>30 seconds</td>
<td>0</td>
<td>CW</td>
</tr>
</tbody>
</table>

Once one side has been polished down to 0.1 um smoothness, and is smooth with no scratches visible in the optical microscope, the sample should be removed, rotation 90 degree, and repeated for the wedge edge side.

Again, remove the sample, rotate 90 degrees, and remount for polishing the final side. On this side, it is imperative that there are no trapped bubbles in the crystalbond under the sample, or any other irregularities that could cause fracture. It is useful to have a few microns of sample on the wedge edge sticking off the stub. This helps to measure the thickness of the sample left in the optical microscope. In this step, it is more important to follow how much of the sample is remaining, as if too much is taken off in the early steps with larger grits, there will not be enough left to polish at each grit to obtain a smooth surface. This is summarized in Table A-2.
Table A-2: Standard polishing procedure for polishing final (front) side. This table describes how much material should be remaining at the end each step, as well as the standard parameters. The green bar at 6 um indicates at what stage to begin to put on the wedge edge.

<table>
<thead>
<tr>
<th>Lapping Film (dia. in µm)</th>
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<th>Sample Remaining (µm)</th>
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<td>2</td>
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<tr>
<td>0.5</td>
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<td>3-0</td>
<td>1</td>
<td>CW</td>
<td>Green lube</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
<td>30 seconds</td>
<td>1</td>
<td>CW</td>
<td>Green lube</td>
</tr>
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</table>

When 75 µm of sample remain, and beginning on the 6 um grit lapping film, the sample should be tilted to begin the wedge edge. Each full rotation of the micrometer on the multiprep is approximately 1 degree of tilt. 0.5 – 1° of tilt is ideal for the highest quality samples with large thin regions, however these are very fragile and can break easily. A wedge angle of 2° often will achieve reasonable samples with much less of a chance of breaking.

After tilting the sample, it is imperative to raise the multiprep head and slowly, manually engage the sample on the polishing pad, as the tilt will have lowered the sample. Again, continue polishing, following the outlined steps until 1 um grit is used. At this step, there should be no scratched visible. It may also be a good idea to switch from water to green lube for polishing. Green lube lowers the drag on the surface from the polishing pad compared to water, but it does not remove excess material from the pad which can come back around and scratch the surface. Therefore, when using green lube it is important to check the sample frequently for any sign of
scratches. Additionally, only use a few droplets on the pad. Using an excessive amount will prevent the sample from coming in contact with the pad and polishing will stop.

In oxide materials, it should be possible to see color fringes at the edge of the material when it becomes sufficiently thin. Silicon begins to turn brown at approximately 10 um, and turns orange at 5 um when viewed in transmission mode. Polishing below this point will save time when ion milling and create a better sample, but at this stage the sample is at its most fragile and may break. The user will need to use their judgement to decide when to stop.

Once the sample has been polished to a wedge, it should be mounted to a molybdenum grid. This is achieved by placing a small drop of EPOTECH epoxy on the thick side of the wedge, and placing a molybdenum grid on top. It should be positioned so that the long opening of the grid is perpendicular to the interface, and the edge of the wedge is roughly in the middle. Care should be taken to avoid putting any epoxy on the pyrex stub itself, as this can glue the sample directly to the stub. In some cases, it can still be removed with a razor, but it is best to use as little epoxy as possible and avoid moving the grid around on the sample to avoid this scenario entirely. Again, heat the sample to cure the epoxy, and then soak the entire stub in acetone for up to 12h to remove the crystalbond. The sample should simply fall of the grid. It is useful to place the stub on top of a piece of filter paper for the sample to fall on, and simply lift the paper to remove the sample.

The final stage of sample preparation is ion milling in the Gatan Precision Ion Polisher (PIPSII). The sample and molybdenum grid should be loaded so that the film is perpendicular to the guns when loaded. Ideally, the stage rotation should be set so that the ion mill is never incident on the wedge edge, as this will cause beam damage to the thin region and blunt the edge. For
thick samples, use 5 kV energy until the fringes are visible on the sample. Then begin stepping
down the voltage to 3 kV, 1 kV, 0.5 kV, and 0.1 kV, polishing for 5 minutes at each stage. If the
sample is sufficiently thin from manual polishing, the 5 and 3 kV step can be skipped entirely.

It is difficult to say with any accuracy how to know from optical images when the sample
is thin enough for imaging. The best method is to simply view the sample in the TEM to see if
further thinning is required, and if so, repeat the ion milling at 1, 0.5, and 0.1 kV until the desired
thickness is reached.
Vita

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Education

2019 PhD in Materials Science, The Pennsylvania State University, University Park, PA
2014 B.S. in Materials Science, The Pennsylvania State University, University Park, PA

Experience

Focus in synthesis of oxide thin films using vacuum deposition techniques, particularly molecular beam epitaxy, and structural characterization via x-ray diffraction and transmission electron microscopy. Developed scripts in MATLAB for automated data analysis. Served as laboratory safety manager overseeing safe handling of chemicals and metalorganic precursors, and ensured proper care and maintenance of UHV equipment.

Selected Publications


