ABSTRACT

BURCH, MATTHEW JAMES. Microstructural Evolution and Domain Structures of Flux-grown Ferroelectric Thin Films. (Under the direction of Dr. Elizabeth Dickey.)

Barium titanate is one of the most commonly utilized dielectric materials for commercial applications. As devices continue to scale smaller, it is necessary to find processing routes that allow for the integration of high-permittivity barium titanate into the thin film geometry. In the bulk, high permittivity barium titanate can be produced at high processing temperatures (>1250° C). This is several hundred degrees higher than many low temperature substrates are able to withstand, which makes integration of high-permittivity barium titanate onto these substrates a challenge. One method to lower the processing temperature and maintain bulk-like permittivity of barium titanate thin films is through the addition of a liquid forming flux. The fluxing agent increases the kinetics of the system while encouraging densification. This increase in kinetics results in large-grained, dense samples, with high dielectric properties at relatively low processing temperatures.

In this dissertation, the underlying mechanisms of how the flux system actually impacts the microstructural evolution of physically vapor deposited barium titanate thin films on sapphire substrates is explored. The flux-system utilized is the barium-borate system (BaO-B₂O₃). It will be shown that the flux system results in large-grained, dense barium titanate thin films grown on sapphire. However, the evolution of the microstructure depends on a complex interaction between the liquid forming flux, a reaction between the sapphire substrate and barium titanate, the resulting reactionary phase of BaAl₂O₄, and {111}-barium titanate twins.

The similar system of barium strontium titanate is known to have a very broad paraelectric-ferroelectric phase transition. This dissertation demonstrates that there exists nano-scale
chemical inhomogeneity between the A-site cations of Ba and Sr. This inhomogeneity is the presumed reason for the residual ferroelectricity above the phase transition temperature.

It has been known since the beginning of ferroelectric research that a large percentage of the dielectric permittivity is dependent on the motion of ferroelectric domain walls. Previous work showed that flux-grown barium titanate thin films exhibit an apparent extrinsic contribution of domain wall motion to the ferroelectric properties. However, despite extensive microstructural characterization, traditional periodic ferroelastic domain structures were never observed. This dissertation utilizes the emerging technique of transmission Kikuchi diffraction of direct observation of abnormal or non-periodic ferroelastic domain structures in polycrystalline barium titanate thin films. Further, this work discusses the origins for these abnormal domain structures in terms of the biaxial strain caused by the substrate constraints.

Further, a technique is demonstrated, which allows for direct quantitative imaging of 180° polarization reversal with electron backscatter diffraction. Direct imaging of 180° ferroelectric domains LiNbO₃ is used as an example. This technique gives rise to an easy, inexpensive and non-destructive way to directly map polarization reversal in crystalline materials.
DEDICATION

To my wife, my Tiffany. And my son, my Isaiah.
BIOGRAPHY

Matthew Burch was born and raised in the small northwest town of Mount Carroll, IL. He attended Mount Carroll Middle School and West Carroll High School, where he graduated salutatorian in 2007. While in high school, he was active in a number of extra curricular activities including golf, basketball, choir and theater. After graduation, Matthew was awarded a scholarship internship at Metform, LLC, a nut and bolt factory in Savanna, IL. This scholarship guaranteed a job during all breaks from school. After high school, Matthew attended Coe College, where he majored in Mathematics and Physics. While at Coe, he met his future wife, Tiffany Myers, whom he wed in 2012. He was also very involved with the Academic Achievement Program, choir, voice competitions, math and physics clubs, and undergraduate research in physics. While at Coe, Matthew began his research career investigating the optical and structural properties of borate glasses.

Matthew graduated Cum Laude from Coe in May 2011. After graduation he immediately went to work for Professor Elizabeth Dickey at North Carolina State University on his dissertation research. While at NCSU, he was very involved with the student organization Allies for Students with Disabilities, of which he was a founding member and served as President and Vice President. The purpose of the group is to promote the awareness and advancement of students with disabilities at NCSU. In December of 2015 his son, Isaiah, was born.
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My many friends I have made at graduate school have helped shape the person and researcher I am today. There are too many to list them all by name but I need to emphasize a few in particular: Dr. Chris Fancher has been one of the best friends and co-workers a person could ask for over the past years. Everett Grimley and Carolyn Jensen, you are truly one of the best couples I know and some of the best friends I will ever have. I have loved
getting to know both of you and am honored to be the best man at your wedding.

My family, who is the foundation for my success, have provided me the support and love to succeed in both my professional and personal life. My parents taught and continue to teach me the power of education, love and faith. They are the reason I was able to turn my short attention span and natural curiosity into a career in physics and engineering. My godmother Cheryl, who was the first person in my life to introduce me to the wonders of science. My sister, Martha, for being the greatest big sister a little boy could hope for. My grandparents, who never missed a single sporting event, concert, performance or graduation when I was growing up and who taught me the value of hard work and determination.

Finally, my wife Tiffany. I gave my heart to you and in return, you gave me a future.
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1.1 Introduction

Barium titanate is one of the most commonly used dielectric materials used in electronic materials [1, 2]. However, integration of these barium titanate ceramics onto low temperature substrates remain a challenge. Generally, to obtain high permittivity in barium titanate ceramics must be annealed or sintered at much higher temperatures than these substrates can sustain. Recently, many strategies have been pursued to lower the processing tem-
peratures to integrate BaTiO$_3$ onto low temperature substrates while achieving dielectric properties approaching high-$T$ processed materials [3, 4, 5, 6, 7]. One particular method to lower the sintering temperature of barium titanate thin films is through the addition of a liquid-forming flux to the synthesis method [6]. Understanding the mechanisms involved in how the flux impacts the microstructure evolution of these thin films is key to eventual integration into electronic devices.

Further, being able to describe and characterize ferroelectric domain structure within barium thin films is crucial to understand the ferroelectric nature of the thin films and maximize performance for future devices.

### 1.2 Outline

Chapter 2 gives a general overview of the history, definition, and physical aspects of ferroelectric materials. Specifically, barium titanate is introduced as well as ferroelectric domains. It exists as a foundation which the original work is built upon.

Chapter 3 discusses how the key concepts in Chapter 2 depend on the microstructure of the processed material. Specifically, how ferroelectricity depends on grain size and processing. This forms the basis for the original work around ferroelectricity in barium titanate thin films.

Chapter 4 gives the history and background on barium titanate thin films. This chapter discusses continuing issues within the literature of scaling barium titanate to the thin film geometry. Also discussed are the advances that have been made in the literature to address these issues.
Chapter 5 gives an introduction to the experimental methods used for the majority of this work. In particular, it addresses the sample preparation methods not explicitly explained in the original work chapters.

Chapter 6 discusses the mechanisms involved when a liquid forming flux is added to the synthesis process of barium titanate thin films grown on sapphire.

Chapter 7 demonstrates that there exists A-site inhomogeneity in barium strontium titanate ceramics through the use of aberration corrected electron microscopy. It discusses this A-site inhomogeneity as a possible reason for the broad ferroelectric-paraelectric phase transition often seen in barium strontium titanate ceramics.

Chapter 8 shows that by utilizing the gnomonic distortion present in all electron backscatter diffraction set-up, an enhancement in indexing sensitivity can be achieved. It is shown that a geometry consistent with transmission Kikuchi diffraction results in improved indexing confidence compared with electron backscatter diffraction set-ups.

Chapter 9 utilizes the results from Chapter 8 by directly imaging abnormal 90° domain structures in polycrystalline barium titanate thin films with transmission Kikuchi diffraction. The origin of these abnormal domain structures is further discussed.

Chapter 10 demonstrates the ability to map 180° polarization reversal in ceramics with electron backscatter diffraction. Periodically poled LiNbO$_3$ is used as an example case.

Chapter 11 gives a summary to the original work and discusses avenues for future work on these projects.
Chapter 2

Ferroelectricity, Ferroelectrics and Domain Walls
2.1 Ferroelectricity

2.1.1 Overview and History

Certain materials, classed as ferroic, are defined by an order parameter that can be reversibly switched between at least two energetically degenerate ground states with the application of certain external stimuli. This order parameter appears suddenly upon cooling through a specific temperature, generally known as the Curie temperature, and disappears suddenly when heated above this temperature. The oldest and probably most well-known of these materials are ferromagnets. Ferromagnets exhibit a spontaneous magnetization in the absence of a magnetic field and researchers have had a cursory understanding of this phenomenon since antiquity. Other classes of ferroics include ferroelastics, which exhibit spontaneous strain in the absence of external stresses, and ferroelectrics, which exhibit spontaneous polarization in the absence of an external electric field. All ferroic materials exhibit the same basic responses with the application of their specific stimuli. With the application of a stimuli higher than a specific valued intensity, the order parameter will switch from one state to the other. This value is known as the coercive field, and the switching of the order parameter is known as hysteresis. Further application of the applied stimulus will result in complete switching of the order parameter. This is known as saturation, when only one of the energetically degenerate ground states are present within the material.

The trademark feature of these ferroic materials is the presence of different areas that exist with only one of the two energetically degenerate order parameters. These areas are known as domains, and the boundaries between these areas are known as domain walls.
These domains occur naturally in ferroic materials upon synthesis. A sample containing domains is known as a polydomain. Samples may then be forced into containing only one of the two possible order parameters through the application of an external stimuli. This is known as a monodomain. Within polydomain samples, one domain can be changed to the opposite order parameter through the application of an external stimuli. This process is known as domain switching. Domain switching occurs through the movement of domain walls, which is known as domain wall motion. The way domain wall motion occurs, the speed at which it occurs and the ability of domains to switch has been shown to be clearly linked to a material’s final device properties and performance [9, 10, 11, 12, 13].

Ferroelectric materials, or more generally ferroelectricity, has its origins in 17th century France where Elie Seignette created what is today known as Rochelle salt ($\text{K Na C}_4\text{H}_4\text{O}_6\text{H}_2\text{O}$), in the small town of La Rochelle, as an alternative to current day laxatives. It was not until the 19th century that Rochelle salt became of interest for its physical properties instead of its medicinal uses. Pierre and Paul-Jacques Curie showed piezoelectricity to be present in Rochelle salt as well as a few other crystals. These early experiments were performed on a class of materials known as pyroelectrics, where an electric polarization is formed from a change in temperature. The experiments on these early piezoelectrics set the groundwork for the work done on ferroelectrics in the middle of the 20th century. One condition, which was readily discovered, is that the crystal structure of a piezoelectric must be non-centrosymmetric (a crystal that contains no center of symmetry). This lack of a center of symmetry implies that when a uniform stress is applied to a piezoelectric, as the atoms are distorted in the unit cell, an electric dipole will result and lead to a net charge or polarization. [14]
In 1920 Joseph Volasek demonstrated that Rochelle salt had a remnant polarization after the application of an electric field that is analogous to a magnet that has remnant magnetism after application of a magnetic field. Thus the term "ferro" in ferroelectric originated. [15, 16] However, the similarities between ferromagnetism and ferroelectricity end at the macroscopic level in that the fundamental physics which cause the two are drastically different. Where ferromagnetism arises from alignment of unpaired electrons within certain atom's electron shells; ferroelectricity is strictly structurally driven.

Despite the apparent breakthrough, interest by the broader community was minimal until the outbreak of World War II when researchers in the United States, Russia and Japan all discovered BaTiO$_3$ contemporaneously [14]. The research into ferroelectrics continued, with many more subsequently being discovered, i.e. strontium bismuth tantalate, bismuth ferrite, relaxor ferroelectrics, etc... [17, 2]. Lead zirconate titanate ((Pb,Zr)TiO$_3$) is one that peeked a lot of interest because of its unusually high dielectric constant and its relatively low processing temperature. Because of this, much research was performed on (Pb,Zr)TiO$_3$ [1, 18, 2]. The applications for these ferroelectric materials are numerous, and include tunable filters, capacitors and memory devices. Generally these ferroelectric devices are composed of patterned layers of ferroelectric materials and electrodes, and much research is ongoing into best practices for processing and fabrication. However, a fundamental understanding of the physics and dynamics of domain structures is key to maximizing device performance as applications continue to drive miniaturization with improved capabilities [19].
Figure 2.1: Example macroscopic polarization vs. applied electric field curve, with the salient points of the curve labeled.
2.2 Ferroelectrics

As previously stated, ferroelectric materials are primarily defined by the presence of a finite electric polarization in the absence of an applied electric field. When an electric field is applied and subsequently reversed, hysteresis results. This example hysteresis of polarization vs. applied electric field is shown in Figure 2.1. Beginning at the origin (1) and applying a positive electric field, the dipoles within the material begin to align. Once they align, saturation is reached (2). If the field is then reversed, some of the dipoles within the material begin to relax until the applied field reaches zero (4). This is where many of the dipoles remain aligned and result in the finite remnant polarization. If the field continues being reversed, the polarization will eventually reach zero (5). This applied field value is known as the coercive field. Further reversal results in opposite saturation (6) and remnant polarization [20].

2.2.1 Thermodynamic explanation - LGD Theory

Landau-Ginzburg-Devonshire (LGD) theory of phase transitions is a theory based on the concept of broken symmetry. According to the theory, the broken symmetry only exists below some critical temperature, \( T_0 \), below which some singular symmetry element is broken. This breaking of symmetry is marked by an order parameter, \( \Psi \), which is zero in the high temperature phase and non-zero in the low temperature phase. The theory holds that near the phase transition, the free energy of the system, \( F \), can be represented as a power series of \( \Psi \), where only the terms allowed by the symmetry of the system are incorporated:
\[ F = F_0 + \sum_n \frac{1}{n} \alpha_n \psi^n \]  

(2.1)

\( F_0 \) is the free energy of the paraelectric phase and is unchanged through the phase transition. The \( \alpha_i \) are the system parameter coefficients [22].

For the system to remain at equilibrium, the derivative of \( F \) must be zero and the second derivative must be greater than zero:

\[ \left( \frac{\partial F}{\partial \psi} \right)_{\psi_{\text{equ}}} = 0 \]  

(2.2)

\[ \left( \frac{\partial^2 F}{\partial \psi^2} \right)_{\psi_{\text{equ}}} > 0 \]  

(2.3)

To further refine the free energy of the system, constraints must be applied to the system. The first and easiest to justify is considering that the two states \( \psi \) and \( -\psi \) are equal. This leads to a cancellation of all the odd terms in the free energy power series. Further, it is generally assumed that higher-order terms (\( \alpha_i \) for \( i > 4 \)) are only slightly temperature dependent and thus can be combined as a real positive constant which is generally neglected in the final equations as these terms do not change the general behavior of the free energy of the system. With this assumption, the above equations become:

\[ F = F_0 + \frac{1}{2} \alpha_2 \psi^2 + \frac{1}{4} \alpha_4 \psi^4 \]  

(2.4)

Again, at equilibrium, the system derivative must be equal to 0:
\[
\frac{\partial F}{\partial \psi} = 0 = \alpha_2 \psi + \alpha_4 \psi^3 \tag{2.5}
\]

If \( T > T_0 \), the second and third terms of equation 2.4 will be zero. As \( T \) becomes less than \( T_0 \), the second and third terms in equation 2.4 may be greater than zero. Using the boundary condition determined in equation 2.2, \( \alpha_2 \) must be zero at the phase transition temperature, which leads to

\[
\alpha_2(T) = \tilde{\alpha}_2(T - T_0) \tag{2.6}
\]

with \( \tilde{\alpha}_2 \) being a non-zero positive real number.

From equation 2.4, \( T > T_0 \) (above the phase transition temperature), the first term in the above equation is positive. This means the only minimum of the system is at \( \psi = 0 \), when at least one coefficient is non-zero. However, as \( T < T_0 \) the solutions to equations 2.4 and 2.5 become

\[
\psi = 0 \tag{2.7}
\]

and

\[
\psi = \pm \left( \frac{\alpha_2}{\alpha_4} \right)^{\frac{1}{2}} \left( T_0 - T \right)^{\frac{1}{2}} \tag{2.8}
\]

Only the non-zero terms are system minima and therefore equilibrium solutions. These equations lead to the famous double-well potential.

The next obvious step in this line of derivation is to understand how the above equations
change with the application of an external electric field. This is simply done by subtracting a positive constant \( h \) (representing the strength of the external field) multiplied by the order parameter \( \psi \):

\[
F = F_0 + \frac{1}{2} \tilde{\alpha}_2 (T - T_0) \psi^2 + \frac{1}{4} \tilde{\alpha}_4 \psi^4 - h \psi
\] (2.9)

If \( h \) is non-zero, then the two minima in equation 2.8 become non-equal and the equation loses its symmetric nature. This loss of symmetry means that one of the solutions in equation 2.8 becomes more energetically favorable under the application of an applied field.

For further information on this derivation please see references [23, 24].

### 2.2.2 Perovskites and Barium Titanate

Before 1949, no ferroelectric was known to exist without a hydrogen bond in the structure. However, in 1949 during the push of research following WWII, barium titanate was found to be a room temperature ferroelectric [16]. This revolutionized the field and possible applications due the cheapness and ease of synthesis, but most of all by the simple structure barium titanate exists as, known as a perovskite. Perovskites are named for the non-ferroelectric CaTiO\(_3\) phase, and the family is composed of a transition metal oxide in the form of ABO\(_3\). The crystal structure is shown in Figure 2.2, where the B-site atom lies at the center of the unit cell and the A-site at the eight corners. The oxygen atoms lie at each face of the unit cell. The reason for the ferroelectricity in perovskite oxides is the possible displacement of the center B-atom from the center of the unit cell and the simultaneous displacement of the oxygen atoms in the unit cell in the opposite direction shown in Figure
2.2. Ferroelectrics  

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Figure 2.2: The crystal structure of a tetragonal unit cell of the perovskite crystal structure. Both polarization directions are demonstrated. The example crystal structure is barium titanate.

2.2. Both average polarizations are demonstrated in Figure 2.2, although local polarization in BaTiO$_3$ are generally considered to be in $<111>$ type direction [25, 26].

As mentioned previously, not all perovskites are ferroelectric. The classic way to determine the possibility of ferroelectricity in crystalline oxides is related to the relative size of the A and B site atoms. This relation is known as the Goldschmidt Tolerance factor:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$  \hspace{1cm} (2.10)

Where $R_A$, $R_B$, and $R_O$ are the ionic radii of the A, B, and O atoms, respectively and $t$ is known as the tolerance factor. If $t > 1$, the B cation has the room to move off center and form the dipole necessary for ferroelectricity. If $t = 1$, the structure is forced into the cubic phase and it is non-ferroelectric. If $t < 1$, then the structure is generally not ferroelectric since the large B site atom does not have the ability to drift off axis with respect to the
oxygen sublattice. However, this is not a guarantee.

Barium titanate has since become one of the most researched ceramics in history because of its incredible dielectric properties (ultra-high permittivity) and its numerous possible applications. The early history of barium titanate focused largely on its very high achievable permittivity after relatively easy processing. The most common way to fabricate BaTiO$_3$ in the early experiments was to use barium hydroxyl and titania and anneal for several hours for at least 1400° C. These early experiments proved that reproducible high-k dielectrics could be fabricated and their potential for industrial applications were numerous [2, 14].

These properties lead to intense academic and industrial research, with the main goals through the 1980’s to increase the dielectric permittivity, lower the leakage current and tune the Curie temperature for a particular application. The latter goal has been seemingly solved with the addition of strontium to barium titanate. It was observed that you can control the Curie temperature of barium titanate and that the phase diagram between BaTiO$_3$ and SrTiO$_3$ (which is not a ferroelectric) was a continuum. This revelation lead to many breakthroughs in numerous applications for tunable filters and capacitors [2, 15, 14]. The previous goals began to be investigated through processing manipulation, whether it was by adding additional additives or manipulating processing environments.

### 2.3 Domains and Domain Walls

The relationship between ferroelectrics and domain walls has been extensively researched after the observation of domains during the early years of ferroelectric research. Domains
2.3. Domains

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are where the average polarization of a non-centrosymmetric crystal are in a certain crystallographic direction. Domain walls are boundaries between two adjacent domains, which are not oriented in the same direction. Domain wall motion was known to be related to ferroelectricity since the first observation of ferroelectricity \[18\]. However, their impact on the dielectric properties is still being investigated today.

There are several types of domains which are relative to the type of structure that is present in the material. For example, in tetragonal barium titanate, there are 2 types of domains: 90° and 180° domains (both are shown in Figure 2.3). Domains in barium titanate orient along the \(\langle 001\rangle\)-type directions, meaning that for 90° domains, the domain wall runs along the \(\langle 1\overline{1}0\rangle\) type directions, as polarization directions \([001]\) and \([010]\) lie 90° apart from one another. For 180° domains, the domain walls run along the \(\langle 001\rangle\) type direction, since \([00\overline{1}]\) and \([001]\) are 180° apart from one another. Generally, it is considered that 180° domain walls are around or even less than 1 unit cell length wide, while 90° domain wall widths can be hundreds of nanometers wide. This is because the strain associated with the formation of 90° domain walls is greater than 180° domain walls. However, it has been shown more recently that the previously held belief of a ‘minimum' 90° domain wall thickness does not seem to exist. Figure 2.4 demonstrates the difference in thickness between a 180° and 90° domain wall. Both of these domains are ferroelectrically active, which means they respond to the external response of an electric field \[29\]. However, since 90° domain walls cause local stress fields in the vicinity of the domain wall and are active under the application of an applied strain, these types are also characterized as ferroelastically active. They will respond to the application of an external mechanical stress. However, there is no localized strain associated with the formation of 180° domain walls, which means they
Figure 2.3: Types of domains in barium titanate. (A) is an example of an in-plane 90° domain wall, (B) is an example of an out-of-plane 90° domain wall, (C) is an example in-plane 180° domain wall and (D) is an example out-of-plane 180° domain wall [28].
are not ferroelastically active [1]. The domain evolution as a function of an applied electric field is shown in Figure 2.5.

It has been known since the 1950's that the ferroelectric response of a material corresponds directly to the switching dynamics of ferroelectric domains. It wasn't until the 1980's when investigators really started to piece together that domain density per unit volume material defines the maximum permittivity, $\varepsilon_r$ within a material [1].

Domain wall motion is generally considered to be completely reversible in phenomenological models. However, this is not always the case. During motion, they may come across pinning centers which prevent further motion and prevent further contribution to the dielectric properties. Some common pinning centers include interfaces (including grain boundaries), impurities (such as dopants or point defects) and other defects. You can visualize the ability of domain motion as an energy landscape with peaks and valleys (shown in Figure 2.6). Domain wall motion is generally considered reversible within a valley and irreversible from one side of a peak to another. The most common technique to examine the relative contribution of reversible and irreversible to the dielectric constant is to use Rayleigh analysis [1].

### 2.4 Domain Walls and Permittivity

A material's permittivity, $\varepsilon_r$, is defined as the ability of a material to store energy in the presence of an electric field. Mathematically, a material's permittivity is described how the electric displacement field $\mathbf{D}$ of a specific material is changes as a function of applied electric field $\mathbf{E}$ [20, 32]:
Figure 2.4: An illustration between the differences between (A) $180^\circ$ domain wall and (B) $90^\circ$ domain walls in barium titanate [19].
2.4. Permittivity

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Figure 2.5: The evolution of domain structures under the influence of an applied field. Shown in the image is domain nucleation, lateral growth and complete polarization reversal. [30].

Figure 2.6: The energy landscape of domain wall motion, with free energy on the y-axis and domain wall location on the x-axis. Demonstrated is both reversible and irreversible domain wall motion locations on the energy landscape diagram [31].
2.4. Permittivity

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\[ D = \varepsilon_r \varepsilon_0 E = \varepsilon_0 E + P \]  

(2.11)

where \( P \) is the polarization, \( E \) is the applied electric field, and \( \varepsilon_0 \) is the permittivity of a vacuum. From the above equation, other relations can be derived with the most common showing that the derivative of polarization, \( P \), with respect to the applied electric field, \( E \) is approximately equal to the relative permittivity:

\[ \varepsilon_r \approx \frac{\partial P}{\partial E} \]  

(2.12)

which directly reflects the previous definition. The permittivity of a material is directly proportional to how the material's polarization changes with respect to an applied electric field.

A material's polarization is broken into 2 distinct parts, the real part \( \varepsilon' \) and the imaginary part \( \varepsilon'' \), with their relation shown below:

\[ \varepsilon_r = \varepsilon' + i\varepsilon'' \]

The real part part of the dielectric constant is related to the amount of potential energy stored in the system, while the imaginary part of the dielectric is related to the dissipation of energy within the material [33].

Ferroelectric domain motion is not the only contribution to the dielectric permittivity. There are several other contributors to the permittivity including electronic and ionic displacements and space charges, the combination of these contributions are generally termed the 'intrinsic' contribution. The main determination factor for which contributions
2.4. Permittivity

are dominant depends on the frequency of the applied field. As you increase the frequency of the applied field, certain contributions begin to freeze out as the field's switching speed prevents the individual polarizing mechanism to react. This means, in general, an increase in frequency will result in a decrease in dielectric constant. These maximum frequencies are typically $10^{15}$ Hz for electronic contribution, $10^{10}$ Hz for ionic contribution, $10^{7}$ Hz for dipole contribution and $10^{3}$ Hz for space charge contribution.
Chapter

3

Ferroelectricity in the Nanoscale

3.1 Permittivity as a Function of Grain Size in Barium Titanate

Understanding how ferroelectricity changes as a function of grain size is an integral part of improving electrical devices and components that include ferroelectric components. A key example of this is demonstrated in the dielectric capacitor, where companies like Shoei Chemical and Murata have vested interest in scaling down component size while maintaining high dielectric properties. This billion to trillion dollar industry tries to continue
3.1. Grain Size

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the push for smaller and faster devices [30, 1, 34]. However, as ferroelectrics scale, multiple factors which generally aren’t considered in bulk production come into play. These include, but are not limited to, the role of interfaces, grain sizes, strains and defects.

3.1.1 Permittivity in Bulk and Thin Film Barium Titanate Based Ceramics

The investigation of how permittivity changes as a function of grain size in bulk ceramics has been carried out by a number of authors [35, 36, 37, 38, 39]. Possibly the most extensive research in how permittivity scales with grain size in bulk ceramics was performed by Arlt in the 1980’s, but he certainly wasn’t alone. Figure 3.1 demonstrates that permittivity is generally constant from grain sizes of 50 \( \mu \text{m} \) to 100 \( \mu \text{m} \). However, from 50 \( \mu \text{m} \) to 1 \( \mu \text{m} \), there is a general increase in permittivity that continues to sharpen as it approaches 1 \( \mu \text{m} \) and then dramatically falls off below 1 \( \mu \text{m} \).

Much work was dedicated to understanding this trend. The theory proposed by Arlt, et. al describes the equilibrium energy (W) of domain wall energy \( w_w \), the mechanical stress field energy \( w_m \) and the electric field energy \( w_e \) with the relation:

\[
w_w + w_e + w_m = W
\]

This relation actually predicted rather well the improved permittivity as grain size decreases. This is due to the increasing extrinsic contribution of domain wall motion to the permittivity because there is an observed higher density of domain walls at smaller grain sizes. Also, the actual width of the domain wall scales with the grain size [27].

Below this 1 \( \mu \text{m} \) grain size regime much work was done to understand the dramatic lowering of permittivity. The bulk of this work was done by Frey et. al., in two very notable
Figure 3.1: Permittivity as a function of grain size in bulk ceramic barium titanate [27].
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Publications by Frey and Payne [37, 38]. These two papers are summarized below in the following few paragraphs. Frey began her investigation by observing that below 1 μm grain sizes in barium titanate ceramics, the permittivity is indeed suppressed. This decrease seems to compress the tetragonal distortion of these ceramics. Frey, et. al proposed several ideas as to why this phenomena is present. One idea is that a depolarizing field forces the polarization to be lowered in smaller grained samples because surface polarization must always remain zero. This depolarizing field disrupts the internal ferroelectricity of the material. In larger grained samples, the field is neglected because well oriented domains, as well as surface charges, are present. However, at small grains sizes, the lack of domain formation would lead to a rise in the depolarization, which could lower the permittivity. However, Frey herself says this is unlikely because the grain boundaries themselves would act as a method to compensate the effect of the depolarization field.

Another, and seemingly more straight-forward concept, is that as grain sizes decrease, the internal stresses within the grains increases which is caused by the increased number of grain boundaries. This stress forces the unit cell to compensate, which forces the normally tetragonal distortion to become a mixture of tetragonal, orthorombic and cubic unit cells. This better facilitates the increase stresses, but also results in a lowered overall permittivity of the system, as switching becomes more difficult [37, 38].

Further work by Frey showed residual ferroelectricity in samples with barium titanate grain sizes as small as 40 nm [37, 38]. This work, and subsequent works, shows that ferroelectricity is present down to very small grain sizes. However, while these grain sizes showed ferroelectricity, the actual permittivity values were quite diminished when compared to larger grain bulk barium titanate ceramics. One very important note from these
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studies is that the Curie temperature does not shift dramatically as grain size decreases. This was surprising as many previous studies had suggested this would be the case in small-grained ferroelectrics. These decreases in ferroelectricity were described with one of the first examples of a core-shell model; a pure ferroelectric center of a barium titanate grain is surrounded by non-ferroelectric barium titanate material, called a ‘brick-wall’ model. Basically, the high permittivity center of the grain is in a parallel configuration with the low-permittivity outside part of the grain. Since they are in parallel, the resultant permittivity can be written just like capacitors in parallel:

$$
\frac{1}{\varepsilon_r} = \frac{V_{center}}{\varepsilon_{center}} + \frac{\omega V_{outer}}{\varepsilon_{outer}}
$$

(3.2)

where $\varepsilon_{center}$ and $\varepsilon_{outer}$ are the permittivity from the center and outer parts of the grain, respectively. $V_{center}$ and $V_{outer}$ are their respective volumes and $\omega$ is simply a form factor [38]. Frey is also one of the first researchers to begin to put together that permittivity is not simply a function of grain size but also a function of sample preparation.

3.1.2 Minimum Grain Size and Film Thickness for Ferroelectricity

Since the inception of ferroelectrics as a class of materials, much debate has existed as to the minimum possible grain or particle size below which ferroelectricity will not exist. The idea is that below a certain grain or particle size, the surface stresses of the particle will prevent the tetragonal distortion from existing and regardless of the applied external field, switching will not occur. Many studies looked at what the minimum grain size is for ferroelectricity and used the results to predict or extrapolate this minimum particle size [40, 41, 42]. Nearly all studies believe that the critical grain size will be below approximately...
45 nm in particle size, with predictions varying from 10 nm to 35 nm. In addition, many studies were performed with epitaxially grown ferroelectric thin films, with multiple studies showing that ferroelectricity will persist down to a few unit cells in thickness [43, 44, 45]. All studies note that this is highly dependent on substrate and contact materials and processing.

In polycrystalline thin films, the problem becomes much more complicated because not only substrate strains, but stresses caused by the additional internal stresses of grain boundaries, complicate the matter. However, previous papers clearly show ferroelectricity in polycrystalline thin films with average grain sizes of 50 nm [6].

### 3.1.3 Permittivity as a Function of Processing Temperature

As mentioned previously, one of the largest, if not the largest, key to maximizing permittivity values is the temperature at which barium titanate based ceramics are processed. This trend is true for thin films as well as bulk ceramics. For many years it was believed that the main driving force for this is that large grain sizes were only achievable at high processing temperatures. Bigger grains are correlated with more and larger domains, corresponding to higher extrinsic contribution to the permittivity [37, 46, 27, 38]. However, it was shown that this is not the case. Grain size is correlated with increasing permittivity, but processing temperature is a much stronger correlation with improved permittivity. This was shown by Aygún et. al. and their analysis is shown in Figure 3.2. The lower line and data points are processed BaTiO$_3$ at low temperatures (700°C), the middle lines is BaTiO$_3$ processed at 900°C and the top line is BaTiO$_3$ processed greater than 900°C. The main reason for the differences in the permittivity shown in Figure 3.2 is that barium titanate is refractory, meaning that high temperatures is necessary for full crystallization. In addition, most processing
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Figure 3.2: Permittivity as a function of grain size at different processing temperatures [47]. The lowest line and data set are processed at low temperatures (700°C). The next lines and datasets are BaTiO$_3$ processed with increasing processing temperature.

Techniques require complex barium and titanium compounds, which include carbon and hydrogen, to fully remove these compounds and prevent secondary or amorphous phases, which further degrade permittivity [47, 38, 48].

3.2 Domain Structures in Small-Grained Ferroelectrics

Domain structures within ferroelectrics have been determined to be of fundamental importance to the available technological applications [49, 19]. However, despite their importance,
a fundamental lack of understanding still exists as to how domain structures are modified as grain sizes decrease in size. The following section will also introduce the reader to the most common domain structures in bulk ferroelectrics and then discuss how these structures change as the geometries and grain sizes are modified. The following section will introduce both 90 and 180 degree domains structures, which are the 2 types of domains in barium titanate thin films in the tetragonal phase.

3.2.1 Traditional Domain Structures in Bulk Ceramics

Figure 3.3 demonstrates the 2 most common types of domain wall structures generally found in bulk and single crystal perovskites. The first is the classic ‘herringbone’ structure, which as the name suggests, exists as periodic needle domains. These domains are 90 degree rotations across the domain wall as demonstrated in Figure 3.3 [50, 51].

The next type of traditional structure is the classic ‘striped’ domain structures, which generally are much larger than the herringbone domains discussed earlier. In most single crystal ferroelectrics, the herringbone domain structures exist within the large striped domain structures, as shown in Figure 3.3 [51].

The structure of 180° domains in barium titanate ceramics are not as easy to pin down. Unlike 90° domain structures, the domain wall does not need to be sharp, but instead can be wavy. The domains themselves appear not to be necessarily periodic, but can exist periodically [51, 28]. Figure 2.3 (shown in previous chapter), demonstrates the qualitative differences between 180 and 90 degree domains. Further, 180° domain walls exist along the [100] type crystallographic direction. However, directly imaging and quantitatively identifying 180° domains is a more complex problem and one that will be discussed in
3.2. Small-Grained Ferroelectrics

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Figure 3.3: Herringbone and striped domains in barium titanate ceramics [51].
3.2. Small-Grained Ferroelectrics

As grain sizes are lowered in bulk ceramic barium titanate, the domain wall density increases until grain sizes of 1 \( \mu \text{m} \) are reached. Below this threshold, the number of domain walls seemingly decreases, but the morphology domain structure slowly changes. As the herringbone pattern becomes less frequent, the striped domains begin to be the only configuration present \[52\]. Figure 3.4 demonstrates how the configurations change as grain sizes decreases. These striped domains exist in grains below 300 nm in size and are easily observed via transmission electron microscopy as shown in Figure 3.4.
Chapter

4

Barium Titanate Thin Films

4.1 Ferroelectric Thin Films Overview and History

As mentioned previously, ferroelectrics are used in a wide-range of applications. More specifically, ferroelectric thin films are used in types of tunable filters, rf devices, and nonvolatile memory. The research into ferroelectric thin films started around 20 years after the discovery of barium titante in 1946, when silicon devices began to rise and it was determined that ferroelectrics could be integrated with silicon for use in non-volatile
memory [53, 54]. Work continued slowly for the next two decades, until in the early 1990’s with the start of the rise of computers, was interest truly revived on a massive research scale.

A more recent driving force for intensive research is the need for ferroelectrics for tunable microwave filters. One reason for this is the so called ‘varactor gap’, where no semiconductor based varactor has a high enough quality factor and tunability for frequencies in the 10-20 GHz range [55, 56]. Through research, it was determined that ferroelectric thin film varactors in this range have a substantially higher Q-factor in this range. In addition, ferroelectrics were determined to integrate very nicely with silicon based devices [57].

A unique aspect of ferroelectric based devices is that both the non-polar paraelectric and polar ferroelectric phase can be used in tunable devices. It is interesting to note that in certain applications the paraelectric phase is actually more desirable because of the lack of hysteretic loss caused by domain wall motion [58]. The most commonly, and seemingly best, ferroelectric to be used for this application is barium titanate in solid solution with strontium titanate. Barium and strontium share the A-site in the perovskite unit cell and the mixture is a continuum without the driving force for phase separation. The reason for barium strontium titanate, being the leading candidate for this application is that strontium titanate is not a ferroelectric and by adding it to barium titanate you lower the Curie temperature of the barium titanate to below room/working temperature of the device. By doing so, you remove the hysteretic loss caused by ferroelectric domain wall switching during field reversal, but retain much of the desirable tunable properties that barium titanate inherently has [56]. Barium strontium titanate is one a very non-linear paraelectric, with the reason for its non-linear response in the paraelectric phase still not completely
understood [59]. However, despite the advantages of using barium strontium titanate in devices, for tunable applications there are some drawbacks that much work has been done to remedy. In particular, the processing temperature required for maximum performance of barium strontium titanate is generally several hundred degrees higher than is possible for integration with common silicon based substrates. Further, residual ferroelectricity leading to high losses is a persistent problem in any of these devices. Both problems and recent work to remedy these problems are described in detail in the following sections.

4.1.1 Residual Ferroelectricity in Barium Strontium Titanate Thin Films

Barium strontium titanate based thin films are used in applications where it is necessary to keep the material in the paraelectric phase but only slightly above the Curie temperature. In this regime, no ferroelectricity should be observed since only the cubic paraelectric phase should be present. However, multiple reports demonstrate that many times there is residual ferroelectricity above the Curie temperature in barium strontium titanate ceramics [60, 61, 8]. Garten et al. performed a systematic study of residual ferroelectricity in barium strontium titanate synthesized with two different processing methods. The first method was chemical solution deposition (CSD), and the other was sputtering. In this paper, Garten measured the tunability and shows the characteristic hysteresis generally associated with domain switching at three different compositions, Figure 4.1.

Garten utilized Rayleigh analysis and determined that residual ferroelectricity was present as much as 65° C higher above the expected Curie temperature. The Curie temperature was determined from the maximum capacitance measurement as a function of temperature. Her conclusion was that nanopolar regions exists within the barium strontium
4.1. Ferroelectric Overview and History

Figure 4.1: Dielectric constant and loss as a function applied electric field of BaSrTiO₃ at 3 different Ba/Sr compositions [8].
titanate and these regions locally have differing Curie temperatures causing the very diffuse phase transition. Chapter 7 discusses how these nanopolar regions likely arise from local inhomogeneity between the A-site cations of strontium and barium [8].

4.1.2 Lowering the Processing Temperature of Barium Titanate Based Thin Films: Liquid Assisted Annealing

Since barium titanate is refractory, the temperatures needed for complete densification, complete crystallization and crystal growth are generally quite high, >1250° C. One method, which is commonly utilized to lower the processing temperature of barium titanate ceramics, is to add a phase to the processing of the bulk material. This will form a liquid phase at the desired sintering temperatures. This phase will provide a method or route for material transport during sintering, thereby moving material quickly and efficiently at lower temperatures than in the solid state. This results in densification and growth of the microstructure. The key to all of this, however, is that barium titanate must be very soluble in the liquid forming phase. There are some obvious problems which generally arise, including secondary phase formation, either from residual flux reacting with the ceramic and residual amorphous regions existing at grain boundaries. In addition, unintentional doping of the ceramic with the flux system could drastically change the defect state of the material and effect performance [62].

Several types of these ‘flux’ systems have been utilized in the past and generally fall into 3 distinct categories: glass-based, lead based and fluorides [63]. The fluoride based systems do seem to dramatically lower the needed processing temperature of barium titanate ceramics while maintaining high permittivity. However, the main flaw with these
systems is the unpredictable fluorine, which is very volatile and makes reproducibility nearly impossible [64]. The lead based systems are also very promising in making high quality ceramics with good permittivity, but the obvious toxic nature of lead has made these processing routes less than optimal [65].

A number of different glass based fluxes have proven effective at lowering the sintering temperature of barium titanate. The first, and most obvious, glass based additive is SiO$_2$, which showed the ability to reduce the sintering temperature of bulk barium titanate by more than 50$^\circ$ C [66]. Another commonly used glass used in fluxes is the B$_2$O$_3$ system since it generally has a very low melting temperature. Also, barium titanate is very soluble in compounds which are boron based [63].

Ihlefeld et al. showed in a number of publications that the addition of a barium borate based flux dramatically improved both the microstructure and dielectric properties of barium titanate thin films[3, 4]. Ihlefeld et al. began by adding $\text{BaO} - 2\text{B}_2\text{O}_3$ at different amounts to chemical solution deposited barium titanate thin films on copper foil substrates without any evidence of secondary phases through x-ray diffraction even though the processing temperature was only 900$^\circ$ C. The resultant microstructures were drastically modified with increasing flux content with the higher flux concentrations having grains several microns in size. Corresponding with each of these flux concentrations is an improvement in dielectric properties. Another interesting characteristic of the higher flux barium titanate films is that it is only polycrystalline barium titanate thin film that shows clear peak splitting in x-ray diffraction. This is clear evidence that the films are in fact tetragonal and there must be ferroelectric domains present, from both the x-ray data and the dielectric properties [3].
4.1. Ferroelectric Overview and History

Ihlefeld et al. further studied the non-linearity within the permittivity as a function of applied field and found a maximum permittivity of 2900 in the highest fluxed sample. Ihlefeld et al. further compared boron and barium borate additives and found that barium borate results in a higher permittivity. However, the pure boron addition resulted in the largest average grain size [4].

Harris et al. progressed these studies further by applying similar techniques to pulse-laser deposited barium titanate thin films on sapphire substrates. Harris found many of the similar results as Ihlefeld. In particular, that the microstructure and dielectric properties of barium titanate thin films with barium borate flux are improved. However, unlike Ihlefeld et al., there appears to be no presence of amorphous secondary phases between grain boundaries. Further, Harris et al. discovered that the thin films were under large bi-axial strain. This strain did not result in any obvious cracking of the thin film. However, a 50° C shift in the Curie temperature was observed and was attributed to the residual strain. Further, the mechanisms for the improvement in microstructure in the barium titanate thin films with the addition of barium titanate thin films will be further discussed in Chapter 6 [6].

It should be noted that neither Harris nor Ihlefeld observed the formation of traditional barium titanate ferroelectric domain structures despite intense microscopy being performed for both. This is despite the fact that both authors attribute the non-linearity in the dielectric response to the extrinsic contribution of domain wall motion [3, 6, 4]. Understanding how ferroelectric domains exist within these thin films is discussed in Chapter 9.
4.2 Domain Structures in Thin Films

Domain structures in barium titanate thin films are actually far more difficult to image than bulk ceramics. Many of the best techniques to image ferroelectric domains, such as optical, PFM, and TEM, do not seem to quantitatively give information about domain structures even in barium titanate thin films regardless of thickness or synthesis method unless the thin films are epitaxial grown. However, even with the lack of direct evidence of domain structure, their presence is unquestionably observed [6, 1, 30]. The observation of domains in the dielectric properties is almost always tied to non-linearity in the dielectric response of the thin film. This non-linearity is usually a direct result of domain wall motion, an exception of course exists with barium strontium titanate, where non-linearity exists in the paraelectric phase [8, 59].

The actual structure of the domains in the thin films has been simulated using phase-field models based on LGD theory. Li and Chen found that the domain structure of ultrathin film barium titanate thin films varied dramatically as a function of biaxial strain within the thin film. They also observed that at high in-plane strain's, the phase diagram is severally modified. Figure 4.2 shows the phase diagram of barium titanate as a function of temperature and biaxial strain. It is interesting to note that at zero applied strain and room temperature Li and Chen predict a mixture of orthorhombic and tetragonal barium titanate phases. Figure 4.3 demonstrates the different domain structures at these different strain states within the material. It is very interesting to note that many of the configurations contain non-periodic domain structures and these abnormal morphologies exist at multiple strains and temperatures [67].
Figure 4.2: Temperature-Strain diagram of ultra-thin epitaxial barium titanate thin films [67].
Figure 4.3: Domain and phases of ultra-thin barium titanate thin films as a function of temperature and strain: (a) Phase $T^F$ at $T = 25^\circ$C and $\epsilon_0 = -1.0\%$, (b) phase $T^F$ and $O^F$ at $T = 75^\circ$C and $\epsilon_0 = -0.05\%$, (c) phase $O^F$ at $T = 50^\circ$C and $\epsilon_0 = 0.2\%$, (d) phase $M^F$ at $T = -25^\circ$C and $\epsilon_0 = -0.05\%$, (e) phase $M^F$ and $O^F$ at $T = -25^\circ$C and $\epsilon_0 = -0.1\%$, (f) phase $O^F$ at $T = 25^\circ$C and $\epsilon_0 = 1.0\%$, (g) phase $O^F$ at $T = 25^\circ$C and $\epsilon_0 = 0.25\%$, and (h) phase $M^F$ at $T = -100^\circ$C and $\epsilon_0 = 0.1\%$. $T^F$ is tetragonal ferroelectric phase, $O^F$ is orthorombic ferroelectric phase, and $M^F$ is monoclinic ferroelectric phase [67].
Obviously, the temperature-strain diagram of Li and Chen cannot be applied directly to a polycrystalline thin film that is several hundred nanometers thick, such as from Harris et al. [6, 67]. However, it may be used as a preliminary evidence that domain structures in barium titanate may not exist in traditional configurations. This hypothesis will be discussed in Chapter 9.
Chapter

5

Common Experimental Methods

This chapter gives a description of common experimental methods used throughout the work. In addition, it gives specific insights into using any novel methods developed during the dissertation research. Each following chapter will discuss specific experimental details relevant for that section.
5.1 Sample Preparation

This section will delve into specific details describing samples examined. This will include samples bought commercially and synthesized at NCSU. In general, the work is based on samples that were not made by the author but were externally bought from a company or synthesized by Jon-Paul Maria's research group at NC State University. These samples were mostly fabricated by Dr. David Harris during the course of his graduate work [68].

5.1.1 Single Crystal Information

For the experiments to map 180° domain structures in ferroelectric oxides, high quality single crystals of lithium niobate and barium titanate crystals were purchased. The lithium niobate crystals were purchased from Deltronic Crystal Industries, Inc. in Dover, NJ and were periodically poled with 180° domains, 12 µm in spacing. A diagram of the lithium niobate crystal is shown in Figure 5.1 This spacing was chosen for its ease of finding the domain structures and mapping with electron backscatter diffraction.

The barium titanate single crystals were purchased from SurfaceNet Gmbh in Rheine, Germany. The crystals were nominally undoped and were not poled, which lead to a large number domain structures evident in the electron backscatter maps and scanning electron microscopy. An optical image of the barium titanate crystal is shown in Figure 5.2.

5.1.2 Pulse Laser Deposition of Thin Films

The main synthesis method for the thin films used in this study was pulse laser deposition (PLD). PLD is a physical vapor deposition technique, where a high-powered laser ablates a
5.1. Sample Preparation  

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Figure 5.1: A diagram of the periodically poled lithium niobate single crystals. The diagram includes the optical applications for the single crystals. Diagram provided by Deltronic Crystal

Periodically-Poled LiNbO$_3$

Positive Polarization  

Negative Polarization

180° Periodic domains
target of material of the desired composition. The material then vaporizes under the impact of the laser and a plume of material (in the form of highly energized plasma) impacts a target a set-distance away. A diagram of PLD is shown in Figure 5.3.

Once the plume impacts the substrate, which many times is heated, nucleation and growth may occur and a thin film is produced. Depending on the substrate, the resulting thin film may or may not be textured. However, if the substrate is not heated above a nucleation temperature, nucleation may not occur, and in this case, the resultant thin film will be amorphous. One of the biggest benefits of PLD, is that the composition of the target and the resulting thin film is considered to be identical [34, 69, 1].
Figure 5.3: A diagram of the PLD system, including the laser, target, substrate and vacuum system.
5.2 Electron Microscopy Based Techniques

The following sections outlines the different electron microscopy based techniques utilized throughout the course of this work. Some of the sections provide a brief outline for how the work was performed, which is intended to provide a general guide for a new user of a technique. The outline should not be used as explicit user manual as each technique will vary for each sample analyzed.

5.2.1 Focused Ion Beam Sample Preparation

Nearly all samples analyzed in the following chapters were prepared by focused ion beam (FIB) sample preparation (except for the few prepared by mechanical polishing, which is discussed in the next section). FIB utilizes a liquid gallium source, which, with the application of an applied electric bias, propels large Ga ions at a target. Depending on the applied field, the gallium ions will mill into a sample at different rates. Generally, a large voltage and amperage are needed initially to mill deep into the sample; I prefer to use 30 kV and 15 nA to make an initial hog out. Once this is preceded by the deposition of a Pt bar to protect the area of interest that will eventually be thinned to electron transparency. Once the initial hog out is performed, subsequent milling is performed by slowly stepping down amperage and voltage until the sample is under 1 µm thick. At this point, lift out is performed and the sample is mounted to a TEM grid, generally made out of copper or molybdenum. At this point final thinning occurs and low voltage and amperages, e.g. 2 kV and 50 pA, are used to limit Ga implantation and surface damage, both of which can lead to artifacts during microscopy and later analysis.
5.2. Electron Microscopy Based Techniques Chapter 5. Common Experimental Methods

Figure 5.4: A focused ion beam prepared TEM or TKD sample. In this case, it was a thin film sample, with the thin film located at the top of the sample. The substrate is sapphire.

Figure 5.4 shows a prepared FIB sample mounted onto a Protochips in-situ chip. The sample at this point is electron transparent and ready for electron microscopy. The general size of a FIB sample is under 20 µm wide and 10 µm tall. This gives a large area for viewing, however, it pales in comparison with the area of view for mechanically polished samples. Also, FIB suffers from a number of potential drawbacks, including surface damage, gallium implantation and material redeposition. Sample redeposition in particular can lead to false impressions during chemical spectroscopy based techniques, such as electron energy loss spectroscopy and energy dispersive spectroscopy. For these reasons, all care must be taken when preparing FIB samples and scrutiny must be applied for each result to be sure results are accurate and not a result of sample preparation.

For this work a FEI Quanta 3D dual beam SEM/FIB with a field emission source for all FIB sample preparation.
5.2.2 Mechanical Polishing

For certain samples, FIB was not the preferred method of sample preparation. This was the case for most of the thin film samples prepared for TEM because during any type of mechanical polishing the films would delaminate from the substrate and prevent further polishing. These samples were prepared with mechanical polishing, where diamond lapping films and an Allied Multiprep system were utilized. In this set-up, large grit-sized (15 \( \mu \text{m} \)-3 \( \mu \text{m} \)) diamond lapping films are initially used to thin and smooth a sample. The grit size is then slowly decreased (3 \( \mu \text{m} \)-0.1 \( \mu \text{m} \)) until the sample is under 30 \( \mu \text{m} \) thick. At this point the polishing is changed to an angle and wedge polishing begins. The sample should continue to thin until fringes are observed, which result from the transmission and interference of light in thin samples. These fringes mean the sample is near to electron transparency. If the sample is showing large amounts of fringing the sample is likely fine for initial viewing in the electron microscope. If the sample requires further thinning, then a liquid suspension with silica particles can be used with a felt polishing wheel to further thinning. If desired thickness is still not reached, ion milling may be used, where low energy ions (0.5-5 kV) are blasted at the sample and small amounts of material is removed and the sample is slowly thinned.

Figure 5.5 shows an optical image of a mechanically polished sample. Notice that the total thin area is several hundred microns long, leading to a large viewing area. There are some drawbacks to mechanical polishing. It is not a site specific technique, unlike FIB, where a particular area is easily chosen to be thin. In addition, diamond and silica particles may contaminate the surface of the sample leading to false feature shapes (however, there are methods to remove these particles). Further, due to the mechanical stress applied during
thinning, changing the strain state of the material is of great concern when the bulk strain state may be of interest during electron microscopy analysis. In general, much thinner sample thickness’ can be achieved with mechanical polishing than with FIB. It should be noted that mechanical relaxation can occur for any sample prep procedure, including FIB.

5.2.3 Transmission Electron Microscopy and Scanning Transmission Electron Microscopy

The electron microscopy contained in this work was performed on a number of different electron microscopes, but particularly the JEOL 2000FX, 2010F and FEI Titan with aberration correction and monochromator were used. In TEM, high energy electrons are focused through a number of magnetic lens onto a sample which is electron transparent. When the sample and electron beam interact, inelastic and elastic scattering of the electrons occur. Both diffraction patterns and images can be formed from these scattering events.
In addition, chemical information can be obtained from the samples due to the inelastic scattering of electrons, as well as from characteristic X-rays produced from the electron sample interactions.

In general, 200 kV electrons were used for all the experiments performed. Bright-field diffraction contrast imaging and electron diffraction were performed on the JEOL 2000FX and JEOL 2010F microscopes. An example bright field image and selected area electron
diffraction (SAED) pattern are shown in Figure 5.6. The diffraction patterns give information on the phase and orientation of the samples examined, while the diffraction contrast images give information on the microstructure of the material.

The FEI titan was used to perform high angle annular dark field (HAADF) imaging and electron energy loss spectroscopy (EELS). The titan has very high quality electron gun (an XFEG 60-300 kV), which leads to very low energy spread while performing EELS.

5.2.4 Electron Energy Loss Spectroscopy

Electron energy loss spectroscopy (EELS) is a very commonly used technique to investigate chemical composition within material systems. A post-column spectrometer measures the energy of transmitted electrons, many of which have lost a finite amount of energy during inelastic interactions between the incident electron beam and the sample. Some of energy loss will correspond to core-shell ionization of the atoms in the material, and from the resultant signals atomic ratios can be calculated. A core shell EEL spectra of BaTiO$_3$ is shown in Figure 5.7.

EELS does have some limitations: without the use of a standard, the use of theoretical cross sections must be used. These cross sections are known to lead to large amounts of error present in any EELS edge higher than L (M-edge, N-edge... etc.), which skews results [70].

In this work, theoretical cross sections were used. More on the technique will be discussed in the appropriate chapters.
Figure 5.7: An example core shell EELS spectra of Ba, Ti, and O core loss shells from a barium titanate sample.
5.2.5 Electron Backscatter Diffraction

Electron backscatter diffraction (EBSD) was performed extensively throughout this work. EBSD utilizes a scanning electron microscope and a EBSD detector, which consists of a phosphorus screen and a camera. The sample is tilted to 70° relative to the horizon and the electron beam impacts the surface of the sample. The electrons diffract and are collected by the EBSD detector. A diagram of the EBSD is shown in Figure 5.8.

Figure 5.8: A pictorial representation of the experimental set-up of EBSD.
EBSD is very sensitive to crystalline phase and orientation information. Further, because of significant dynamical diffraction, it can give information about orientation in non-centrosymmetric crystal systems (i.e., it can, in theory, distinguish between \((h k l)\) and \((\bar{h} \bar{k} \bar{l})\).

From the EBSD patterns (an example pattern is shown in Figure 5.9), the phase and orientation can be determined. Indexing algorithms typically utilize a Hough transform based indexing method, where the bands locations are determined in Hough space. Hough space is advantageous for indexing, because through a hough transform, lines are transformed into points. From these points the band widths and inter-bandular angles are determined and compared to look-up tables. The orientation and phase information is gathered from this comparison. For each identified orientation a quality factor is given, which is a goodness of fit and generally relates how the experimental pattern fits the simulation and this value varies among commercial softwares.

### 5.2.6 Transmission Kikuchi Diffraction

Transmission Kikuchi Diffraction (TKD) is very closely related to EBSD. The data collected in TKD is mostly identical to EBSD. The primary difference between the two techniques is that TKD is performed in a transmission geometry and EBSD is a back-scatter geometry typically from a bulk sample. For TKD, this results in a lowered interaction volume than EBSD. The differences are demonstrated in Figures 5.10 and 5.11, respectively. This lowered interaction volume leads to an improved spatial resolution, as low as 5 nm in most experimental set-ups (vs. 50 nm for most EBSD set-ups for bulk specimens).

For the experimental set-up, the TKD sample, is tilted 20° relative to the horizon and
Figure 5.9: An example EBSD pattern of barium titanate.
Figure 5.10: Monte Carlo simulation of the electron beam interacting with a thin sample, which simulates TKD. Simulation performed in the software CaSiNO.
Figure 5.11: Monte Carlo simulation of the electron beam interacting with a bulk sample, which simulate EBSD. Simulation performed in the software CaSiNO.
the forward scattered electrons are collected by the EBSD detector as shown in Figure 5.12. To further enhance spatial resolution, small working distances are used. For instance, the author generally recommends a working distance of 2 mm. This drastically changes the geometry of the pattern collection, which will be shown to have a significant impact on the indexing sensitivity as explained in Chapter 8.
Mechanisms for microstructure enhancement in flux-assisted growth of barium titanate on sapphire

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Chapter 6. Mechanisms for microstructure enhancement in flux-assisted growth of barium titanate on sapphire

6.1. Introduction

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A low-temperature thin-film processing method for BaTiO₃ is studied to understand microstructure development in the presence of a liquid-forming phase. The addition of a eutectic barium borate flux is found to prevent nucleation of BaTiO₃ during pulsed-laser deposition on sapphire substrates at 400 °C. Subsequent thermal annealing above the flux's eutectic temperature dramatically enhances the film's microstructural development and crystallinity. A secondary reaction phase of barium aluminate is identified at the substrate interface in both unfluxed and fluxed films, although it is more pronounced in the fluxed films. This barium aluminate phase in conjunction with the liquid flux serves to nucleate {111} twins in the barium titanate, which subsequently lead to enhanced grain growth. The resulting large-grained and dense thin films result in markedly improved dielectric properties.

6.1 Introduction

Nonlinear thin-film dielectrics are of great interest for their applications in, for example, tunable and memory devices [71, 72, 73]. One common material of interest is BaTiO₃, which exhibits a large permittivity and nonlinear dielectric response and has been widely used in multilayer ceramic capacitors [74]. Thin-film BaTiO₃, while attractive for device integration, typically does not realize bulk-like properties due mainly to restrictions in processing
temperature and thus crystalline perfection [47]. Efforts have been made to enhance the dielectric and tunable properties of these films by a variety of methods including doping and alternate synthesis approaches [73, 75, 76, 5, 77]. For example, liquid-phase sintering, a commonly used method for promoting densification and grain growth in bulk ceramics and metals, has recently been applied to thin-film BaTiO$_3$ with promising results [47, 3, 6]. The addition of a liquid-forming flux increases grain size and film density, enabling improvements in dielectric properties to an extent that they are comparable to bulk BaTiO$_3$. As in any fluxed material, residual amorphous and secondary phases may be found at grain boundaries and triple junctions, which dilute the ferroelectric and dielectric properties [3, 63, 78]. Recently, Harris et al. demonstrated the ability to produce dense, large-grained BaTiO$_3$ thin films without residual amorphous or secondary phases at the grain boundaries and triple junctions; these films were grown on sapphire substrates by pulsed laser deposition (PLD) at processing temperatures as low as 900 °C using a eutectic BaO - B$_2$O$_3$ (BBO) flux [6]. The resulting films exhibited an increase in relative dielectric tuning from 20 % for the unfluxed films to as much as 70% for the fluxed compositions. Even though the flux leads to an improved overall larger grain size, enhanced crystalline perfection, and hence tunable properties, a reaction phase of BaAl$_2$O$_4$ is observed at the interface between the sapphire substrate and BaTiO$_3$ thin film [6]. The formation of BaAl$_2$O$_4$ is expected, as BaAl$_2$O$_4$ is an intermediate compound between BaO and Al$_2$O$_3$ [79] and has been found to form between other barium containing thin films and sapphire substrates under similar synthesis conditions [80, 81, 82, 83]. In this study, we investigate the formation of the BaAl$_2$O$_4$ interphase and its role in the overall thin-film microstructure evolution.
6.2 Experimental Procedure

All samples were fabricated using PLD from single targets that were either pure BaTiO$_3$, or incorporated the barium borate flux with the ratio 94.5 mol% BaTiO$_3$, 1.36 mol% BaO, and 4.13 mol% B$_2$O$_3$ powders and the unfluxed targets containing pure BaTiO$_3$. Both un-fluxed and fluxed samples were deposited onto c-sapphire substrates at 400 °C. Further details on flux and film preparation as well as dielectric and strain measurements are available in Harris et. al [6]. The thickness of the deposited films ranged between 350-500 nm. Samples were annealed subsequently for 1 h at 900 °C in air. Specimens were prepared for transmission electron microscopy (TEM) utilizing a FEI Quanta 3D-FEG dual-beam focused ion beam (FIB; FEI, Eindhoven, Netherlands). FIB thinning of the samples was performed by systematically stepping down the voltage from 30 to 2 kV to minimize sample damage caused by the ion milling. Samples were then examined in a JEOL 2000FX TEM for diffraction-contrast imaging, a JEOL 2010F TEM for high-resolution transmission electron microscopy (HRTEM; JEOL Ltd., Tokyo, Japan) and electron energy loss spectroscopy (EELS), and a FEI Titan for scanning transmission electron microscopy, energy dispersive x-ray spectroscopy, and EELS. Average grain size and thin-film morphology were assessed from the TEM images. Secondary phases were identified by selected area electron diffraction, EELS, and fast Fourier transforms of HRTEM images. Hot-stage x-ray diffraction (XRD) was performed on a PANalytical Empyrean system with Cu Ka radiation in the Bragg-Brentano geometry with a ramp rate of 5 °C/min and a scan taken every 30 s.
6.3 Results

The microstructures of the as-deposited fluxed and unfluxed BaTiO$_3$ thin films are shown by the representative TEM images in Fig. 6.1. The unfluxed samples [Fig. 6.1a] exhibit conically shaped microcrystalline regions that nucleate as close as 70 nm from the substrate interface. The electron diffraction pattern (inset) and XRD patterns (not shown) indicate that these microcrystals are perovskite BaTiO$_3$. The fluxed samples [Fig. 6.1b] appear completely amorphous in the as-deposited state, as evidenced by the uniform intensity in the TEM images, the diffuse electron diffraction patterns and by further XRD studies (not shown). Local chemistry of the sapphire-BaTiO$_3$ interface in the as deposited state was studied by performing EELS maps across the interface at a step size of 4 nm. Figure 6.2 shows...
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6.3. Results

Figure 6.2: EELS intensity profiles of Ti (blue) and Al (black) in the as-deposited (a) unfluxed BaTiO$_3$ and (b) fluxed thin films across the interface region of the BaTiO$_3$ thin film and sapphire substrate demonstrating the intermixing that occurs during deposition. The interface region denoted by vertical black lines was defined as deviation of more than 10% from the bulk EELS intensity.

representative profiles of the integrated intensities of the Ti $L_{2,3}$ and Al K EELS edges across the interfaces in a typical pure and fluxed film. The chemical width of the interface in the pure sample is approximately 8-12 nm, whereas the fluxed sample showed a width of 13-20 nm, indicating that the flux impacts the extent of the initial interfacial mixing layer.

XRD patterns from an in situ heating measurement of flux-modified BaTiO$_3$ thin films are shown in Fig. 6.3. BaTiO$_3$ appears to form around 530 °C as indicated by the broad, diffuse peak at 31.5°. This low-order BaTiO$_3$ peak corresponds to the 110-type reflections and remains relatively broad until sharpening dramatically and shifting to higher scattering angles around the flux melting temperature of 870 °C; this is concomitant with the sharpening of higher order 111 and 200 BaTiO$_3$ diffraction peaks. At the same temperature, 0004 peak from hexagonal BaAl$_2$O$_4$ become evident. The diffraction peaks associated with both
BaTiO$_3$ and BaAl$_2$O$_4$ become more intense and sharper at the final annealing temperature of 900 °C.

Figure 6.4 shows TEM cross-sectional images of the post-annealed BaTiO$_3$ fluxed and unfluxed samples after annealing in air for 1 h at 900 °C. The average grain size of the unfluxed sample is 55 nm and the film contains substantial porosity. In contrast, the fluxed films are fully dense with an average grain size of 330 nm. These large grained fluxed samples contain {111} twin lamellae, as can be observed in Figs. 6.4(b) and 6.4(c) with many of the {111} twins sharing a boundary with the substrate interface.
6.3. Results

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Figure 6.4: Microstructures of the post-annealed (a) unfluxed BaTiO\textsubscript{3} and (b) fluxed BaTiO\textsubscript{3} thin films. (c) An electron diffraction pattern showing an example of a \{111\} twin, which are found in many of the larger grains of the fluxed BaTiO\textsubscript{3} thin films.

Figure 6.5: Bright-field cross-sectional TEM and HRTEM micrographs demonstrating the occurrence of BaAl\textsubscript{2}O\textsubscript{4} in (a) the unfluxed BaTiO\textsubscript{3} (inset) and (b) the fluxed BaTiO\textsubscript{3} thin films. (c) An electron diffraction pattern showing the crystallographic orientation relationship between the BaAl\textsubscript{2}O\textsubscript{4} and the sapphire substrate.
In annealed BaTiO₃ thin films with and without flux, a crystalline reaction phase is present at the film-substrate interface as is outlined in Fig. 6.5. In the unfluxed samples [Fig. 6.5(a) inset], the reaction results in a continuous reaction layer, identified as BaAl₂O₄, about 3-5 nm in thickness between the BaTiO₃ and Al₂O₃ substrate. In the fluxed samples [Fig. 6.5(b)], BaAl₂O₄ is also present at the interface but occurs in discrete pockets that may penetrate up to 190 nm into the BaTiO₃ layer. A representative electron diffraction pattern in Fig. 6.5(c) shows that the interface phase is BaAl₂O₄ and that it adopts an epitaxial relationship with the underlying sapphire substrate. The orientation relationship is

\[(2\bar{4}20)BaAl₂O₄//(1\bar{2}10)Al₂O₃\]

\[\{10\bar{1}0\}BaAl₂O₄//(10\bar{1}0)Al₂O₃\]

The phase and orientation relationship is consistent for all of the BaAl₂O₄ grains examined in the fluxed samples.

Figure 6.6 is a HRTEM image showing the presence of c-alumina at the interface between the sapphire substrate and a region of BaAl₂O₄ in a fluxed BaTiO₃ sample. The c-alumina is observed in the as-deposited fluxed films and the annealed fluxed and unfluxed films.

### 6.4 Discussion

Diffraction, microstructure, and microchemical analyses provide insight into the role of the BBO flux in the BaTiO₃ microstructural evolution in terms of both nucleation and growth, both of which appear to be significantly affected by the presence of this flux. The unfluxed BaTiO₃ films in the as-deposited state exhibit crystalline regions with a conical morphology
Figure 6.6: A HRTEM micrograph showing the occurrence of c-alumina in the substrate of a post-annealed fluxed BaTiO$_3$ sample with its accompanying FFT’s demonstrating the secondary phase.
that shares microstructural similarities to amorphous silicon. In the case of amorphous silicon, a roughening transition during growth induces crystalline nucleation at the film-vacuum interface [84, 85]. Importantly, however, the addition of hydrogen during deposition has been shown to delay or prevent crystallite nucleation in amorphous silicon [86]. In the BaTiO$_3$ system, BBO appears to prevent crystallite nucleation; therefore, we speculate that the mechanism that retards nucleation is related and attributed to the glass network forming capabilities of boron oxide. The metastable amorphous state of the fluxed samples may increase the energy barrier to nucleation thereby reducing the homogeneous nucleation density during subsequent annealing while promoting heterogeneous nucleation at the substrate interface.

While full crystallization and the formation of a discrete BaAl$_2$O$_4$ interphase are not evident until post-deposition annealing, interdiffusion at the interface is present in both the unfluxed and fluxed as-deposited state. After annealing at 900 °C for 1 h, the unfluxed films exhibit a continuous 3-5 nm thick layer of crystalline BaAl$_2$O$_4$, which is approximately the same thickness as the as-deposited mixing layer. In contrast, the formation of BaAl$_2$O$_4$ in the fluxed BaTiO$_3$ is not restricted to the thickness of the initial mixing layer of the as-deposited samples, instead forming as a patchy interface layer that can extend as deep as two-hundred nanometers into the thickness of the film. Hot-stage XRD of these samples shows a direct correlation between the BaAl$_2$O$_4$ crystallization and the melting point of the BBO at 870 °C, indicating that the liquid-phase flux is associated with the BaTiO$_3$ reaction kinetics.

The microchemical and microstructural data also suggest that diffusion of Al and O out of the sapphire substrate toward the BaTiO$_3$ film dominates the mass transport. This is
especially evident in the fluxed samples, where the BaAl\textsubscript{2}O\textsubscript{4} grows away from the interface into the BaTiO\textsubscript{3} film. Even in the as-deposited state, depletion in the EELS Al signal is evident within the sapphire adjacent to the interface [Fig. 6.2(b)]. Furthermore, EDX and secondary ion mass spectrometry analysis of annealed samples (not shown) confirm the presence of Al throughout the BaTiO\textsubscript{3} film. The Al and O transport out of the sapphire substrate results in a relatively disordered region in the sapphire; these disordered regions accommodate the Al and O vacancies and converts locally to c-alumina when the vacancy concentration is high enough (Fig.6.6), as c-alumina is less dense than sapphire.

In addition to affecting the formation of the interface reaction layer, the BBO flux also has a dramatic influence on the final microstructure of the BaTiO\textsubscript{3} film. The hot-stage XRD data indicate increased ordering in the BaTiO\textsubscript{3} beginning at temperatures as low as 530 °C, as evidenced by the 110 BaTiO\textsubscript{3} reflection at 31.5° 2h. Around the melting temperature of BBO, 870 °C, a marked sharpening of the 110 reflections is accompanied by a shift to higher scattering angles and the appearance of higher order diffraction peaks, which is consistent with a marked increase in crystallinity and grain size. Importantly, these changes in the BaTiO\textsubscript{3} crystallinity are directly correlated with the nucleation of crystalline BaAl\textsubscript{2}O\textsubscript{4}.

The authors surmise that the BBO liquid-phase influences the nucleation of both the BaAl\textsubscript{2}O\textsubscript{4} interface phase and the BaTiO\textsubscript{3}, and we believe that these two nucleation events may be coupled with the BaAl\textsubscript{2}O\textsubscript{4} serving as a heterogeneous nucleation site for the BaTiO\textsubscript{3} in the presence of a liquid phase. While unconfirmed experimentally, this hypothesis is supported by the fact that the fluxed samples have \{111\} twins in the large BaTiO\textsubscript{3} grains, many of which appear to emanate from the BaAl\textsubscript{2}O\textsubscript{4} regions. \{111\} BaTiO\textsubscript{3} twin formation has been observed and studied since the 1950s in both bulk ceramics and single crystals.
grown from a liquid flux[87]. The \{111\} twin formation is typically associated with excess Ti, but this has been shown to be an indirect effect via the formation of Ti-rich polytitanate phases, e.g., \( \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \). Lee et al. demonstrated that in an oxidizing atmosphere, \( \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \) grains act as nucleation sites for \{111\} twins in \( \text{BaTiO}_3 \); the resulting twinned grains exhibit abnormal growth with a preferred \{111\} growth direction[88]. The BBO-fluxed \( \text{BaTiO}_3 \) films in the present study exhibit a large size distribution with the larger grains containing \{111\} twins, however our processing temperature is several hundred degrees below the minimum temperature needed for \( \text{Ba}_6\text{Ti}_{17}\text{O}_{40} \) formation, but we believe that the \( \text{BaAl}_2\text{O}_4 \) interphase in the presence of a liquid phase acts as a similar nucleation site for the \( \text{BaTiO}_3 \) and \{111\} twins. It has previously been suggested that abnormal grain growth is promoted by the existence of \{111\} twins and that through seeding of twins a larger microstructure can be realized [87, 88, 89]. Kang notes that grains containing a \{111\} twin will grow preferentially in that direction because of a reduction of the critical driving force for boundary migration where the \{111\} twin intersects a grain boundary [90]. The existence of the \{111\} twins in the fluxed \( \text{BaTiO}_3 \) suggests a possible mechanism that drives the growth of the large \( \text{BaTiO}_3 \) grains, i.e., the addition of the flux to our system promotes \( \text{BaAl}_2\text{O}_4 \) formation, which leads to nucleation of \{111\} \( \text{BaTiO}_3 \) twins, and thus results in improved grain size by lowering the energy barrier for grain boundary migration and providing a liquid phase for enhanced transport.
6.5 Conclusion

The presence of barium borate during the deposition and annealing of pulsed laser deposited BaTiO$_3$ on sapphire has both direct and indirect effects on nucleation and growth. The flux prevents nucleation of crystalline BaTiO$_3$ during deposition, while the melting of the eutectic barium borate during post-deposition annealing facilitates the nucleation and growth of a BaAl$_2$O$_4$ interface reaction phase. This interface phase, in combination with the liquid phase flux, appears to nucleate $\{111\}$-twinned BaTiO$_3$ grains, which are typically associated with abnormal grain growth, or fast grain-growth kinetics. The resulting dense, large grained, and highly crystalline BaTiO$_3$ microstructure leads to dielectric properties equivalent to materials processed at much higher (1200 °C) temperatures.

6.6 Acknowledgments

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Chapter 7

Investigation of the A-Site Chemistry of Barium Strontium Titanate Thin Film and Bulk Ceramics

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7.1 Introduction

Barium strontium titanate (BST) is an important dielectric material because of its high tunability (dielectric constant as a function of applied voltage) and low loss, with specific applications in tunable microwave circuits. However, regardless of processing technique, additives, or synthesis temperatures some remnant ferroelectricity is always observed beyond the paraelectric phase transition [1]. One possible explanation for this remnant ferroelectricity, which has been hotly debated, is that the local stoichiometry of the A-site cations (Ba and Sr) is globally homogeneous, but not locally homogeneous. This hypothe-
sis surmises that local areas, which are barium rich, may result in remnant polarization [8]. The remnant polarization is the result of certain areas having slightly different Curie temperatures than other areas, resulting in a broad phase transition, where ferroelectricity will persist well below the paraelectric-ferroelectric phase transition.

In this work, we use an aberration corrected scanning transmission electron microscope (STEM) and electron energy loss spectroscopy (EELS) to investigate the local stoichiometry of arguably the best-engineered barium strontium titanate samples ever fabricated in comparison to BST thin films showing some of the best tunability in thin-film form [8, 91].

### 7.2 Experimental Procedure

Electron energy loss spectroscopy was used to measure the chemical homogeneity of the BST samples. Cross-sectional electron transparent samples were prepared for EELS by either focused ion beam (FIB) preparation or mechanical polishing and subsequent ion milling. The ceramic BST sample was prepared by both methods and no variation in chemistry between the two sample preparation methods were detected within the experimental error. FIB samples were prepared from the thin films using a FEI (Hillsboro, OR) Quanta 3D-FEG dual-beam FIB, including a final mill of 2 kV to minimize sample damage. Ion milling was performed on the mechanically polished samples using an EA Fischione Model 1010 (Export, PA) ion mill at a voltage of 0.7-2.5 kV, current of 5 mA, and milling angles of 6° to 10° at 100° C to minimize sample damage. A probe-corrected FEI Titan G2 60-300 kV S/TEM equipped with an X-FEG source and a Gatan Enfinium electron energy loss spectrometer (Pleasanton, CA) were used to take these measurements. The microscope was operated
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at 200 kV and the energy resolution was 0.8 eV for all spectra obtained. Gatan Digital Micrograph TM software was used to perform EELS spectral analysis. For this work, EELS spectrum images were taken from the bulk of the samples with pixel sizes around 2 nm x 2 nm and an image over an area of over either 192 or 384 nm². Contributions of plural scattering contributions to the spectra were removed using the Fourier-ratio method, where the Fourier transform of the core-loss spectrum is divided by the Fourier transform of the low loss spectrum. Quantification of EEL spectra was then performed by using the ceramic sample as a reference to calculate a sensitivity factor assuming a 0.7 Ba:Ti ratio. This was done because of known problems with the Ba M-edge's theoretical partial scattering cross section. The equation to calculate the relative concentration is shown below:

\[
\frac{C_{Ba}}{C_{Ti}} = K_{Ti:Ba} \times \frac{(I_{Ba}(\beta, \Delta))}{I_{Ti}(\beta, \Delta)}
\]

where \(K_{Ti:Ba}\) is the experimentally determined sensitivity factor, \(b\) is the collection angle, \(D\) is the edge integration width, \(C_i\) is the calculated concentration, and \(I_i\) is the integrated intensity from the background-subtracted EEL spectra. The Ba\(_M\) and Ti\(_L\) edges were used as an indirect measure of the Ba to Sr variation due to limitations in the quantification of the Sr L-edge. If the Ti site occupancy was assumed to be one, then \(\text{Ba:Sr} = (\text{Ba:Ti})/(1-\text{Ba:Ti})\). Any variation observed between the Ba and Ti concentrations would thus correspond to variation in the A-site occupancy [70]. An example EELS spectrum image is shown in Figure 7.1.

The sample we used as a reference was fabricated in the 1990’s by Texas Instruments (TI) and later given to Dr. Cross at Penn State for electrical characterization [91]. It has long been deemed as one of the best-engineered bulk BST sample ever synthesized and
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7.2. Experimental Procedure

Figure 7.1: An example of an EELS spectrum image with the plot showing the variation of Ba/Ti concentration.
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7.2. Experimental Procedure

Figure 7.2: An example of an EELS spectrum of barium strontium titanate.

shows excellent electrical properties, including a very sharp phase transition. We used this sample as a baseline and compared the result to modern-day synthesized BST thin films on a ceramic alumina substrate, which shows the best tunability to-date in a thin film geometry but with a much broader phase transition than the TI sample. An example EELS spectra is shown in Figure 7.2. The thin films were processed with radio-frequency sputtering and chemical solution deposition [8, 7].
7.3 Results and Discussion

Local variations in the composition were assessed by EELS analysis. Table 7.1 shows the EELS results for the different samples analyzed (ceramic and CSD film). Overall, the bulk ceramic sample showed the smallest Ba:Ti deviation over the scale analyzed, with a relative standard deviation of less than 2.55% and a maximum Ba:Ti ratio variation of just 10.49% (The maximum Ba:Ti variation represents the maximum percentage deviation from the average composition between any two pixels in the EEL spectral image). Assuming the A to B site ratio to be 1:1, which we believe to be justified because no secondary phases are evident, we attribute the compositional variation to be from variations in the A-site cation ratios, i.e., Ba:Sr. The CSD film showed a slightly higher average Ba:Ti ratio with a relative standard deviation of 2.61% and a maximum Ba:Ti ratio variation across the sampled area of 14.97%. The sputtered film, which had a lower average Ba:Ti ratio of 0.516, showed the highest relative standard deviation of 5.75%, and a maximum Ba:Ti variation of 35% across the sampled area. We also sampled a larger area of the sputtered film, to assess the inhomogeneity at larger length scales, although these measurements were taken with a larger pixel size. The results of the larger sampled area are very similar for the sputtered film, although there is a small decrease in the observed standard deviations and maximum variations. This may suggest that the chemical fluctuations are on a length scale slightly smaller than the 6.7×6.7 nm² pixel size, which just begins to average over the compositional inhomogeneities.

The results from Table 7.1 demonstrates that there is an apparent difference in A-site stoichiometry between the Texas Instruments sample and the thin film sample. This differ-
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7.4. Conclusion

Table 7.1: The EELS result showing the difference in Ba:Ti stoichiometry in the two barium strontium titanate samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sampled area (pixel size)</th>
<th>Ba:Ti avg. Std. Dev.</th>
<th>Ba:Ti % Rel. Std. Dev.</th>
<th>Ba:Ti % variation</th>
<th>Maximum Ba:Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ba_{0.7}Sr_{0.3}TiO_3$ (Ceramic)</td>
<td>32 nm x 12 nm (2×2 nm)</td>
<td>0.7002</td>
<td>0.0179</td>
<td>2.55</td>
<td>10.50</td>
</tr>
<tr>
<td>$Ba_{0.7}Sr_{0.3}TiO_3$ (Thin Film)</td>
<td>32 nm x 6 nm (2×2 nm)</td>
<td>0.729</td>
<td>0.0190</td>
<td>2.61</td>
<td>14.97</td>
</tr>
<tr>
<td>$Ba_{0.5}Sr_{0.5}TiO_3$ (Sputter)</td>
<td>32 nm x 12 nm (2×2 nm)</td>
<td>0.525</td>
<td>0.0302</td>
<td>5.76</td>
<td>35.92</td>
</tr>
<tr>
<td>$Ba_{0.5}Sr_{0.5}TiO_3$ (Sputter-Large)</td>
<td>100 nm x 100 nm (6.7×6.7 nm)</td>
<td>0.516</td>
<td>0.0235</td>
<td>4.55</td>
<td>33.27</td>
</tr>
</tbody>
</table>

ence between the A-site stoichiometry could account for the more broad phase transition that is observed in the BST thin film samples than the Texas instrument sample. As the areas with high barium content will have a different Curie temperature that the areas with a high strontium content. This will broaden the phase transition and in doing so lead to ferroelectricity below the predicted Curie temperature. Further, over the length scales analyzed, the variation seems to be over the nano-meter length scale. As the stoichometry over larger areas of the sputtered thin film begins to approach theoretical values.

7.4 Conclusion

In conclusion, we used electron energy loss spectroscopy to describe the differences in A-site stoichiometry between a reference highly engineered barium strontium titanate sample with a sharp phase transition to a modern thin film barium strontium titanate thin
film with broad phase transition. We found that the A-site chemical variation in the modern thin film sample is much larger than the reference sample leading to the conclusion that the broad phase transition is the result of local chemical inhomogeneity.

### 7.5 Acknowledgments

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Chapter 8

Utilizing Gnomonic Distortion for Enhanced Indexing in Electron Backscatter Diffraction and Transmission Kikuchi Diffraction

Matthew J. Burch¹, Chris M. Fancher¹, Srikanth Patala¹, and Elizabeth C. Dickey¹
8.1 Introduction

Electron backscatter diffraction (EBSD) is one of the most commonly used characterization techniques for orientation analysis in crystalline materials [92]. In addition to EBSD, the relativity new technique of transmission Kikuchi diffraction (TKD) has shown to give nearly identical information as traditional EBSD, but at a much greater spatial resolution (5 nm) [93, 94]. Both techniques are commonly used for texture analysis in large-grained crystalline materials, however, traditional indexing methods claim to only be able to distinguish interband angle differences of approximately 0.5°. Multiple distinct orientations with interband angles within this tolerance have classically been considered impossible to differentiate. The recently developed high-resolution EBSD (HR-EBSD) methods utilize cross correlation to identify slight angular differences in patterns to extract strain information. The angular resolution for HR-EBSD is as small as 0.01° [95, 96], however, this technique is computationally intensive [97, 98, 99, 100, 101].

Most commercial indexing software utilizes the Hough transform, which is a transformation primarily designed to identify lines in an image through the parametric equation:

\[ \rho = x \cos(\theta) + y \sin(\theta) \]  

(8.1)

where \( \rho \) is the distance of the origin (generally the center of the pattern) to a point and \( \theta \) is the angle between the x-axis and this point [102]. Performing a Hough transform
on the two-dimensional patterns (Figure 8.1) transforms the information into $\theta$-$\rho$ space, where lines becomes points. These points are then identified using a butterfly mask. The angles between the points in Hough space, are computed and compared to a table of simulated orientations for the input material and the best-fit orientation is obtained [103].

The geometric differences between EBSD and TKD are shown in Figure 8.1. Generally, the working distance for EBSD is set to minimize the distance between the sample and the EBSD detector, which for many systems is 5-15 mm with the pattern center lying approximately in the center of the detector [104, 105]. A shorter working distance (2-4 mm) are commonly used in TKD to maximize signal incident upon the detector [93, 105, 106]. The difference in sample location leads to a drastic change in pattern center with respect to the detector, as is illustrated in the figure. The differences between the two geometries changes the angular range observed (by as much as $20^\circ$) and also changes the projection distortions onto the EBSD detector, as will be shown later.

The projection of the diffraction sphere project onto the two-dimensional detector is known as a gnomonic projection. In a gnomonic projection, the location of the projection is at the center of the sphere, which means in a gnomonic projection great circles are mapped to approximately straight lines. The impact of the gnomonic distortion on EBSD/TKD indexing sensitivity is addressed in depth in the Discussion section. In this work we simulate kinematical electron diffraction patterns to demonstrate that the indexing sensitivity can be improved by taking advantage of gnomonic distortions, which are exaggerated for typical TKD geometry. This enhanced sensitivity is a direct result of the change in pattern center associated, which results from the change in position of the sample with respect of the detector. The results presented in this manuscript show that the enhanced gnomic
Figure 8.1: Illustration of the different geometries for TKD and EBSD. Demonstrated are the different locations of the pattern centers as well as the different radii of the diffraction sphere.
8.2 Simulation Procedure

For simplicity, the different geometries of electron diffraction will be referred to as EBSD geometry, i.e. a backscatter geometry with the pattern center near the center of the detector, and TKD geometry, in a forward scatter geometry with the pattern center far above the detector. A 70° sample tilt relative to the incident electron beam direction and towards the detector was used for both the TKD and EBSD geometries to isolate the detector geometry effects. We simulated EBSD and TKD patterns for a hypothetical tetragonally distorted aluminum (c/a of 1.025-1.005) using the open source code OpenXY [107]. Diffraction patterns were simulated for a crystal with the hypothetical tetragonal distortion along the [010] or [001] direction and Euler angles $\phi_1=0$, $\Phi=45$, and $\phi_2=0$. Example simulated EBSD and TKD patterns are shown in Figure 8.2. These settings were chosen to roughly simulate the geometry of the SEM and EBSD system at the Analytical Instruments Facility at North Carolina State University, which is placed 10 mm below the pole-piece and at an angle 70° from the horizontal plane, for TKD the sample was placed 2 mm from the pole-piece. Turn page

To facilitate sensitivity analysis of EBSD and TKD patterns, cross correlation and Hough transforms were performed in MatLab. The cross correlation is defined as:

$$\gamma(u, v) = \frac{\sum_{x,y}[f(x, y) - \bar{f}_{u,v}][t(x - u, y - v) - \bar{t}]}{(\sum_{x,y}[f(x, y) - \bar{f}_{u,v}]^2\sum_{x,y}[t(x - u, y - v) - \bar{t}]^2)^{1/2}}$$

where $f$ is the image and is summed over $(x,y)$ under the window containing the feature
Figure 8.2: (Left) An example of a simulated EBSD pattern. (Right) An example of a simulated TKD pattern. Both patterns have Euler angles of $\phi_1=0$, $\Phi=45$, and $\phi_2=0$, with the only change between the two patterns being the pattern center location with respect to the detector plane.
8.3 Results

During pattern indexing, the Hough transform of the pattern is performed to identify different Kikuchi bands. Two patterns with tetragonal distortions oriented 90° apart for
the distorted-Al unit cell were simulated for TKD and EBSD geometries and the Hough transform was performed. Representative diffraction patterns, and their respective Hough transforms is shown in Figure 8.3. The Hough transforms for TKD and EBSD were then cross-correlated for several different c/a ratios and these results are shown in Figure 8.4. The correlation of the TKD-based geometry is lower than the EBSD-based geometry for all c/a ratio greater than 1, which shows that even though the Euler angles are the same for both EBSD and TKD, the differences between the two patterns is magnified in the TKD based geometry.

EBSD and TKD patterns of cubic aluminum were simulated for various uniaxial strains, then cross-correlated with an unstrained pattern to determine the influence of sample geometry on the sensitivity to identify strains, the differences are shown in Figure 8.5. Figure 8.5 shows that EBSD and TKD are nearly identical sensitivity to $\epsilon_{22}$ and $\epsilon_{22}$ strains, with the exception of very high strain values (>2%) where EBSD is slightly more sensitive than TKD. For the simulated grain orientation TKD is more sensitive to the changes in $\epsilon_{11}$ strain than EBSD.

We performed an analogous analysis of the same patterns and geometries in Hough space instead of diffraction space. Figure 8.6 summaries the strain dependence of the obtained cross correlation index. For all strains the TKD geometry is more sensitive to the difference between strained and unstrained patterns than the EBSD geometry. Further, in Hough space the cross correlation coefficient drops off at a much steeper rate than in diffraction space. Which means that at small strains Hough space analysis results in a much higher sensitivity than diffraction space.
Figure 8.4: The cross correlation coefficients EBSD/TKD patterns of the tetragonally distorted Al unit cell oriented 90 degrees apart.
Figure 8.5: This figure shows the effect of strain on the two different geometries of EBSD and TKD by direct comparison of an unstrained pattern and a strained pattern in diffraction space.
Figure 8.6: This figure shows the effect of strain on the two different geometries of EBSD and TKD by comparison of an unstrained pattern and a strained pattern in Hough space.
8.4 Discussion

It should be reiterated that the only difference in simulated patterns for the EBSD and TKD geometries is a change in pattern center and how this change in pattern center influences the projection of the diffraction sphere onto the detector. In the projection present for EBSD, the diffraction sphere originating at the sample is projected onto the EBSD detector as shown in Figure 8.7. This type of projection is known as a gnomonic projection. In Figure 8.7, the z-axis is along the vector joining the sample and pattern center on the detector. This projection can be described with the transformation equations described below:
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8.4. Discussion

\[(R, \Phi) = (r \tan(\theta), \phi)\]  

\[(X, Y) = (r \tan(\theta) \cos(\phi), r \tan(\theta) \sin(\phi))\]  

where \(\theta\) and \(\phi\) are the polar and the azimuthal angles, respectively and \(r\) is the distance between the sample and the pattern center, as shown in Figure 8.7. In a gnomonic projection, great circles are mapped from the sphere to bands on the projection. One consequence of the gnomonic projection is demonstrated in Figure 8.7, where equidistant points on the diffraction sphere are projected to non-equidistant points on the EBSD detector. Other consequences of the gnomonic projection in EBSD are the loss in intensity of the Kikuchi patterns and an increase in the bandwidth as the polar angle \(\theta\) is increased. The loss of intensity incident on the detector is one reason why gnomonic distortions are viewed as being undesirable for the indexing EBSD patterns [18]. In TKD, small working distances are generally used to minimize spatial resolution. This decreased working distance increases the distance between the sample and EBSD detector. In EBSD geometry, this increased sample-detector distance would degrade pattern intensity. However, in TKD the intensities and the quality of the projected Kikuchi pattern remains excellent despite the larger sample-detector distance [2], [15]. This results in the TKD geometry having little impact on overall pattern quality.

When obtaining an EBSD map within a single grain and the grains orientation (Euler angle) is perturbed slightly (\(\pm 2^\circ\)), the position of the zone axis within the EBSD/TKD pattern (i.e. the point where multiple Kikuchi bands intersect) is perturbed. The sensitivity of the
technique depends on how small the differences between two patterns can be confidently distinguished by the indexing software. From the equations above it can be shown that a perturbation (i.e. $ds = \sqrt{(d\theta^2 + d\phi^2)}$) of the zone-axis on a unit sphere is related to the change in its position ($dR$) on the detector as:

$$\frac{dR}{ds} = rs\sec^2\theta. \quad (8.5)$$

Therefore the perturbation is magnified by the distance of the pattern center from the sample (by a factor of $r$) and polar angle (through $\sec^2\theta$). In the TKD geometry both $r$ and $\theta$ are increased. This increase in $r$ and $\theta$ results in greater distortion, which improves the sensitivity of band indexing. This effect can be magnified with larger values of $R$ and $\theta$, however, Nowell and Wright demonstrated that there is a limit on how far the detector can be moved farther away before the loss of intensity will deteriorate the pattern quality to a degree that prevents confident indexing [18]. Since gnomonic distortion is nearly ubiquitous in all EBSD set-ups, it is useful to understand how this distortion affects indexing confidence. This is especially true as EBSD detector companies are designing set-ups which reduce or remove gnomonic distortion from EBSD patterns [19]. The impact of gnomonic distortion on indexing sensitivity may be applied to a number of different applications. One specific example is the imaging of ferroelastic domains in ferroelectric oxides. The $c/a$ of many ferroelectric oxides are less than 1.02, which makes determining $90^\circ$ domain structures difficult through traditional EBSD. These small $c/a$ ratios makes the difference in indexing confidence of multiple orientations very small [18]. The resulted presented in this work suggest that utilizing a working distance that enhances gnomonic distortions is a potential avenue for discriminating between differently oriented domain in these materials. It should
be noted that this is only true for 90° domain structures in ferroelectrics, as Hough transform based indexing is insensitive to inversion symmetry. Further, to demonstrate the impact of geometry for strain analysis. Patterns were simulated for various principle strains, then compared to it to an unstrained pattern. In diffraction space, for most strains analyzed the differences between TKD and EBSD were very small, and which geometry was more sensitive depended on the strain applied. For the same analysis is performed in Hough space instead of diffraction space the TKD geometry is more sensitive to detect differences between strained and unstrained patterns. Currently HR-EBSD strain analysis is performed via cross correlation in diffraction space. Our results indicate that the differences between a strained and unstrained pattern are more apparent in Hough than in diffraction space. We conclude this because the cross correlation coefficients are much lower for the strain analysis for Hough space regardless of the geometry. These results suggest that researchers should consider performing strain analysis in Hough space instead of diffraction space. This work demonstrates that the TKD based geometry identifies slight differences between two patterns more confidently than an EBSD based geometry. It should be noted, that indexing confidence may depend on many factors beyond what is presented in this work. This work only demonstrates that Hough transform based indexing sensitivity depends dramatically on sample-detector geometry.

8.5 Conclusion

It has been shown that genomic distortions can be used to amplify anisotropic strain sensitivity in EBSD and TKD. The increase in sensitivity of TKD is quantified through cross
correlation of the Hough transforms of the diffraction patterns. It was further determined that as a function of c/a and Gaussian noise, the TKD geometry always indexes with a higher confidence compared to the EBSD geometry. These results demonstrate that indexing confidence and sensitivity is highly dependent on the sample detector geometry.

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Chapter 9

Characterization of Abnormal Domain Structures in Barium Titanate Thin Films via Transmission Kikuchi Diffraction

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9.1 Introduction

The domain structures of small-grained ferroelectrics has been shown to be of dramatic importance to the performance of ferroelectric devices [39, 109, 110, 27]. However, despite the known importance of this domain structures, characterizing these domain structures in barium titanate thin films has proven very difficult. Traditional techniques that are generally used to examine domain structures have proven insufficient to completely unravel how the domain structure is present [100, 111, 112]. Many journal articles discuss the presence of domain wall motion (generally through hysteresis or tunability plots) in polycrystalline barium titanate thin films, including articles with intense microstructural investigations that have not shown any evidence of traditional domain structures [6, 113, 4, 7]. In bulk barium titanate ceramics, ferroelectric domain structures are clearly evident in barium titanate ceramics with average grain sizes as little as 200 nanometers [52]. This is at odds with the thin film geometry, where some modern day flux-grown barium titanate thin films have average grain sizes more than double this value, with no traditional domain structure demonstrated [6, 113, 4, 3]. One major problem with characterizing the domain structure of thin film polycrystalline barium titanate thin films is the lack of techniques that have all the requisite functionality to complete the investigations. Techniques, such as XRD, has great sensitivity to structure and orientation within samples, but is limited severally in spatial resolution and in samples with small grain sizes and small volumes, diffraction peaks become diffuse, which makes characterizing even phase information
difficult. Other techniques, such as convergent beam electron diffraction (CBED), give very detailed information about local structure and orientation, however, gaining even moderate scale, multi-grain spatial information (greater than 10's of nm's) from a sample is severally limited by time and experimental parameters [114, 25]. Probably the most common technique for imaging ferroelectric domains is piezoresponse force microscopy (PFM). PFM is limited in spatial resolution to generally less than 20 nm in the best of cases and this is very probe and sample dependent. So for nanodomain structures which may exist smaller than 20 nm, PFM would not be sensitive [115, 97, 43]. Another candidate is electron backscatter diffraction (EBSD), which is very sensitive to orientation changes; however, it again is limited in spatial resolution, due to the dispersive scattering from the geometry of the technique. Recently, a new technique, Transmission Kikuchi Diffraction (TKD), gives the same information as EBSD, however, with much greater spatial resolutions (≈5 nm). Unlike EBSD, TKD is more limited by the optics of the microscope then with the type of sample that is being analyzed [106, 116, 94, 117]. This technique has proven useful in the small-grained metals community, but has rarely been utilized by the electro-ceramics community. EBSD has been shown to easily characterize domain structures in bulk single crystal barium titanate samples [99, 98]. Traditional thinking is that the small deviation in c/a (1.01) ratio of barium titanate is not visible in traditional EBSD indexing techniques due to the deviations in angles between Kikuchi bands to be less than the resolution of the indexing software of 0.5°. However, through a previous investigation of understanding the relationship between indexing sensitivity and sample geometry, it became clear that domain structures could be characterized with both EBSD and TKD, with the TKD geometry resulting in a slightly greater sensitivity to small perturbations between two patterns. The specifics of how are
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9.2 Experimental Procedure

explored in depth in a previous publication (Chapter 8). In short, our ability to observe domain formation is that due to the nature of the projection of an EBSD pattern onto the phosphorus screen, known as a gnomonic projection, at higher scattering angles, the pattern is distorted, so the zone axis and band position change between diffracting planes across a 90° domain boundary will be exaggerated. This will lead to an enhanced sensitivity to small perturbations between 2 diffraction patterns. Further, TKD patterns show this distortion to even a higher degree due to the nature of the sample placement relative to the EBSD detector (Chapter 8). In this work, we directly image the abnormal 90° domain structure of flux-grown barium titanate thin films with TKD. Further, we discuss the possible origins of the abnormal domain formations in terms of the effect of biaxial strain imposed on the thin films by the substrate.

9.2 Experimental Procedure

The samples used in this work were made by pulsed laser deposition. More on sample preparation can be found in reference [6].

Transmission Kikuchi diffraction was performed on a FEI Quanta Dual Beam SEM/FIB. The TKD detector used was a Oxford NordlysNano EBSD detector and was operated at 20 kV and between 3-9 nA.

Transmission electron microscopy was performed on a Jeol 2000FX. TEM and TKD samples were prepared on a FEI Quanta Dual Beam SEM/FIB.
9.3 Results

Figure 9.1 shows an inverse pole figure (IPF) map of a grain within a flux-grown barium titanate thin film. The IPF of the grain shows that the bottom left corner (the mostly red area) is oriented 90° away from the rest of the grain (the green area). The band contrast image is also shown. The difference in patterns is shown in Figure 9.2.

To confirm that we indeed were observing a 90°-domain within the thin film, we utilized transmission electron microscopy. Through tilting to a 2-beam condition, where the 110 type reflections are the only strong reflectors, we are able to see contrast within in the grain that is consistent with our TKD results, shown in Figure 9.3. In addition, within the diffraction pattern, the 110 type reflection is splits, as one would expect to observe with the presence of a 90° domain. This type of splitting is utilized extensively in bulk barium titanate to identify 90° domains [28].
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Figure 9.2: TKD Patterns across a 90° domain boundary in barium titanate thin films. The different orientations are shown here, which demonstrate a 90° domain rotation.

Figure 9.3: A TEM micrograph of the large grain shown in Figure 9.1 and its corresponding diffraction pattern showing the spot splitting in the 220 reflection.
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Figure 9.4: The microstructure of a flux grown barium titanate thin film shown through band contrast image. The next two images show the IPF’s with respect to the Z and X orientation. The circled areas show the areas with a 90° wall.

With the confirmation that we are sensitive to 90° domain structures in barium titanate thin films, we set out to map 90° domain structures over a large area of a flux-grain barium titanate thin film with TKD, in order to understand how domain structures exist over microns of the thin film. Figure 9.4 shows a band contrast image of TKD demonstrating the microstructure of a flux-grown barium titanate thin film. The next two are IPF’s corresponding to the microstructure in the band contrast image. The circled areas are the areas where clear evidence of a 90° rotation is present. These areas were confirmed by directly comparing the experimental EBSD patterns on either side of the apparent 90° domain wall and verifying that the change in interband angles were consistent with the simulated 90° domains (Chapter 8).
9.4 Discussion

This is the first report of direct imaging of 90° domain structures in polycrystalline ferroelectric barium titanate thin films. The domain structures support the preponderance of evidence in the literature that the non-linearity and hysteresis observed during tunability and permittivity measurements are a direct result of domain wall motion [6, 7, 3, 47, 118]. The authors surmise that previous attempts at observing 90° domain structures were unsuccessful because the domains within these thin films do not exist in the traditional geometries i.e. periodic herringbone or striped domains. The domains observed in the thin films exist more as pockets within a grain and do not appear to be periodic in nature. We believe the reason for these abnormal domain structures is the large amounts of strain (0.15 biaxial strain) that is present within these thin films. This strain may prevent the formation of traditional periodic domain structures and instead results in the pocketing of domains as observed here. Further, there is evidence in previous literature that abnormal domain structures will exist in strained thin films. Li and Chen performed phase field simulations of
9.5 Conclusion

In conclusion, we demonstrate the first direct imaging of 90° domain structures in barium titanate utilizing transmission Kikuchi diffraction. We found that domains do not exist in the traditional periodic arrangements that occur in bulk barium titanate, but instead exist as individual pockets within certain grains of the microstructure. We confirmed the presence of these 90° domain structures with transmission electron imaging and diffraction, where we observe peak-splitting consistent with a 90° domain wall. Further, we map the presence of 90° domain walls over several microns of flux-grown barium titanate thin films, where we found many 90° domains to exist within the microstructure. We surmise that the existence of the domains in a non-traditional or abnormal formations is the result of the biaxial strain the thin films are constrained by.
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Chapter 10

Direct Observation of 180° Ferroelectric Domains Using Electron Backscatter Diffraction

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10.1 Introduction

The extrinsic contribution of ferroelectric domain wall motion is an important mechanism for large permittivity within ferroelectric ceramic oxides \[109, 110, 119, 9, 50\]. Due to the importance of domain structures in ferroelectric materials much work has been devoted to understanding these structures since the discovery of barium titanate, the first perovskite ferroelectric \[9, 50, 120, 28\]. Through these various studies 90° domain structures within barium titanate ferroelectrics have been identified and well characterized, with one of the most common techniques based on diffraction contrast imaging \[120, 28\].

In addition to the imaging techniques, various diffraction based techniques are used to characterize 90° domain structures, where clear peak splitting will occur when observing 90° domain structures \[28\]. While 90° domains have been thoroughly investigated in bulk ferroelectrics, the characterization of 180° domain structures is challenging, since diffraction based techniques are not sensitive to the unit cell inversion associated with a 180° domain wall. This is due to Friedel's law, which states that the intensities between two reciprocal diffraction peaks is equal, such that \(I(hkl) = I(\bar{h} \bar{k} \bar{l})\) are known as Friedel's pair. This holds true except for anomalous or dynamical diffraction of non-centrosymmetric crystal structures. Any diffraction based techniques which are not heavily influenced by dynamical scattering will not be sensitive to 180° domain structures \[28, 121, 122, 39\]. Other techniques do exist, which allow direct imaging of 180° domain boundaries. The most common technique is piezo-response force (PFM) microscopy. In PFM, an atomic force microscope (AFM) is used in conjunction with the application of an applied bias to observe how the polarization direction changes at the surface of a sample. The sample must be mounted
with a bottom ground electrode and then the AFM probe tip with a small voltage applied rasters across the top of the sample. As the field interacts with the polarization direction, it will lead to changes in the measured field, and from the point by point measurements, a map of polarization direction can be generated [115, 123, 97, 100]. However, PFM is limited in that a bottom electrode must usually be present for the measurement to take place. In addition, PFM is susceptible to artificial contrast, which may be interpreted as polarization contrast, due to poor probe tip shape and sample preparation [124]. Another technique to image 180° domains is to chemically etch the surface of a material and then image the surface topography with SEM. This will bring contrast to the domain structure as each of the domain orientations will etch with slightly different rates and through the topography one can characterize both 90° and 180° domain structures [28]. The obvious problem with this technique is that it is destructive. Optical birefringence in ferroelectrics can also be used to directly image 180° domain structures through polarized light microscopy [125]. However, not all 180° domain walls are visible with this technique, such as barium titanate, where the 180° domain walls are only visible with an applied electric field and once the field is removed the contrast disappears [125, 126, 127]. Further, with this technique there is no way to determine the polarization direction on either side of a domain wall. In this work, we present a method to directly image 180° domain structures in ferroelectric oxides through electron backscatter diffraction (EBSD) and dynamical diffraction based simulations. Recently, Marc De Graef from Carnegie Mellon University developed software, which uses dynamical diffraction theory to simulate EBSD patterns and through these patterns we developed a post-analysis technique to directly image 180° domain structures [128].
10.2 Experimental Procedure

10.2.1 Materials

To develop the experimental approach we chose a material system which contains well-defined 180° domains. Periodically poled LiNbO₃ single crystals were chosen because of the predictable pattern of the 180° domains within the system. The single crystals were purchased from Deltronic Crystal Industries, Inc. in Dover, NJ USA. The grating period was 11.2-12.0 µm and the crystals were left un-polished and were coated with a thin coating of carbon to prevent charging.

10.2.2 Equipment

An Oxford NordlysNano EBSD detector was used to collect EBSD maps with a full resolution of 1344×1024 pixels. The sample was mounted to a 70° pre-tilted stage. A field-emission FEI Quanta Dual Beam SEM/FIB was operated at 20 kV and between 3-9 nA.

10.2.3 Software and Simulation Methods

To dynamically simulate EBSD patterns, the EMsoft software was used [128]. The simulated patterns orientations (euler angles) and pattern center were optimized to fit the experimental patterns. Further, both the positive and negative polarization direction were simulated for each crystal orientation by inverting the Euler angles. To map the 180° domain structures from the obtained EBSD maps, a direct mean intensity variation from a simulated pattern and experimental pattern was calculated. This relation is shown in Equation 10.1.
\[ I_{x,y} = \text{Mean}(I(SIM_{x,y}) - I(EXP_{x,y})) \] (10.1)

Experimental patterns with the same orientation as the simulated patterns will have a lower mean intensity variation than when the incorrect orientation is subtracted from the simulated orientation. This procedure was performed for each pattern within an EBSD map and the resultant values were plotted. Areas with lower overall mean intensity difference from experimental to simulation correspond to a particular polarization orientation and areas with a higher overall intensity variation correspond to the opposite variation. The opposite polarization orientation was then simulated and the routine was performed again to confirm the previous results.

10.3 Results

Figure 10.1 presents EBSD patterns from the two domain orientations from the LiNbO$_3$ sample, which are oriented 180° apart. The difference in the patterns is observable to the naked eye, with the center of the middle zone axis inverted with respect to the opposite orientation. It should be noted, that there is no change in band location or angles, the only difference between the patterns arises from variation within the Kikuchi bands between the two different orientations.

Figure 10.2 presents the simulated LiNbO$_3$ with the same orientations shown in Figure 10.1A. Figure 10.2A corresponds to the positive polarization direction, while the negative polarization direction is shown in Figure 10.2B.

Figure 10.3A shows an SEM micrograph of the LiNbO$_3$ single crystal. The 180° domains
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Figure 10.1: Experimental EBSD patterns from LiNbO$_3$ with (A) and (B) being inverse polarization directions and the inset boxes emphasizing the difference in the patterns.

Figure 10.2: Simulated EBSD patterns with the same orientations as Figure 1.
10.4 Discussion

The technique demonstrated in this work may become very popular in a number of communities for a variety of applications. The technique opens the possibility to map 180° and 90° ferroelectric domains over a many 10’s × 10’s of µm, thus being able to understand relative populations of ferroelastic and non-ferroelastic domain structures, which has been an area of debate for decades [51, 27, 109]. Further, this technique would benefit from in-situ capabilities to observe how the population and structure of non-ferroelastic domain structures changes at different locations on the hysteresis loop. Further, this technique
Figure 10.3: (A) An SEM micrograph of periodically poled LiNbO$_3$ showing the 180° domains. The polarization direction (B) The corresponding IPF maps from EBSD, showing that traditional indexing is not sensitive to polarization inversion. (C) A mean intensity variation map; where comparing experimental EBSD patterns to simulated of a [0001]-oriented domain (Dark areas are domains oriented in [0001] orientation). (D) The same type of image as (C), but the simulated pattern is the [0001] direction.
could be applied and used in transmission Kikuchi diffraction on ferroelectric thin films, which is a technique similar to EBSD, but is able to achieve much smaller spatial resolutions.

While demonstrated for ferroic oxides, the developed methodology is broadly applicable and can be utilized for studying all non-centrosymmetric structures. For example, the nitrides community grows GaN thin films with either Ga-polarity or N-polarity with two of the most common techniques utilized to determine the polar direction being chemical etching or convergent beam electron diffraction, both of which are destructive techniques \[20\], \[21\]. The use of the shown technique for these kinds of applications will lead to a quick, easy, and non-destructive ways to determine polar direction.

10.5 Conclusion

In conclusion, we demonstrated the ability to directly map polarization reversal in a ferroelectric oxide with electron backscatter diffraction (EBSD). Using periodically poled LiNbO$_3$ as an example, we clear map the polarization direction from a known 180$^\circ$ domain configuration. To facilitate the polarization mapping, the mean intensity variation between experimental patterns and dynamical diffraction simulations of EBSD patterns is calculate. Further applications for this technique are discussed.

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Conclusions and Future Directions

The work presented in this dissertation gives major new insights into the microstructures and ferroelectric nature of barium titanate thin films. The purpose of this chapter is to highlight the major conclusions from the original work presented in this dissertation and discuss future directions this research.
11.1 Summarized Conclusions

1. The microstructural evolution of flux-grown barium titanate thin films on sapphire substrates is dependent on a series of interconnected mechanisms based on the addition of the liquid forming flux. First, during annealing the liquid forming flux drives a reaction between the sapphire and barium titanate, resulting in \( \text{BaAl}_2\text{O}_4 \) forming at the interface. Next, the \( \text{BaAl}_2\text{O}_4 \), in the presence of the liquid-phase causes the nucleation and growth of \{111\} type twins in the barium titanate. The grains containing these \{111\}-type grains grow abnormally, resulting in grain structures that are far larger than would just occur for flux grown \( \text{BaTiO}_3 \) thin films grown on substrates other than c-sapphire.

2. In barium strontium titanate thin films there exists nano-scale A-site inhomogeneity. This was shown with aberration electron microscopy and electron energy loss spectroscopy. This A-site inhomogeneity is believed to be responsible for the broad paraelectric-ferroelectric phase transition commonly observed in barium strontium titanate ceramics.

3. It was determined that the sensitivity of indexing in electron backscatter diffraction is based on the geometry of the sample and detector. Further, it was shown that sensitivity of the indexing for the geometry common to transmission Kikuchi diffraction is superior than the geometry common to electron backscatter diffraction. The reason for the improvement of transmission Kikuchi diffraction is the increased amount of gnomonic distortion present in the geometry for transmission Kikuchi diffraction.
4. Abnormal ferroelastic domain structures in flux-grown barium titanate thin films were mapped using transmission Kikuchi diffraction. These abnormal domain structures were confirmed with transmission electron diffraction. The authors surmise that the reason for these abnormal domain structures is due to the large amounts of strain present in these barium titanate thin films, which prevents the formation of periodic domain formations.

5. Electron backscatter diffraction patterns were utilized to directly map $180^\circ$ polarization reversal in ceramics. We utilize dynamical diffraction electron backscatter diffraction pattern simulations in order to create intensity variation maps between the simulated and experimental patterns. These maps directly show the orientation of the polarization direction. The method is demonstrated on periodically poled LiNbO$_3$ single crystals. Other possible uses for this technique is discussed.

11.2 Future Work

11.2.1 Transmission Kikuchi Diffraction

The work demonstrated here shows the power of transmission Kikuchi diffraction for electroceramic research. Previously, electron backscatter diffraction was considered to have too large of a spatial resolution to be useful for applications in nano-grained ceramic samples. However, transmission Kikuchi diffraction (TKD) is not limited by spatial resolution, as resolution better than 10 nm can easily be achieved. TKD can be shown to be incredibly versatile in that it can directly map all the zone-axis present in a thin sample designated
for S/TEM, thereby allowing a microscopist to know what zone axes are close to tilt too. It is also incredibly powerful in its own right as tool to determine orientation and phase information of a very sensitive level. As this technique is embraced by the electroceramics community, new and exciting applications are sure to be discovered.

### 11.2.2 Abnormal Ferroelastic Domain Structures in Ferroelectric Oxides

The work presented in this dissertation demonstrated the first observation of abnormal domain structures in polycrystalline barium titanate thin films. Further, we discuss the possibility of strain as an explanation for the abnormal structures. However, to confirm that strain is truly the culprit intense simulations would have to be conducted of strained polycrystalline barium titanate thin films. Currently, it is not known if such simulations are possible that would accurately describe the evolved domain structures of these complicated thin films.

Additionally, it is currently not known how these abnormal domain structures evolve and move under the application of an electric field. It is possible that the motion would be distinct from that observed in bulk ceramics. This could be shown through in-situ microscopy experiments with the application of an electric field. Currently, sample preparation is the main limiting factor preventing these experiments.

### 11.2.3 Utilizing Electron Backscatter Diffraction for Direct Mapping of 180° Polarization Reversal

The ability to map polarization reversal in an inexpensive, non-destructive way should not be understated. Currently, in many applications, the cheapest and easiest way to deter-
mine polarization direction is to severely chemically etch the sample, which is of course destructive. The method described in this work would remove this destructive part of the characterization procedure.

Further, our method could give researchers the ability to map polarization reversal globally in a sample over 10's or 100's of microns. This could be useful in many communities, but in particular, the ferroelectric community could utilize this technique to great effect. This technique may lead to the ability to characterize the relative populations of ferroelastic and non-ferroelastic domain structures in ferroelectrics.
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