Microstructure and magnetism in ferrite-ferroelectric multilayer films

Natalie A. Frey

University of South Florida

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Microstructure and Magnetism in Ferrite-Ferroelectric Multilayer Films

by

Natalie A. Frey

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science Department of Physics College of Arts and Sciences University of South Florida

Major Professor: Srikanth Hariharan, Ph.D. George Nolas, Ph.D. Myung K. Kim, Ph.D.

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Microstructure and Magnetism in Ferrite-Ferroelectric Multilayer Films

Natalie A. Frey

ABSTRACT

Composite magneto-dielectric materials have been investigated over the years because of their potential applications in RF and microwave devices as the dielectric constant and permeability can be individually changed in these materials. In the recent past, there is a renewed interest in systems classified as ferroelectromagnets or multiferroics, which possess simultaneous ferroelectric and magnetic ordering as well as interesting magnetoelastic phenomena. In all these ferrite-ferroelectric materials, the coupling between the permeability ($\mu$) of the magnetically ordered phase and permittivity ($e$) of the ferroelectric phase make them attractive candidates for multifunctional applications.

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BSTO) is a ferroelectric with potential applications in tunable filters, antennas, and thin film capacitors. $\text{BaFe}_{12}\text{O}_{19}$ (BaF) is a hard ferromagnet with large in-plane anisotropy which makes it promising for use in microwave and RF devices that need permanent magnets for biasing requirements. We have used magnetron sputtering to deposit multilayer films of BSTO and BaF on $\text{Al}_2\text{O}_3$ and heated Si/SiO$_2$. To our knowledge this is the first attempt at combining these technologically important materials in multilayer form. The as-deposited films were amorphous and post-annealing was optimized until distinct BSTO and BaF x-ray peaks could be identified. Surface and
images were obtained by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The multilayer structure and BSTO/BaF interfaces were identified using cross-sectional SEM. Magnetic properties of the multilayer films were measured using a Physical Properties Measurement System (PPMS) by Quantum Design at 10K and 300K over a range of magnetic field (0 < H < 7T). We have attempted to correlate some of the magnetic characteristics with the film microstructure.

In addition, we have deposited layers of Fe$_3$O$_4$ nanoparticles onto both bare Si/SiO$_2$ substrates and the surfaces of the multilayers using Langmuir-Blodgett technique. Preliminary images of monolayer Fe$_3$O$_4$ particles reveal some ordering present. We have also used the PPMS to look at the magnetic properties of the particles, both by themselves and deposited onto the multilayers to see what magnetic effects the particles have on ferrite-ferroelectric systems.
Chapter One

Background and Motivation

The main driving force for the interest in ferroelectric and ferrite materials in tunable high-frequency devices is the potential for substantial miniaturization of microwave and radio frequency (RF) components accompanied by a large cost reduction. There is also potential for integration with microelectronic circuits due to the development of thin film ferroelectric and ferrite technology. [1.1, 1.2] Furthermore, materials that exhibit properties associated with both ferroelectric and ferromagnetic characteristics (multiferroic materials) allow an extra degree of freedom in the design of high-frequency components [1.3].

1.1 Dielectric Materials

Dielectrics are materials (often oxides) that are poor electrical conductors. In most instances the properties of a dielectric are caused by the polarization of the material. When the dielectric is placed in an electric field, the electrons of an atom or ions of a unit cell reorient themselves. As a result of this polarization, the dielectric is under stress and
it stores energy that becomes available when the electric field is removed. This polarization is analogous to the polarization that takes place when a magnetic material (section 1.3) is magnetized. As in the case of a magnet, a certain amount of polarization remains when the polarizing force is removed. [1.4]

The effectiveness of a dielectric material is measured by its relative ability, compared to a vacuum, to store energy, and is expressed in terms of a dielectric constant, or permittivity, e. The term dielectric constant is misleading in that it is actually a frequency dependent function composed of real and imaginary parts. The ratio of the imaginary part to the real part of the dielectric constant is the loss tangent. [1.5]

The ability of a dielectric to withstand electric fields without losing insulating properties (a point known as dielectric breakdown) is its dielectric strength. A good dielectric must return a large percentage of the energy stored in it when the field is reversed. Dielectrics exhibiting high dielectric constants at high frequencies, high dielectric strengths and have low loss tangents are desirable for many applications. [1.4]

As mentioned above, a dipole moment may be induced in response to an applied electric field, but disappears when the field is removed. If the unit cell has a spontaneous electric dipole moment in the absence of an electric field, it is called a polar crystal. Polar crystals may be classified as being pyroelectric, ferroelectric, or antiferroelectric. In a pyroelectric crystal the dipole moment remains fixed and is largely unaffected by external fields. In a ferroelectric crystal the dipoles of neighboring unit cells are aligned in the same direction. When an external electric field is imposed, these dipoles orient themselves parallel to the applied electric field. The direction of the polarization vector
may be reversed by applying a field of sufficient strength in the opposite direction, creating a ferroelectric hysteresis loop. [1.6]

In ferroelectricity there is a competition between the ferroelectric exchange interaction (i.e. chemical forces), which tends to produce aligned dipoles in neighboring cells, and thermal agitation, which will destroy this alignment. The Curie temperature, $T_c$, is determined by which of these tendencies dominates. For $T < T_c$ there is ferroelectricity, whereas for $T > T_c$ there is a paraelectric (nonpolar) phase and the dipoles either become randomly oriented or disappear. However, the relative dielectric constant remains large and can be changed with the applied electric field. In an antiferroelectric crystal the dipole moments of neighboring cells point in opposite directions, so there is no net polarization. [1.6]

### 1.2 Ferroelectric Materials

The main attraction of ferroelectric materials is the strong dependence of their dielectric permittivity $\varepsilon$ on the applied bias electric field $E_0$. This characteristic is commonly described by the tunability $n$ defined as the ratio of the dielectric permittivity of the material at zero electric field to its permittivity at some non-zero electric field [1.1]:

$$n = \varepsilon(0)/\varepsilon(E_0)$$

Ferroelectrics in thin film form are of particular interest in microwave and radio frequency (RF) tunable applications due to the low tuning voltages and relatively low production cost. Two examples of tunable ferroelectric components are the tunable capacitor (or varactor) and microwave ferroelectric phase shifters. [1.1]
Barium Strontium Titanate, \((\text{Ba}_{x}\text{Sr}_{1-x})\text{TiO}_3\) or BSTO is an extremely attractive candidate for many ferroelectric applications due to its exceptionally high tunability, high breakdown field and relatively low loss tangent at microwave frequencies [1.7]. Figure 1.1 shows sample data of the field dependence of the dielectric permittivity of BSTO. The Curie temperature is composition dependent, which implies that by choosing the ideal value of \(x\), BSTO can be made tunable at room temperature [1.8]. What makes BSTO even easier to work with is that polycrystalline BSTO films have been shown to have dielectric and electrical properties that are competitive with epitaxial thin films [1.7]. This opens up a broader choice of deposition techniques as well as lowering production costs.

BSTO has the perovskite structure \(\text{ABO}_3\), which is shown in figure 1.2. It derives its high dielectric constant from an ionic displacement and therefore differs from lower dielectric constant materials that only experience an electronic displacement with changing applied voltage. The Ti ions are each surrounded by six oxygen ions. At zero applied voltage, the Ti ions are centered in the oxygen octahedra and the dipole moments cancel. With the application of a voltage, the Ti ions will be displaced and a dipole moment will be induced. [1.9]

The BSTO thin film is a well-studied system which makes it ideal for experimentation with doping, forming composites and in our case, forming multilayer structures with other materials.
Figure 1.1. Typical field dependence of the dielectric permittivity of BSTO. (Adapted from reference [1.1].)

Figure 1.2. The structure of (Ba$_{x}$Sr$_{1-x}$)TiO$_{3}$. Ba and Sr occupy the center position with Ti at the cube corners, surrounded by oxygen octahedra. (Adapted from reference [1.9].)
1.3 Magnetism in Materials

Magnetism is exhibited in all materials. The magnetic nature of a material is determined by the magnetic moments of the electrons, atoms and ions in the material. The magnetic responses of electrons and of atoms and ions can exhibit a variety of behaviors in materials due to the wide range of interactions that can occur between the magnetic moments and their environment. [1.6]

The magnetic moment of an atom has three sources: Electron spin, electron orbital momentum about the nucleus and the change in the orbital momentum induced by an applied magnetic field ($H$). The magnetization of a material, $M$, is defined as the magnetic moment per volume. The magnetic susceptibility, $x$, is defined as

$$x = M/H.$$ 

$B$ is the macroscopic field intensity and can be related to $H$ by

$$B = \mu H$$

where $\mu$ is a parameter characteristic of the medium called the magnetic permeability. The relative permeability is given by the ratio of the magnetic permeability to that of free space [1.5].

$$\mu_r = \mu/\mu_0$$

Diamagnetism arises because of the induced currents set up when an external magnetic field is applied. These currents tend to screen the applied field from the interior of the material, therefore it is present is all materials to some extent. Diamagnetism is characterized by a negative susceptibility and a magnetic permeability less than $\mu_0$. [1.10]
Paramagnetism is characterized by a positive susceptibility and a magnetic permeability greater than $\mu_0$. It corresponds to the magnetic behavior found in materials in which localized magnetic moments are present but in which no net macroscopic magnetization exists in zero applied field. There are two forms of paramagnetism. In one, the magnetic moments are present at sufficiently low concentrations so that they are well separated from each other, and the spins do not interact. Paramagnetism can also exist when there are interactions between the magnetic moments as long as the interactions are weak enough so that there is no net magnetization when the applied field is zero. This occurs in ferromagnetic materials (discussed below) above their critical temperatures. [1.10]

At low temperatures, many paramagnetic materials possess a finite magnetization in the absence of an applied field. This spontaneous magnetization is due to the alignment of the permanent dipole moments and indicates that each dipole is aware of the direction in which other dipoles are pointing. The interaction between dipoles results in what is known as magnetic ordering. Ferromagnetic ordering occurs when all the moments contribute equally to the spontaneous magnetization. It will be discussed in further detail in section 1.4. Antiferromagnetism is ordering such that there is no net spontaneous magnetization because half of the dipoles are aligned in one direction and the other half in the opposite direction. In ferrimagnetism, there are oppositely directed moments which do not completely cancel resulting in a net spontaneous magnetization. [1.10] Figure 1.3 is schematic of the different types of magnetism that have been discussed.
1.4 Ferromagnetism and Ferrite Materials

In a crystal, each atom having a magnetic moment has a magnetic field about it. If the magnetic moment is large enough, an applied dc magnetic field can force a nearest neighbor to align in the same direction provided the interaction energy is larger than the vibrational energy, $k_B T$, of the atoms in the lattice. The interaction between atomic magnetic moments is of two types: the dipolar interaction and the exchange interaction,
which represents the difference in the Coulomb energy between two electrons with spins that are parallel and antiparallel. This interaction is usually the dominant of the two types. The Curie temperature, Tc, as in ferroelectrics, is the temperature at which the interaction energy is greater than the thermal energy and ferromagnetism is present. Ferromagnetic materials exhibit paramagnetism above the Curie temperature. [1.11]

For a bulk ferromagnetic material below Tc, the magnetization is less than what would be exhibited if every atomic moment were pointing in the same direction. This is due to the existence of domains, which are regions where all the atomic moments point in the same direction so that within each domain the magnetization is saturated (possessing its maximum possible value). However, the magnetization vectors of different domains in the sample are not all parallel to each other, so the total magnetization is less that the value for the complete alignment of all moments. [1.11]

Applying a dc magnetic field can increase the magnetic moment of a sample. Initially, as H increases, M increases until a saturation point, Ms, is reached. When H is decreased from the saturation point, M does not decrease to the same value it had when the field was increasing. It is higher on the curve of the decreasing field, creating a hysteresis. This effect occurs because the domains that were aligned with the increasing field do not return to their original orientation when the field is lowered. When H is returned to zero, the material still has a magnetization, referred to as the remnant magnetization, Mr. In order to remove the remnant magnetization, a field Hc has to be applied in the opposite direction to the initial applied field. This field is the coercive field. [1.11]
A full cycle of magnetization is called a hysteresis loop and is somewhat analogous to the one that occurs in ferroelectrics (in fact ferroelectrics were given the name due to this similarity). A sample hysteresis loop is shown in figure 1.4. $M_s$, $M_r$ and $H_c$ are all strongly dependent on the ferromagnetic material and the conditions by which they are synthesized. [1.11]

Ferrites are mixed metal oxides with iron oxides as their main component. Ferrites crystallize into three crystal types: spinel, garnet and magnetoplumbite [1.12]. The first two have a cubic structure, while the magnetoplumbite has a hexagonal structure [1.12]. Ferrites are characterized not only by their magnetic ordering but also by their large electrical resistivity and low induction current [1.13]. This makes them especially conducive to use in electromagnetic devices in the radio frequency region [1.13].

Figure 1.4. Plot of the magnetization $M$ versus an applied magnetic field $H$ for a hard ferromagnetic material (Adapted from reference [1.11].
Hexagonal ferrites (those exhibiting the magnetoplumbite structure) also have potential in high-density recording media, both perpendicular and longitudinal [1.14]. Barium Ferrite (written as $\text{BaFe}_{12}\text{O}_{19}$ or $\text{BaO}\cdot 6\text{Fe}_2\text{O}_3$ to stress the iron oxide main component [1.15]) in particular has shown promise in all of these areas. It is characterized by large anisotropy and coercivity, excellent durability and hardness, and resistance to corrosion [1.14]. Its Curie temperature is extremely high (350°C) so it is in the ferromagnetic phase at room temperature. It is also known to have a high magnetic permeability which is variable with growth conditions, temperature and doping [1.2].

Barium Ferrite’s complicated magnetoplumbite structure is presented in figure 1.5. It is symbolically described as $\text{SRS}^{*}\text{R}^{*}$, where $\text{R}$ is a three-layer block ($\text{O}_4$-$\text{BaO}_3$-$\text{O}_4$) with composition $\text{BaFe}_6\text{O}_{11}^{2-}$ and $\text{S}$ is a spinel-like two-layer block ($\text{O}_4$-$\text{O}_4$) with composition $\text{Fe}_6\text{O}_8^{2+}$. Here the asterisk means the corresponding block has been turned 180° around the hexagonal c-axis. In this structure, the iron cations are distributed within five different sites: three octahedral, one tetrahedral and one trigonal-bipyramidal site. The ordering of the magnetic moments of the iron cations and their interactions with the oxygen anions (a phenomenon known as superexchange) are responsible for the excellent magnetic behavior of Barium Ferrite. [1.16], [1.6]

Like BSTO, Barium Ferrite ($\text{BaF}$) has been studied extensively in thin film form. Groups have brought these two technologically important materials together through doping $\text{BaF}$ with BSTO [1.17] and growing $50\%$ BSTO/$50\%$ BaF composite thin films [1.18]. However, to our knowledge this is the first project to use BSTO and BaF in multilayer thin films.
Figure 1.5. Unit cell of Barium Hexaferrite based on two formula units of $\text{BaFe}_{12}\text{O}_{19}$. (Adapted from reference [1.16]).
1.5 Ferroelectric-Ferrite Multilayer Films

There are several reasons for wanting to combine BSTO and BaF in multilayer thin film form. As mentioned above, BSTO has excellent dielectric tunability. In the past, efforts have been made to “tune” the magnetic properties of BaF through deposition methods, deposition temperature, substrate and chemical composition [1.17]. Huang et al. have shown that an increase in the permittivity and permeability of hexaferrites can be achieved through a 1.5% doping with BSTO. They also observed a change in coercivity and anisotropy with BSTO content, which implies a possible method of manipulating the microstructure of BaF by integrating it with BSTO.

A concern in the development of tunable microwave circuits is the large change in the characteristic impedance ($Z_0$) of the device, which occurs when the dielectric constant of the ferroelectric is reduced by a factor of four or more with an applied dc bias field. A poor impedance match at the device will increase the reflection and total insertion loss of the device. Ferroelectric-ferrite multilayers may lead to active adjustment of the characteristic impedance by changing both the permittivity of the ferroelectric and the permeability of the ferrite. [1.19] Ferroelectric-ferrite multilayers of BSTO and $Y_3Fe_5O_{12}$ grown by Kim et al have been shown to be electrically and magnetically tunable, realizing the goal of dual tuning with a multilayer structure.

Lastly, exciting progress is being made in the field of multiferroics, materials that are simultaneously ferromagnetic and ferroelectric. For a single material to be multiferroic, its allowed physical, structural, and electronic properties are restricted to those which occur both in ferromagnetic and in ferroelectric materials. Such materials
have all the potential applications of both ferroelectric and ferromagnetic materials. In addition, a whole range of new applications are possible. The ability to couple either to the electric or the magnetic polarization allows an additional degree of freedom in the design of conventional actuators, transducers, and storage devices. Other potential applications include multiple state memory elements, in which data is stored both in the electric and the magnetic polarizations, or novel memory media, which might allow writing of a ferroelectric data bit, and reading of the magnetic field generated by association. Finally, the physics of multiferroics is not well understood, providing much opportunity for contribution. [1.3]

While multiferroic materials show tremendous technological promise, they are extremely rare. This is not surprising given that the mechanisms that lead to ferroelectricity and ferromagnetism are not usually compatible. The conventional mechanism driving ferroelectricity in perovskite $\text{ABO}_3$ structure oxides requires vacant $d$ orbitals in the B cation. In contrast, occupied $d$ orbitals are required in order to have any kind of magnetic ordering. This makes it surprising that there are multiferroic materials at all. [1.3]

A proactive way of finding multiferroic materials is to synthesize them by combining ferroelectric and ferromagnetic materials. In thin film form this can be done by making multilayers structures. It is our hope that not only can we electrically and magnetically tune these films by external electric and magnetic fields, but that we may observe other interesting phenomena associated with multiferroics.

The magnetoelectric effect is the induction of magnetization by means of an electric field and the induction of polarization by means of a magnetic field [1.20]. This
implies a new property of reverse tunability for our materials. Another manifestation of coupling between a ferroelectric and a ferromagnet is a change in magnetization at the ferroelectric Curie temperature. This has been observed in multiferroic nanostructures of BaTiO$_3$ and CoFe$_2$O$_4$ [1.21]. The reverse, dielectric anomalies at the magnetic transition temperatures are also possible [1.22].

Optimizing the growth parameters and characterizing the resulting multilayer films is the most time consuming aspect of this project. Huang et al’s results indicate that we need to look carefully for changes in the BaF microstructure after the BSTO is incorporated. Our Physical Properties Measurement System (PPMS) will enable us to examine the magnetic properties of the multilayer films, giving us crucial information needed to progress our study. Finally, the last part of the project is to deposit magnetic nanoparticles on the multilayers to bring an even wider range of applications to our structures.

1.6 Magnetic Nanoparticles

Nanoparticles (particles with a radius less than 100nm) are currently the focus of much technological interest. The nanometer length scale is comparable to an electron’s mean free path, or the average distance that an electron will travel between collisions with the vibrating atoms or impurities of the solid. When the size of the particles are less than a characteristic length such as the mean free path, it is possible to see different physical or chemical characteristics than those exhibited by their larger counterparts. Electrical resistivity, reactivity, melting temperature and optical absorption have all been shown to be dependent on particle size when particles reach the nanometer scale. [1.11]
With this in mind, one can immediately deduce that magnetic properties will be affected by particle size, especially when particle size is of the same length scale as the magnetic domains of the material. At the nanometer scale, magnetic particles have been shown to behave differently than in bulk magnetic materials. As particle size decreases, remnant magnetization and saturation magnetization increases. This implies that scaling particles down to the nanometer scale can greatly improve the quality of magnets fabricated from them. [1.11]

When the size of the magnetic nanoparticles reaches single domain, a new type of magnetism can be achieved, called superparamagnetism. When this occurs, the coercivity and remnant magnetization go to zero. For superparamagnetic particles, the net magnetic moment in zero field at T >0K will average to zero. In an applied field, there will be a net statistical alignment of magnetic moments. This is analogous to paramagnetism, except now the magnetic moment is not that of a single atom, but of a single domain particle containing $10^5$ atoms. Hence the term superparamagnetism, which denotes a much higher susceptibility value than that for paramagnetism. [1.23]

Superparamagnetism can improve the efficiency of systems that are subjected to rapidly alternating AC magnetic fields like transformers and rotating electrical machinery. In a traditional magnet exposed to an AC magnetic field, the magnet cycles through its hysteresis loop often causing a loss of efficiency and a rise in temperature. This rise in temperature is due to the frictional heating that occurs when magnetic domains are varying their orientation. The amount of energy loss in each cycle is proportional to the area enclosed by the loop, so a small or non-existent coercivity is desirable. [1.11]
It has also been shown that particle size has a large effect on microwave absorption. Particles of nanometer size greatly improve the absorptive efficiency and broaden the bandwidth. [1.24]

It is our hope that by coating our electrically and magnetically tunable multilayer films with magnetic nanoparticles, we will produce a novel structure with the advantages associated with ferroelectric, ferromagnetic and nanostructured films. The multilayer films can be used as base substrates whose tunability is a variation in frequency dependent material parameters such as impedance, permeability and dielectric constant through external electric and magnetic fields. The nanoparticle arrays will add even more versatility. They can be ferromagnetic, ferrimagnetic or antiferromagnetic, all possessing different properties. We anticipate that there will exist coupling between the hard ferrite component (BaF) and the magnetic nanoparticles which will be revealed through frequency dependant measurements.

Although many of the experiments discussed above to reveal multiferroism and how the nanoparticles may interact with the tunable components are in various stages of progress in our Materials Physics Laboratory, the scope of this thesis is limited to the microstructure and magnetism of these systems. The synthesis, characterization and examination of magnetic properties of these films in itself is a major undertaking that gives us a glimpse into the underlying fundamental properties of these little-studied systems.
Chapter Two

Growth of Ferrite-Ferroelectric Multilayers by Magnetron Sputtering

Depositing oxides in thin film form can be challenging due to the very nature of these materials. High melting temperatures rule out evaporation and high resistivities make DC sputtering impossible. Other considerations like brittleness and complicated stoichiometry make bulk sample targets vulnerable to deposition conditions. With these characteristics in mind, we concluded that radio frequency (RF) sputtering is the ideal technique for depositing our chosen ferrite-ferroelectric thin film oxides. While pulsed laser deposition (PLD) is known for yielding stoichiometric films, its highly unidirectional deposition makes it less preferable for producing film batches consisting of several samples. [2.1]

RF sputtering makes it possible for dielectric materials to be sputtered at relatively low voltages. However, due to the inherent difficulty of passing current through a dielectric, sputtering rates for oxides are extremely slow and inefficient. Magnetron sputtering helps alleviate this problem by introducing a magnetic field in addition to the usual electric field present in the plasma. This helps confine electron
motion to the target area, improving plasma intensity and thus deposition rate. The fact that the plasma is more confined to the area between the target and the substrates improves the efficiency by reducing the amount of material wasted during deposition.

2.1 Growth of films at Oak Ridge National Laboratory

Our continued collaboration with Dr. Nancy Dudney’s group in the Condensed Matter Sciences Division provided us access to sputtering facilities and characterization equipment at Oak Ridge National Laboratory (ORNL). My work at ORNL was supported by a Southeastern Universities Research Association (SURA) Fellowship. The plan was to deposit multilayer thin films of Barium Strontium Titanate (BSTO) and Barium Hexaferrite (BaF) on three types of substrates: Polished alumina (Al₂O₃), thermally oxidized Silicon (Si/SiO₂), and kapton, a polyimide commercially available in a variety of thicknesses. While the first two choices are quite standard in oxide film growth, the idea was that kapton would provide mechanical flexibility and good thermal conductivity if we could successfully grow the BSTO/BaF films on it.

Films of pure BSTO and pure BaF were deposited using a non-commercial magnetron sputtering vacuum chamber equipped with two guns holding the BSTO and BaF targets and attached to RF power supplies. The BSTO and BaF targets were 2-inch ceramic sputter targets with copper back plates from SCI Engineered Materials. The two targets were set up vertically and a movable substrate holder could be positioned over either target (figure 2.1). In addition, a quartz crystal oscillator could be placed over either of the targets to measure deposition rates. Unfortunately, the thickness
monitor and substrate holder could not be placed simultaneously over the same target to measure the film thickness as it was being deposited. Thicknesses had to be inferred from deposition rates measured before and after the deposition and then later verified with a profilometer.

Figure 2.1. Sputter Chamber at ORNL.
Initial films of BSTO and BaF were grown on Al₂O₃ substrates with a Pt buffer layer as well as glass substrates to investigate post-annealing conditions. The target thickness of each film was 2µm. Using x-ray diffraction (discussed in chapter three) good crystalline peaks of both materials were obtained when as-grown films were subjected to post-annealing in an O₂ atmosphere at 1000°C for 10 hours.

The first attempt at growing multilayer films was done on a set of four substrates: glass, kapton, bare alumina and bare Silicon. The presence of two guns allowed the multilayer structure to be grown in situ by simply rotating the substrate holder to be in position above the desired target. The films consisted of four layers of alternating BSTO and BaF. The bottom layer was BSTO, and each layer was grown approximately 1µm thick. Upon removing the films from the chamber, an immediate adhesion problem was observed with the films on Silicon. The kapton substrate had curled up, causing the film to flake off. The curling was most likely due to the substrate being too small for the holder and the kapton being susceptible to the sputtering conditions. It is likely that kapton may not be suitable given the proximity to the high voltage plasma in the chamber. In any case, we had to abandon the plan of using kapton as a viable substrate for magnetron sputtering.

Annealing this batch of multilayers under the same conditions as the pure films proved insufficient and flaking off of the films occurred (figure 2.3a). A systematic investigation of annealing conditions revealed that the films were unable to adhere at temperatures higher than 200°C. The possible explanations for this problem are that the films were too thick, causing interfacial strain between the layers, or the mismatch in thermal expansion between BSTO (10.5 x 10⁻⁶°C⁻¹ [2.2]) and BaF (12.2 x 10⁻⁶°C⁻¹ along
the a-axis, $10.0 \times 10^{-6}\text{C}^{-1}$ along the c-axis [2.3]). It is also to be noted that flaking is usually not a problem for single layer thin or thick films. Our studies underscore the complexities in growing multilayers.

If a chemical reaction was responsible for the films flaking off, X-ray diffraction might have signaled the presence of any impurity phases that were greater than 5% by volume. Unfortunately, at the time of film deposition at ORNL, the machine was out of order and we had to rely on other methods to investigate this problem. Scanning electron microscope (SEM) images of the film grown on Silicon revealed fragments of film lying on a smooth background. Energy dispersive spectroscopy (EDS) scans showed the presence of Barium, Strontium, Titanium and Oxygen as well as Silicon, implying that what we thought to be the substrate still contained some of the bottom BSTO layer.

Due to time constraints and the fact that the magnetron sputtering system was off-campus and available to us only for a limited time, we were unable to perform a systematic study to determine which of the sputtering parameters was the main reason for the films flaking off. When we tried to grow multilayers with BaF as the bottom layer, the adhesion problems were much worse. However, there was marginal improvement with the BSTO as the bottom layer, so we decided to continue using this configuration for all of the films. We decided another step would be to integrate a heated substrate holder into the system and try growing the multilayers at a temperature above the post-annealing breakdown temperature of $200\degree C$. Substrate heating is quite common in growth of oxide films and several groups have used this process for successful growth of individual oxide films.

The magnetron sputtering system at ORNL did not have a substrate heater. As
part of this research project, a substrate heater was designed and integrated into the
deposition chamber. The old substrate holder was replaced with a larger holder that
contained a resistive heating element. The new holder could be mounted to the rotator in
the same manner as before. Copper wires insulated with ceramic beads were mounted
from the holder to the inside wall of the chamber where they terminated at a socket.
Plugged into the outside wall of the chamber was a voltage source and attached to that, a
temperature controller. These connections were designed to maintain the vacuum and
isolation conditions of the sputtering chamber. The substrate holder was a disk three
inches in diameter and was beveled so that two 1" x 1" substrates could smoothly lie
under masks that were screwed in (figure 2.2). To monitor the temperature of the
substrates under the two different masks, two chromel-alumel thermocouples were made
and insulated with nylon. Divots were machined into the masks so that the
thermocouples could fit tightly between the substrates and the masks. Under this
arrangement, two sets of four substrates (each substrate $\frac{1}{2}" \times \frac{1}{2}"$) could be placed in the
substrate holder at a time.

Four batches of multilayer films were made successfully with heated substrates
(figure 2.3b). We limited the substrates to $\text{Al}_2\text{O}_3$ and Si/SiO$_2$ because the kapton would
not have survived the substrate heating followed by post-annealing requirements. Onto
some of the substrates we deposited thin layers of Ti and Pt so that capacitance and
ferroelectric hysteresis loop measurements could be made later. Table 1 summarizes the
optimized sputtering conditions for the separate depositions.
Figure 2.2. Modified substrate holder.
Figure 2.3. a) Photograph of initial multilayer deposition without heated substrate holder. Clockwise from upper left: multilayers on kapton, multilayers on glass, multilayers on Si, multilayers on Al$_2$O$_3$ (sample was broken in half with the left side having been annealed and the right side remaining as deposited). b) Successful films grown after substrate holder was modified to include a heater. Clockwise from upper left: multilayers on Al$_2$O$_3$, multilayers on Si/SiO$_2$, multilayer on Si/SiO$_2$ with Ti and Pt layers, multilayers on Al$_2$O$_3$ with Ti and Pt layers.
<table>
<thead>
<tr>
<th>Batch Number</th>
<th>Substrates</th>
<th>Layers</th>
<th>Argon Pressure (mtorr)</th>
<th>Argon Flow (sccm)</th>
<th>Power (BSTO, BaF) (W)</th>
<th>DC Bias BSTO, BaF (V)</th>
<th>Substrate Temp (°C)</th>
<th>Deposition Rate (BSTO, BaF) (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al₂O₃ w/Pt, glass</td>
<td>BSTO</td>
<td>19.9</td>
<td>20.0</td>
<td>30, —</td>
<td>78, —</td>
<td>room</td>
<td>15, —</td>
</tr>
<tr>
<td>2</td>
<td>Al₂O₃ w/Pt, glass</td>
<td>BaF</td>
<td>20.3</td>
<td>20.0</td>
<td>—, 39</td>
<td>—, 91</td>
<td>room</td>
<td>—, 28</td>
</tr>
<tr>
<td>3</td>
<td>Al₂O₃, Si/SiO₂</td>
<td>BSTO, BaF, BSTO, BaF</td>
<td>19.8</td>
<td>57.2</td>
<td>59, 59</td>
<td>248, 242</td>
<td>306</td>
<td>55, 40</td>
</tr>
<tr>
<td>4</td>
<td>Al₂O₃, Si/SiO₂</td>
<td>BSTO, BaF, BSTO, BaF</td>
<td>20.0</td>
<td>55.9</td>
<td>63, 60</td>
<td>135, 236</td>
<td>316</td>
<td>48, 37</td>
</tr>
<tr>
<td>5</td>
<td>Si/SiO₂ w/Ti &amp; Pt, Si/SiO₂</td>
<td>BSTO, BaF, BSTO, BaF</td>
<td>20.0</td>
<td>56.2</td>
<td>68, 64</td>
<td>138, 239</td>
<td>303</td>
<td>73, 46</td>
</tr>
<tr>
<td>6</td>
<td>Al₂O₃, Al₂O₃ w/Ti &amp; Pt, Si/SiO₂, Si/SiO₂ w/Ti &amp; Pt</td>
<td>BSTO, BaF, BSTO, BaF, BSTO</td>
<td>20.0</td>
<td>56.3</td>
<td>68, 63</td>
<td>143, 235</td>
<td>340</td>
<td>79, 43</td>
</tr>
</tbody>
</table>

Table 2.1. Details for batches yielding viable films. For all batches, sputtering was done in an Argon atmosphere after a base pressure of ~10⁻⁷-10⁻⁶ was reached. Temperatures given are averaged. Temperatures fluctuated during depositions by about ±25°C.
2.2 Growth of films at the University of Central Florida

A second set of films was grown through a collaboration our group recently started with the University of Central Florida, in Orlando. Professor Kevin Coffey of the Advanced Materials Processing and Analysis Center (Ampac) worked with us to try to grow more multilayers to be used for a variety of experiments.

Unlike the system at ORNL, Dr. Coffey’s magnetron sputtering system is a commercial system built by AJA International, Inc. It is equipped with six guns, four connected to DC power sources and two connected to RF power sources. The default geometry of the chamber allows simultaneous deposition of several materials by having each target tilted at an angle from the normal. One large substrate holder is placed in the middle of the chamber and rotated to promote uniform material deposition from each target.

Initial calibration runs with this system indicated that some modification would need to be done. With the substrate holder held so far from the targets and the targets themselves being tilted, we were getting such poor efficiency that the targets would have completely eroded before enough material was sputtered to deposit a 0.5µm film. Clearly we needed a substrate holder that could be placed directly above the targets and therefore allow the targets to sit upright in the chamber.

We designed a new substrate holder that could be integrated into Dr. Coffey’s system by attaching to the same piece that rotated the previous substrate holder. The new holder, machined here at USF, consists of two aluminum bars connected perpendicularly at the center, effectively making four arms at 90° intervals (figures 2.4 and 2.5). Screwed into each arm is an aluminum spacer and on the other side of the spacer is attached the
actual substrate holder, enabling the user to deposit four sets of films that could have variety in terms of materials.

We decided to take advantage of these features and deposit two different sets of multilayers, each set consisting of three layers (BSTO/BaF/BSTO and BaF/BSTO/BaF). We used the remaining two arms to deposit pure BSTO and pure BaF. The target

Figure 2.4. Substrate holder designed to be integrated into the sputtering system at UCF.
thickness for the multilayer films was 0.9µm total and for the plain films 0.6µm each. The choice of three layers instead of four and making the total films thinner was a result of constraints imposed upon us by the sputtering parameters. Sputtering rates were slower than at ORNL and we were also hoping that thinner films might make post-annealing easier. One thing we were not able to include in our new substrate holder was a heater. Since all sputtering systems are different, we essentially had to re-optimize the
parameters. We decided to start at the beginning once again and try depositing on polished Al₂O₃ at room temperature. As before, some of the substrates had a platinum layer on them for capacitance and ferroelectric measurements. Table 2.2 contains the parameters used for this deposition.

Our assumption that we could grow multilayers successfully on Al₂O₃ substrates at room temperature proved to be wrong as our initial attempts at post-annealing failed. Slow ramping up to 1000°C in O₂ caused the BSTO/BaF/BSTO multilayers to disintegrate and we were left with a fine powder. Though we knew annealing needed to be done above 800°C to see any x-ray peaks, systematic annealing studies showed that the films could not even tolerate 400°C.

The BaF/BSTO/BaF multilayers on Al₂O₃ and the pure BaF and BSTO films survived annealing to 1000°C. It was surprising that the pure BSTO on Al₂O₃ tolerated the high temperatures while the multilayers with BSTO on the bottom did not, especially since x-ray diffraction data has not indicated chemical phases consistent with a reaction. If there was a BSTO/Al₂O₃ reaction, the region of the film containing the by-product was too thin to produce a signal. One possibility is the porosity of the Al₂O₃ combined with the overall thinner multilayers compared to those grown at ORNL may have resulted in our failure to obtain good quality continuous multilayers. We are still exploring options for depositing and post-annealing the BSTO/BaF/BSTO. Some of these include depositing a thin BSTO layer on heated substrates using Dr. Coffey’s heated holder and his original geometrical set-up followed by our films using our own four-arm configuration. Unfortunately, this would involve breaking vacuum between layers.
Another option is experimenting with different initial buffer layers as well as using different substrates.

Almost the opposite situation occurred with the films deposited on $\text{Al}_2\text{O}_3$ with Platinum. Immediately after deposition the Pt/BaF/BSTO/BaF multilayers as well as the Pt/BaF films peeled off in large flakes leaving only the bare substrate. Pt/BSTO/BaF/BSTO and Pt/BSTO films have been successfully annealed.

<table>
<thead>
<tr>
<th>Arm Number</th>
<th>Layers</th>
<th>Argon Pressure (mtorr)</th>
<th>Argon Flow (sccm)</th>
<th>Power (BSTO, BaF) (W)</th>
<th>DC Bias BSTO, BaF (V)</th>
<th>Substrate Temp (°C)</th>
<th>Deposition Rate (BSTO, BaF) (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BSTO, BaF, BSTO</td>
<td>4</td>
<td>20</td>
<td>70, 70</td>
<td>196, 302</td>
<td>room</td>
<td>57, 38</td>
</tr>
<tr>
<td>2</td>
<td>BSTO</td>
<td>4</td>
<td>20</td>
<td>70, —</td>
<td>235, —</td>
<td>room</td>
<td>57, —</td>
</tr>
<tr>
<td>3</td>
<td>BaF, BSTO, BaF</td>
<td>4</td>
<td>20</td>
<td>70, 70</td>
<td>196, 302</td>
<td>room</td>
<td>57, 38</td>
</tr>
<tr>
<td>4</td>
<td>BaF</td>
<td>4</td>
<td>20</td>
<td>—, 70</td>
<td>—, 322</td>
<td>room</td>
<td>—, 38</td>
</tr>
</tbody>
</table>

Table 2.2. Conditions for film growth at the University of Central Florida. Different targets were used from the ones at ORNL. Deposition rates were calibrated without the use of a thickness monitor before all the films were deposited.
In summary, we can draw some important conclusions based on our experience in growing multilayers with two distinct sputtering systems. First and foremost, systems are very different from each other and conditions for growing multilayers need to be re-optimized every time one wishes to use a different system. While individual films of high quality can be easily optimized and routinely grown, multilayers of BSTO/BaF have issues such as interfacial and overall film stress that need to be carefully addressed. This is time consuming and can best be handled by a systematic approach of varying sputtering parameters and post-annealing conditions followed by characterization of structure and physical properties until quality films are achieved. Considering that to our knowledge this is the first ever attempt at growing BSTO/BaF multilayers, our work has already yielded insights into key parameters that need to be controlled. We expect from what he have learned so far that the quality of multilayers we grow will improve with time.
Chapter Three

Structural Characterization of Ferrite-Ferroelectric Multilayers

In this chapter we present the structural characterization of the sputtered multilayer samples. Before annealing, profilometry was used to find the thicknesses of the as-deposited films. X-ray diffraction (XRD) was used to help optimize post-annealing conditions. After the films showed peaks consistent with crystalline phases of both materials, XRD was also used to gain insight into possible preferred orientations of the film.

Two different methods were used to image the films: atomic force microscopy (AFM) and scanning electron microscopy (SEM), each method providing different and valuable information. AFM, primarily used for topographical imaging, was used to look at the structure of BaF as the top layer. SEM was used to further image the surface and zoom in individual BaF particles. SEM was also used to image the BSTO and provided us with the first known cross-sectional images of BSTO/BaF multilayer films.
3.1 Thickness Measurements

3.1.1 Thickness measurements of films grown at Oak Ridge National Laboratory

The target thickness for all multilayer films was 2µm. Sputtering times were determined by deposition rates measured before depositions and calculated to yield 0.5µm per layer. Deposition rates were measured using a thickness monitor inside the sputtering chamber so that rates could be measured in vacuum. The thickness monitor was a quartz crystal oscillator that detected a change in frequency due to the mass of the film deposited on the sensor. It used the density of the film material (an input parameter) to calculate the film’s thickness [3.1]. Though quartz crystal oscillators can yield exceptional thickness accuracy when used during a deposition, the one used in the chamber at ORNL could not be placed over the target while film was being deposited, providing some room for error. However, from the aspect of functional properties of the multilayers, there is no requirement for a critical thickness. As long as the entire structure is reasonably thick (approximately 1µm or greater), mechanical stress induced problems are not expected to be significant.

Deposition rates vary slightly even within the same target as a target erodes due to sputtering. As we were witness to, deposition rates measured before and after a deposition sometimes were not in perfect agreement. Even though rates were measured by collecting and averaging over five minute depositions onto the monitor, this averaging did not smooth out the tendency for the rates to increase over time. When total deposition times are on the order of hours, as was the case here, these effects can become
significant. As a result, other methods of measuring film thickness (profilometry, cross-sectional imaging) yielded thinner films than anticipated.

Thickness measurements on a selected number of films were taken at ORNL before annealing was done. A Sloan Dektak profilometer gave average step heights as the stylus scans across the substrate-film edges.

Films deposited on Al$_2$O$_3$ tended to give smooth profiles with a visible step where the bare substrate ends and the film begins (figure 3.1). Using profilometry, thickness measurements of the films were between 1.0 and 1.3µm, much thinner than our original targeted thickness. Measuring the thicknesses of films grown on Si/SiO$_2$ was more troublesome. In a few cases, the step was close to what we were getting for the films on Al$_2$O$_3$ (figure 3.2a), but in most cases there was a step followed almost immediately by a gradual decline in surface height (figure 3.2b). Often when one is using a profilometer, a

![Figure 3.1. Profilometry data for film grown on Al$_2$O$_3$.](image)
similar phenomenon will occur, but this is due to improper leveling of the stage. After repeated trials, we were convinced that the decline was real and present on the substrate. It is possible that the thin Si/SiO$_2$ wafers were warped during the deposition from the plasma conditions in the sputter chamber.

A more straightforward method was employed on one sample. While trying to investigate the layered structure, we took an SEM image of the cross-section of a film cleaved in half with a diamond scribe (figure 3.9b). While structural results from this experiment will be discussed later (section 3.4.2) this brute-force method of measuring thickness gave us 1.66µm, midway between results from the profilometer and what we calculated from deposition rates.

![Figure 3.2a.](image-url)
3.1.2 Thickness measurements of films grown at the University of Central Florida

The sputtering system at UCF was not equipped with a thickness monitor, so deposition rates had to be determined by other means. The BSTO and BaF targets were new as the ones used at ORNL had eroded significantly in the meantime. It is always tricky finding the deposition rates for new targets because the rates will change dramatically as the targets are used over time. First, we let the targets sputter without a substrate present for a couple of hours. Then, we used a permanent marker as a crude lithography tool to create a mask, drawing a few intersecting lines on a glass substrate. We sputtered each of the targets for a fixed amount of time and then removed the marker with a solvent. The films were then coated with gold and an optical interferometer was
used to measure the thickness of the deposited films. However, even after a couple hours of sputtering the new targets the deposition rates were probably still variable.

The thickness we were attempting to achieve for the multilayer films was 0.9µm and for the pure BSTO and BaF films it was 0.6µm. Post deposition (and pre-annealing) thickness measurements done at USF with a Tencor Instruments profilometer indicated that the multilayer films of BSTO/BaF/BSTO had a thickness of about 0.7µm while the BaF/BSTO/BaF films were about 0.8µm (figure 3.3 a and b). Pure BSTO and BaF films had thicknesses of around 0.5µm and 0.45µm respectively (figures 3.3 c and d).
Figure 3.3. Profilometry data for films grown at UCF. a) BSTO/BaF/BSTO multilayers. Thickness is measured as 715nm. b) BaF/BSTO/BaF multilayers. Thickness is measured as 800nm. c) Pure BSTO. Thickness is measured as 505nm. d) Pure BaF. Thickness is measured as 455nm.
3.2 X-Ray Diffraction Data

3.2.1 X-ray diffraction of films made at Oak Ridge National Laboratory

X-ray diffraction is a technique used to determine the crystal structure of sample in which a collimated beam of x-rays is directed at the sample and the angles at which the beam is diffracted are measured [3.2]. Initial x-ray scans of the BSTO and BaF films on Al₂O₃ with Platinum were done at ORNL and are shown in figure 3.4. In the BSTO scan, the majority of BSTO peaks are present, though not all. The strong (220) peak is completely missing, suggesting a tendency for the BSTO not to crystallize in that orientation on that particular substrate. The peaks that are not labeled are all accounted for by the Al₂O₃ substrate except for the strongest line, which is the characteristic peak for Platinum. This implies that there was no significant chemical reaction between the BSTO and the substrate since there are no peaks indicative of a different compound.

Similar conclusions can be drawn for the BaF on Al₂O₃/Pt film. While almost all of the strongest BaF peaks are present, a strong (220) peak at 63º is clearly missing. As above, all other peaks are accounted for either by Al₂O₃ or Platinum.
Figure 3.4. X-ray diffraction scans of films grown at ORNL. a) Pure BSTO. BSTO peaks are indexed; all others are from Al$_2$O$_3$ except for the sharpest peak which is from Platinum. The widening at the base of the Pt peak is due to the BSTO (111) peak. b) Pure BaF. BaF peaks are indexed; all other peaks are from the substrate.
The x-ray diffractometer was out of order for the rest of the time at ORNL and scans of the multilayers had to be taken here at USF after all other films were made. Sample scans of multilayer films grown on $\text{Al}_2\text{O}_3$ and $\text{Si}/\text{SiO}_2$ are shown in figure 3.5.

What is immediately noticeable about the multilayer films grown on $\text{Si}/\text{SiO}_2$ is the intense peak around $17^\circ$. This along with peaks present at $14^\circ$, $18.5^\circ$ and $25.5^\circ$ all seem to be associated with an impurity $\text{Sr}_3\text{Si}_3\text{O}_9$ phase which might explain some of our adhesion problems. Evidently, the bottom BSTO layer was chemically reacting to the $\text{Si}/\text{SiO}_2$ substrate. This reaction possibly was damaging to the top layers of the films, forcing them to flake off. This reaction must have occurred somewhere above room temperature but below the substrate heating temperature so the BSTO and $\text{Si}/\text{SiO}_2$ could react during the deposition and not disturb the films during post-annealing.

Film growth (both BSTO and BaF) reported in literature tend to have underlayers such as Titanium and Platinum that could be buffer layers preventing this interaction with the substrate. Our initial idea was that in a thick multilayer, a thin interfacial layer at the substrate would not significantly affect the overall films properties. While this may be true for physical properties, it appears that the buffer layers are critical to establish good mechanically robust films. We will attempt these experiments in the future, and study the influence of buffer layers.

While not all the BSTO peaks are present that were seen in the pure BSTO scan, there are three distinct peaks that are seen in both (a) and (b) of figure 3.5. For BaF, the peaks present in the multilayer on $\text{Al}_2\text{O}_3$ scan match up well with the peaks of pure BaF on $\text{Al}_2\text{O}_3$. There are a couple of weak peaks that are not seen in the multilayers that are present in figure 3.4b. The (0014) and (220) peaks are present in the multilayer scan but
not in the pure BaF scan. As we will explain later, it turns out that the presence of BSTO in the multilayers plays a huge role in the growth of BaF. This could explain some differences in the XRD data between pure BaF and the multilayers.

The scan of multilayers on Si/SiO$_2$ has different BaF peaks than that of the pure BaF on Al$_2$O$_3$ or even the multilayers on Al$_2$O$_3$. There are peaks present in figure 3.5a that are not in 3.5b ((106) and (2011)) and that are not in 3.4b ((106), (205), (0014) and (220)). Also, there are peaks present in 3.5b that are not in 3.5a ((102) and (104)). This suggests that the BaF grain orientations are strongly dependent on the substrate used even when BaF is used as the second and fourth layers in the multilayer structure and not directly in contact with the substrate. We note that this trend of using substrates and buffer layers to tailor the grain growth mechanism in BaF is of topical interest and other groups are attempting this while growing pure BaF films. In particular, c-axis orientation of BaF grains in epitaxial films is expected to hold excellent potential for perpendicular recording media [3.3].
Figure 3.5. X-ray diffraction scans of films grown at ORNL. a) Multilayers on Si/SiO2. b) Multilayers grown on Al2O3.

3.2.2 X-ray diffraction of films made at the University of Central Florida

X-ray diffraction of films grown at UCF was done at USF using a Philips PW2-4-Pro diffractometer. The pure BSTO on Al₂O₃ analysis revealed four peaks of moderate strength and width ((100), (110), (111) and (200) in figure 3.6a). The difference between this film and the pure BSTO film from ORNL is most likely due to the UCF films being much thinner and the use of a new target. Only two BSTO peaks are present in the scan of the multilayer films ((110 and (200) in figure 3.6c).
The pure BaF on polished Al₂O₃ grown at UCF (figure 3.6b) has different peaks than the pure BaF film grown at ORNL on Al₂O₃ with Platinum. The pure BaF from UCF has the (108), (300) and (220) peaks which are not present in figure 3.4b and the pure BaF from ORNL has the (202), (102), (006), (217) and (2011) peaks which are not present in figure 3.6b. This again suggests how sensitive grain orientation can be. It is possible that in this instance the Platinum buffer layer affected the grain orientation enough to create different peaks than those seen for the BaF on bare, polished Al₂O₃.

Overall, the peaks seen in the multilayer films made at UCF are not as sharp and strong as the ones seen in the films made at ORNL. We attribute these differences to film thickness and the fact that the post-annealing procedure has not been completely optimized. Work continues through our collaboration on the UCF sputtering system to improve the quality of the multilayers there. Since access to the sputtering system at UCF (in Orlando) is much more convenient than the one at ORNL (in Tennessee), we are hoping the materials growth work will progress more rapidly and optimization should not take too much time.
Figure 3.6. X-ray diffraction scan of films made at UCF. a) Pure BSTO. b) Pure BaF. c) Multilayers.

3.3 Atomic Force Microscope Images

The atomic force microscope (AFM) is an example of a scanning probe microscope which is known for directly imaging surfaces. Unlike other electron beam-based imaging tools, there are few restrictions on what may be imaged. Metals, semiconductors and insulators are all imageable. The AFM employs a probe tip that is etched to a small radius (< 10nm) and mounted at the end of a soft cantilever spring. This tip scans along the surface of the sample and an interferometer detects deflections of the cantilever due to
surface features of the sample. A feedback system monitors and controls the force applied by the cantilever onto the sample and a display converts the force-position data into an image. [3.1]

A Digital Instruments AFM available to us at USF was used to take images of both batches of films (figure 3.7). Surface images of the films made at ORNL show sharp, needle-like particles characteristic of BaF. Images of films grown at UCF also show the elongated BaF particles but in general they appear to be shorter in length. It is documented that BaF grain shape can be highly dependent on substrate temperature [3.4]. When the substrate is heated, the grain nuclei can align better, giving more room for grains to grow large. During room temperature depositions, the nuclei are randomly oriented and the grains do not grow as large due to space restrictions.

Another thing to notice is the large dark spot on the upper right-hand corner of the AFM image of the film grown at UCF (figure 3.7d). This was our first indication that not only were the UCF films thinner than we thought but they might not have even covered the substrates completely. Also, the gradual change in color from the lower left to the upper right of the image suggests that the film might be thinly deposited over a rough surface. Later, SEM images revealed islands of bare and porous Al₂O₃ (section 3.4).
a.

b.
Figure 3.7. AFM images of multilayers with BaF as the top layer. a) Surface image of multilayers on Si/SiO$_2$ deposited at ORNL. b) Profile image of multilayers on Si/SiO$_2$ from ORNL. c) Profile image of multilayers on Al$_2$O$_3$ deposited at ORNL. d) Surface image of multilayers on Al$_2$O$_3$ deposited at UCF.
3.4 Scanning Electron Microscope Images

In a scanning electron microscope (SEM) electrons are thermionically emitted from a tungsten or LaB$_6$-cathode filament to an anode and focused by two successive lenses into a beam with a very fine spot size. Pairs of scanning coils located at the objective lens deflect the beam either linearly or in raster fashion over a rectangular area of the sample surface. When the electron beam impinges on the surface, the primary electrons decelerate and lose energy, transferring it to other electrons in the sample. Through continuous random scattering events, the primary beam spreads and fills a small volume. The result is a distribution of electrons which leave the sample with an energy spectrum. Various SEM techniques are based on what part of the energy spectrum is detected and imaged. In our samples, the secondary (lowest energy) electrons are detected and imaged. [3.1]

The SEM at ORNL and the two available to us at USF have revealed some of the most important information about our films. They have not only been used to image BaF and BSTO surfaces, they have also given us an idea of the cross-sectional structure of the films, verified thickness measurements and grain-size measurements and shown us what needs to be done differently in the future. It should be noted that this the first study of multilayers of BSTO and BaF. The fact that we were able to get good cross-sectional scans is a major success in our project.
### 3.4.1 Surface images

A Hitachi S-800 SEM at USF was used to image some of the films grown at ORNL. Surface images of films grown at ORNL gave us images consistent with AFM data. The post-annealed BSTO surface deposited at room temperature is homogeneous with symmetrical, irregular shaped particles on the order of 1µm across (figure 3.8a). The BaF surface shows in greater detail the elongated particles with high aspect ratio, which we measured to be on average 1.2µm x 0.3µm (figure 3.8b).

Surface images of those films grown at UCF were taken with a Philips 515 SEM. High magnification images of BSTO surfaces grown at UCF were very similar to those of the films grown at ORNL. The BaF surfaces of films grown at UCF were different from those grown at ORNL due to the sensitivity of BaF grain size and shape to deposition conditions and substrates. The particles seem not as well-defined and have a much greater size-distribution than those grown on heated Si/SiO$_2$ substrates. The size distribution could be a consequence of their tendency to prefer different orientations on Al$_2$O$_3$ versus Si/SiO$_2$, or heated versus room temperature substrates. The longest and thinnest particles visible in figure 3.8c are the same size as most particles in 3.8b, but there are many more particles that appear smaller or altogether shapeless.

A low magnification surface image of one of the multilayers deposited at UCF proved what we had already suspected, namely that the films were not uniformly covering the entire substrate (figure 3.8d). Further investigation points to the Al$_2$O$_3$ substrates having pores deeper than the thickness of our multilayers, creating discontinuous films thus limiting the experiments that can be performed on them.
Figure 3.8. SEM surface images.  a) Multilayers with BSTO as top layer grown at room temperature on Al₂O₃ at ORNL magnified 30000x.  b) Multilayers with BaF as top layer grown on heated Si/SiO₂ at ORNL magnified 20000x.  c) Pure BaF grown at room temperature on Al₂O₃ at UCF magnified 20800x.  d) Multilayers with BaF as top layer grown at room temperature on Al₂O₃ at UCF magnified 326x.
3.4.2 Cross-sectional Images

Cross-sectional images were taken of representatives of both batches of multilayers. Figure 3.9a shows an SEM image taken at ORNL with a JEOL JSM-840. The image is a multilayer film deposited at room temperature pre-annealing. This particular film had partially flaked off and the imaged piece was peeling away from the bottom BSTO layer and underlying Silicon substrate. Even though the film itself was considered a “failure” due to its lack of adhesion, it was well-suited for cross-sectional imaging and indicated that clear BaF/BSTO interfaces could form. The features associated with BaF grains are clearly visible in the top and bottom layers and the more continuous structure in the center can be identified as the middle BSTO layer.

The cross-section of the best quality multilayer film on Si/SiO$_2$ that we could obtain is presented in figure 3.9b. The image was taken after the film was annealed and XRD verified crystalline phases. The film still contains visible interfaces between the grainy BaF and relatively smooth BSTO. Though four layers were deposited, five are seen. It is believed that the bottom layer is in fact the Sr$_3$Si$_3$O$_9$ formed during deposition onto the heated substrate. This image also provides another means of measuring the total thickness of the film as well as a way to measure the thicknesses of each individual layer.

Cross-sectional images were taken of one of the multilayer films grown at UCF. Again, the excessive porosity of the Al$_2$O$_3$ substrate was seen, but the individual layers could not be made out. The main conclusion to be drawn from SEM images taken of the UCF films is that either total film thickness or substrate material should be experimented with in future depositions.
Figure 3.9. Cross-sectional images of films deposited at ORNL. a) A multilayer film before annealing. Magnification is 20000x, imaged with a JEOL JSM-840 SEM. b) A different multilayer film after annealing, imaged with a Hitachi S-800. Total thickness of film is measured on the far left with measurements of each layer throughout. Magnification is 40000x.
3.5 Conclusion

Profilometry, x-ray diffraction, AFM and SEM are powerful tools that enabled us to learn a great deal about the multilayer films deposited at ORNL and UCF. All films deposited seem to be thinner than anticipated, though film thickness in general is not a critical parameter as far as properties are concerned unless the films are thinner than around 0.1µm.

Due to the fact that BaF particles are easily affected by many deposition variables, we see different BaF x-ray peaks for each set of films. Other evidence suggests that substrate (and buffer layers), deposition temperature and the presence of BSTO all determine which peaks are present.

When BSTO is used as the top layer, the films appear to be isotropic with irregular shaped particles of consistent size. When BaF is deposited as the top layer we can clearly see the long, needlelike grains characteristic of BaF. These images are consistent with what is already known about these materials, though it is highly likely that the presence of one material affects the exact size and shape of the particles that make up the other.

Images also confirmed that the films grown at ORNL are in general of higher quality than those grown at UCF, probably due to the incompleteness of the optimization process. It is fortunate that an ongoing collaboration with such a close facility will let us further optimize these films.

Most importantly, cross-sectional images of the multilayers both prior to and after annealing show that BSTO and BaF when deposited in multilayer form can have distinct, clean interfaces, indicating that overall, the goal of growing multilayers was achieved.
Due to its potential for magnetic recording, magnetic properties of BaF thin films grown by a variety of techniques have been studied extensively. It has been shown that a number of parameters (e.g. substrate material, deposition time and temperature, post-annealing conditions and even sputtering power) have a huge influence on the magnetic properties that BaF exhibits [4.1, 4.2]. The fact that there has been no documented work of BaF/BSTO multilayers makes investigating the magnetic properties of this system even more important. The films grown at ORNL and UCF have enabled us to conduct our own study of magnetic properties comparing pure BaF to BaF/BSTO multilayers while also examining the effects of substrate material and \textit{in situ} heating versus post-annealing. Since BaF has a distinct and interesting microstructure, we will also attempt to correlate the magnetic properties with the microstructure presented in chapter three.

The DC magnetic properties of ferrite-ferroelectric multilayers were measured with a Physical Properties Measurement System (PPMS) from Quantum Design. The ferromagnetic Curie temperature ($T_c$) of Barium Ferrite is quite high (350°C). Since the
temperature range of our PPMS covers 300K to 2K, we made no effort to study the ferromagnetic-paramagnetic transition. In all of our measurements reported here, the samples are well below $T_c$ and we focus mainly on the variation of DC magnetization with applied magnetic field. Plots of magnetization versus applied magnetic field (M-H loops) were done at 10K and 300K for all samples. These two temperatures were chosen to compare parameters such as coercivity in detail. Some samples were examined with the applied magnetic field perpendicular to the sample (out-of-plane) as well as the traditional parallel applied field (in-plane). Since the polycrystalline BaF films have elongated needle-like grains, by doing the anisotropy measurements with the field in-plane and out-of-plane, we can detect any preferred orientation of the BaF grains (if present) in the films.

Figure 4.1 shows M-H loops for pure BaF on Al$_2$O$_3$ grown at UCF. Recall that these samples were grown at room temperature. Magnetization measurements were taken at three temperatures to make sure that magnetic trends are consistent with what is already documented about BaF thin films. Panels (a) and (c) show the raw magnetization data in units of emu x 10$^{-3}$. The 300K raw magnetization data (figure 4.1a) has a diamagnetic background due to the Al$_2$O$_3$ substrate expressed as a negative slope on top of the ferromagnetic hysteresis signal. The 100K raw magnetization loop (figure 4.1c) also has a diamagnetic background though when the temperature is decreased to 100K, the slope has decreased. In figure 4.1e one can see a positive slope consistent with a paramagnetic background. This trend has also been reported in BaF/BSTO composite films [4.3].
The slopes associated with the diamagnetic background can be subtracted from the loop leaving just the magnetic response of the hard ferromagnetic BaF. To do the background subtraction we fit the high field (> 20kOe) part of the curve to a straight line, obtain the slope and then subtract the line with this slope from the entire curve. The corrected loops are shown on the right panels.

Table 4.1 summarizes the magnetic properties given in the corrected M-H loops. The values for the saturation magnetization, remnant magnetization and coercivity are comparable to those reported by other groups that have deposited BaF films by rf sputtering [4.1, 4.4].

<table>
<thead>
<tr>
<th>BaF on Al₂O₃ (room temperature)</th>
<th>10K</th>
<th>100K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_r ) (emu/cc)</td>
<td>120</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>( M_s ) (emu/cc)</td>
<td>&gt;400</td>
<td>180</td>
<td>120</td>
</tr>
<tr>
<td>( H_c ) (Oe)</td>
<td>2100</td>
<td>2000</td>
<td>1900</td>
</tr>
</tbody>
</table>

Table 4.1. Magnetic Properties of pure BaF on Al₂O₃ grown at UCF.
Figure 4.1 (a-e). M-H Loops for BaF on Al₂O₃.

a. [Graph showing M-H loop for BaF on Al₂O₃ at 300K in plane.

b. [Graph showing M-H loop for BaF on Al₂O₃ at 300K in plane.

c. [Graph showing M-H loop for BaF on Al₂O₃ at 100K in plane.

d. [Graph showing M-H loop for BaF on Al₂O₃ at 100K in plane.

e. [Graph showing M-H loop for BaF on Al₂O₃ at 10K in plane.
Figure 4.2 (a-c) shows M-H loops for BaF/BSTO multilayers, also grown at UCF under conditions identical to those of the pure BaF. Graph (a) represents the raw magnetization data with the diamagnetic background present. This time the diamagnetic background is due to the Al₂O₃ and also the presence of the dielectric BSTO. Graph (b) has the background subtracted out and represents the hysteresis associated with BaF, which is the only magnetic phase of the system. The results are summarized in table 4.2.

Note that due to the error in estimation of the total thickness of BaF layers alone in the multilayer samples and also considering the possibility of interdiffusion at the interfaces, it would not be prudent to convert the measured values of Mr and Ms to absolute values in emu/cc.

<table>
<thead>
<tr>
<th>Multilayers on Al₂O₃ (room temperature)</th>
<th>10K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mr (emu x 10⁻³)</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Ms (emu x 10⁻⁴)</td>
<td>&gt;3.5</td>
<td>0.9</td>
</tr>
<tr>
<td>Hc (Oe)</td>
<td>1800</td>
<td>2100</td>
</tr>
</tbody>
</table>

Table 4.2. Magnetic properties of BSTO/BaF multilayers on Al₂O₃ grown at UCF.
Figure 4.2 (a-c). M-H Loops for BaF/BSTO/BaF on Al₂O₃.
What is immediately apparent from comparing the magnetic properties of BSTO/BaF to those of pure BaF is that at 10K, the coercivity is less in the multilayers films than in pure BaF films. However, at 300K, the coercivity of the multilayer films is comparable to the coercivity of pure BaF films at 10K. While the pure BaF films show a small decrease in coercivity with increase in temperature, the multilayer films show a large increase in coercivity with increase in temperature. The increase in coercivity with decrease in temperature seen in the pure BaF is consistent with conventional behavior in bulk magnetic materials.

We believe that the competition between the shape and magnetocrystalline anisotropies is responsible for the increase in coercivity with increase in temperature seen in the multilayer samples. The theoretical coercivity of a random array is given by

$$H_c = 0.48 \left( \frac{2K}{M_s} - NM_s \right)$$

where $2K/M_s$ is the crystal anisotropy and $NM_s$ is the shape anisotropy [4.5]. As $M_s$ decreases with increase in temperature, the contribution from the shape anisotropy decreases and $H_c$ increases with temperature. While this effect is not seen in the pure BaF films, the decrease in $M_s$ with the addition of the BSTO layers may be enough to favor high $H_c$ with high temperatures. It is interesting to note that Huang et al reported the same behavior in coercivity with BaF doped with up to 1.5% BSTO. They cited that the BSTO increases the crystal anisotropy, thus producing the effect [4.6].

Substrate temperature has been known to have a huge effect on many properties of thin films including the magnetic properties [4.7]. Recall from chapter two that multilayer films grown at ORNL were deposited around 300°C. M-H loops of
multilayers on Al₂O₃ grown at ORNL on heated substrates are presented in figure 4.3(a-f). Here we have included data taken in-plane and out-of-plane. Comparing magnetic properties with applied magnetic field parallel to and perpendicular to the substrate can lead one to determine whether or not there is a preferential orientation of magnetization for the sample.

Figures 4.3a and c are the raw magnetization data for the samples at 300K. Figures 4.3b and d are the corresponding corrected loops. Again, a diamagnetic contribution can be seen in these loops. In this case however, the raw magnetization loop is slightly asymmetric about the x-axis. At low signal level, the centering of the sample in the AC coil of the magnetometer becomes very important. Slight offset combined with the diamagnetic background subtraction can give an offset to the M-H loop in the x-axis. Note that since the diamagnetic contribution is negligible at 10K and corrections did not have to be made for these loops. Figures 4.3e and f are the raw magnetization data for the loops taken at 10K in (e) and out of (f) the substrate plane.

Table 4.3 summarizes the results of figure 4.3. The decrease in remnant magnetization and saturation magnetization is even more pronounced in the samples that were grown on heated substrates. The coercivities of these samples are much greater than those grown at room temperature and again we see an increase in coercivity with temperature. This is most likely another example of the competition between shape and magnetocrystalline anisotropy.
Figure 4.3 (a-f). M-H Loops of BSTO/BaF multilayers on Al₂O₃ grown at ORNL.
It is important to note that while the pure BaF films, the multilayers grown at UCF and the multilayers grown at ORNL all had different target thicknesses (0.6, 0.9 and 2µm respectively) this should not be the primary reason for the differences in magnetic properties for all three sets of samples. Research performed by Capraro et al revealed that while substrate material as well as deposition and post-annealing temperatures play crucial roles in the microstructure and magnetic properties of BaF films, (as well as rf power and Argon pressure, to a lesser extent), films with varying thicknesses up to 10µm exhibited the same magnetic properties [4.1].

It has been postulated that any substrate heating during deposition leads to more organization for particle nuclei and as a result particles will have a preferred growth direction. This ordering should also affect average particle size as particles aligned in one direction will not be restricted by the presence of surrounding randomly-oriented particles [4.2]. If this is true, then films grown on heated substrates should have bigger particles and thus smaller coercivity [4.8]. We should also see a large magnetic anisotropy for films grown on heated substrates [4.2]. Magnetic data for the multilayers grown on heated Al$_2$O$_3$ does not appear to coincide with these notions. While a change

<table>
<thead>
<tr>
<th>Multilayers on Al$_2$O$_3$ (heated substrate)</th>
<th>10K in plane</th>
<th>10 K out of plane</th>
<th>300K in plane</th>
<th>300K out of plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$ (emu x 10$^{-3}$)</td>
<td>0.7</td>
<td>0.6</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>$M_s$ (emu x 10$^{-3}$)</td>
<td>1.6</td>
<td>1.4</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>2300</td>
<td>2400</td>
<td>3300</td>
<td>2900</td>
</tr>
</tbody>
</table>

Table 4.3. Magnetic properties of BSTO/BaF multilayers on Al$_2$O$_3$ grown at ORNL.
in coercivity with magnetic field orientation is present at 300K, there is no significant change in coercivity at 10K. Therefore, it is difficult to deduce magnetic anisotropy in these samples. There is also no decrease in coercivity with increase in substrate temperature. Such large increase in coercivity gives evidence to the opposite conclusion, that particles grown on the heated substrates are actually smaller than those grown at room temperature. It also cannot be ruled out that the overall discontinuity of the UCF films on the Al$_2$O$_3$ did not have some influence on the magnetic properties. We are still exploring how their discontinuity may have played a role in observed differences between the films.

The last set of films to examine is those grown at ORNL on heated Si/SiO$_2$. Figures 4.4(a-f) and 4.5(a & b) show M-H loops for these films. Figure 4.4a is the raw in plane magnetization data taken at 300K. Once again there is a strong diamagnetic background from the substrate and the dielectric BSTO present in the multilayers. There is also the vertical shift in the loop that was present for the films on heated Al$_2$O$_3$. Figure 4.4b is the same loop corrected for these effects. Figure 4.4c is the raw data for the film at 300K, this time out of plane. Figure 4.4d is the corrected loop. 4.4e is the raw magnetization data taken at 10K in plane. In this case, as before, the data is sufficient to not require correction. Similarly, figure 4.4f is the raw data taken at 10K out of plane. Figures 4.5a and 4.5b are comparisons of the loops at 300K and 10K. The in plane and out of plane data are overlapped to make the difference in coercivities clear.
<table>
<thead>
<tr>
<th>Multilayers on Si/SiO$_2$ (heated substrate)</th>
<th>10K in plane</th>
<th>10K out of plane</th>
<th>300K in plane</th>
<th>300K out of plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$ (emu x 10$^{-3}$)</td>
<td>1.5</td>
<td>1.0</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>$M_s$ (emu x 10$^{-3}$)</td>
<td>3.2</td>
<td>3.3</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>$H_c$ (Oe)</td>
<td>1500</td>
<td>1200</td>
<td>2000</td>
<td>1700</td>
</tr>
</tbody>
</table>

Table 4.4. Magnetic Properties of BSTO/BaF multilayers on Si/SiO$_2$ grown at ORNL.
Figure 4.4(a-f). M-H Loops of BSTO/BaF multilayers grown on Si/SiO$_2$ at ORNL.
Figure 4.5 a & b. Comparisons of in-plane and out-of-plane loops at 300K and 10K.

Multilayers on Si/SiO₂
300 K Comparison

H (kOe)
M (emu × 10⁻³)

-1.5 -1.0 -0.5 0.0 1.0 1.5

-5 -4 -3 -2 -1 0 1 2 3 4 5

-1.5 -1.0 -0.5 0.0 1.0 1.5

-5 -4 -3 -2 -1 0 1 2 3 4 5

In-plane
Out of plane

Multilayers on Si/SiO₂
10K Comparison

H (kOe)
M (emu × 10⁻³)

-2 -1 0 1 2

-5 -4 -3 -2 -1 0 1 2 3 4 5

-2 -1 0 1 2

In-Plane
Out-of-plane

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There is a substantial difference in magnetic properties between multilayer films grown on Al₂O₃ and multilayers grown on Si/SiO₂. The remnant magnetization and saturation magnetization are much greater in the films grown on Si/SiO₂. This agrees well with Capraro et al’s study of differences in substrate material as they conclude that films on silicon substrates present better magnetic characteristics than those obtained on alumina [4.1]. With the films grown on Si/SiO₂ we also see the smallest coercivities yet, even smaller that the pure BaF films on Al₂O₃. However, the general trend of increase in coercivity with temperature present in the other multilayers appears with the multilayers on Si/SiO₂ as well.

The smaller coercivities in the films on Si/SiO₂ imply a larger particle size than the multilayers on Al₂O₃, which is supported by the images in chapter three. The difference in coercivities with applied field orientation is definitely noticeable with these films at both 10K and 300K, which points to magnetic anisotropy. Comparison of the hysteresis loops with respect to applied field orientation is shown in figure 4.5a & b. There the difference in shape of the loops is apparent, most notably in the 10K graphs. Closer examination of the shapes of these loops show that the film is more easily saturated as the field is applied parallel to the plane. When the increasing field is applied perpendicular to the plane, the magnetization increases more slowly and the film is saturated at a larger field. This behavior indicates that the effective easy axis of magnetization is parallel to the film plane. Since the easy axis of BaF is parallel to the c-axis, on average the c-axis of much of the film must lie parallel to the substrate plane. This is also verified in the SEM and AFM images of the multilayers on Si/SiO₂ where we can distinctly see most of the grains lying with their c-axes parallel to the substrate.
Whether the texturing of the BaF layers in the multilayer films is due to the substrate heating or the substrate being single crystal silicon with a thin oxide layer versus polycrystalline alumina is unclear. It is unfortunate that adhesion problems prohibited multilayers from being grown on Si/SiO$_2$ at room temperature, or a more comprehensive study could be performed. Our future attempts will include use of Platinum and Titanium buffer layers on Si/SiO$_2$ substrates that are expected to aid film adhesion as well as prevent interaction with the substrate. What is interesting is that the ordering of BaF particles can be achieved with a buffer layer of BSTO between it and the substrate. The fact that we can visually see this happening on the top layer with three layers underneath is all the more interesting and needs further investigation.

The magnetic properties of the four sets of films examined in this chapter have revealed a lot about the nature of BSTO/BaF multilayers. The fact that the properties of the pure BaF agree well with other published results reaffirmed that our technique was sufficient for attempting to grow multilayer structures. Two major differences were seen between the pure BaF films grown on Al$_2$O$_3$ and the multilayer films grown on Al$_2$O$_3$. One was a lowering of remnant magnetization and saturation magnetization. The other was a trend for the coercivities of the films to increase with increasing temperature, which is contrary to the general behavior of ferromagnetic materials. We believe that the presence of BSTO in the multilayer films is responsible for both of these effects although the exact mechanism is difficult to pinpoint with our present experiments. It is also possible that these effects are linked in that the decrease in saturation magnetization is enough to let the coercivity increase with temperature as shown by the simple equation relating coercivity to shape and magnetocrystalline anisotropy.
Growing multilayers on heated $\text{Al}_2\text{O}_3$ resulted in a further decrease in remnant magnetization and saturation magnetization. The increase in coercivity with temperature is also present in these films, further suggesting that this is a general feature of BSTO/BaF multilayers. Studies of in plane and out of plane $M-H$ loops could not confirm or rule out magnetic anisotropy of the films as the 10K coercivities agreed, but there was a difference in 300K coercivities. It is likely that the substrates were not heated enough to obtain highly oriented films. Overall, the results of films grown on $\text{Al}_2\text{O}_3$ heated to 300°C versus films grown on room temperature $\text{Al}_2\text{O}_3$ are inconclusive with respect to anisotropy studies.

On the other hand, there are clear differences between the films grown on Si/SiO$_2$ and the films grown on $\text{Al}_2\text{O}_3$. The films deposited on Si/SiO$_2$ have higher remnant magnetization and saturation magnetization than any of the films deposited on $\text{Al}_2\text{O}_3$, including the pure BaF. The coercivities in general were much lower, and a difference seen in coercivities with applied field orientation at 10K and 300K suggest magnetic anisotropy of the films. This anisotropy is believed to be from the c-axis lying parallel to the substrate. Whether or not the more textured films are a result of substrate heating or material is unclear though other studies seem to point towards silicon being a preferable choice for BaF films. Further work will focus more on using Si/SiO2 substrates and studying the correlation between microstructure and magnetic properties.
Chapter Five

Nanostructured Thin Films

In chapters two three and four we discussed growing and characterizing BSTO/BaF multilayer films. In addition, we also explored techniques for depositing and characterizing nanostructured thin films of Fe$_3$O$_4$, both on Si/SiO$_2$ substrates and on the BSTO/BaF multilayers. Though our ultimate goal is to understand the effects of the tunable BSTO/BaF substrates on nanoparticle arrays, finding the best deposition methods for the nanoparticles, examining the resulting microstructure has itself been challenging.

Drop casting and spin coating are two common methods for depositing nanoparticles suspended in a solvent. However, it is the Langmuir-Blodgett technique that provides maximum ordering of particles and control over film thickness. This chapter describes the Langmuir-Blodgett process and our ongoing efforts at depositing and characterizing nanoparticle arrays on multilayer substrates.
5.1 Introduction to Langmuir-Blodgett Films

Although experiments involving spreading thin layers of oil on water date back to Benjamin Franklin, it was Irving Langmuir and Katharine Blodgett who developed the modern Langmuir-Blodgett (LB) film [5.1]. A Langmuir-Blodgett film is a monolayer of material transferred from a subphase (in most cases water) to a substrate by dipping the substrate through the monolayer into the subphase either once or a number of times to create a monolayer or multilayer stacked films.

A monolayer-forming material has two distinct regions in the molecule: a hydrophilic head group which is easily soluble in water, and a long alkyl chain which provides a hydrophobic tail. When such a material is in a solution with a water-immiscible solvent, the solution can be spread on a water surface. It will spread out to cover the area of the surface and as the solvent evaporates, the amphiphilic molecules will arrange themselves so that the head groups are submerged in the water and the tails remain out of the water, thus forming a monolayer. [5.1]

When the distance between the molecules is large, they have little effect on each other and the monolayer can be regarded as a two dimensional gas. If a barrier pushes on the sides of the monolayer, forcing the distance between molecules to decrease, the molecules will exert a repulsive force on each other, resulting in a two dimensional analog of pressure (surface pressure, measured in mN/m). This results in a phase change from a two-dimensional gas to a two-dimensional liquid. Further compression results in another phase change to an ordered solid like arrangement of a two-dimensional array of molecules (figure 5.1). These phase transitions are clearly visible in a surface pressure/area isotherm that is collected during the compression of the molecules (figure
Figure 5.1. Expanded and compressed monolayers on a water surface. (Adapted from reference [5.3]).

Figure 5.2. A stearic acid isotherm on pure water. (Adapted from reference [5.3]).
It is important to compress the monolayer slowly and only to a suitable surface pressure. Compressing too fast or past the desired surface pressure can result in a collapse of the monolayer, in which the molecule layers ride up on top of each other and disordered multilayers are formed. [5.1]

Compression of the layer is done in a Langmuir-Blodgett trough (figure 5.3). This consists of a well for the subphase and one or two barriers to compress the monolayer. The barriers may be moved by a gearing system to an electric motor. All parts of the trough that come in contact with the subphase and the monolayer must be chemically inert and able to withstand the organic solvents used for cleaning, the most popular choice being Teflon. [5.2]

A common method for measuring the surface pressure is a Wilhelmy plate attached to the trough. The plate is calibrated and then immersed in the subphase. As the solution is spread on the subphase, the Wilhelmy plate will measure the change in force due to the monolayer. It will then relate this force to the change in surface tension [5.2]. After the monolayer is compressed to a desirable surface pressure, it is ready for deposition onto a substrate. A substrate can be dipped vertically into the trough through the monolayer into the subphase. The molecules will attach to the substrate depending on whether the substrate itself is hydrophilic or hydrophobic [5.1]. The dipping and removing of the substrate through the interface can be repeated to build ordered stacks of molecule layers (figure 5.4). This can be achieved consistently through a motorized dipping mechanism attached to the trough. Alternatively, the substrate can be lowered horizontally by hand until the substrate touches the surface and picks up the monolayer.
Figure 5.3. The Langmuir-Blodgett trough in the Materials Physics Lab at USF.
Figure 5.4. Langmuir-Blodgett deposition. a) Deposition of the first layer onto a hydrophobic substrate. b) The substrate reverses. c) The second layer is deposited. (Adapted from reference [5.3].)

5.2 Synthesis of LB films

Fe$_3$O$_4$ nanoparticles were synthesized by members of our Materials Physics Lab using a chemical method outlined by Massart [5.4]. Particles had an average diameter of around 12 nm with a size distribution of ± 3 nm. Their stoichiometry was confirmed by x-ray diffraction and they have been shown to be superparamagnetic at room temperature. The particles were coated with oleic acid (C$_{17}$H$_{33}$CO$_2$H) to enable them to form monolayers as well as to prevent aggregation. They were then suspended in hexane to form a solution. Figure 5.5 is a transmission electron microscope (TEM) image of these particles taken with a Philips CM-10 TEM after they were drop-cast onto a TEM grid.
Figure 5.5. TEM image of nanoparticles synthesized at USF.
Our Materials Physics Lab is equipped with a NIMA™ Technology 30 x 10cm Langmuir trough (figure 5.3). This setup is entirely software controlled with motorized Teflon barriers and mechanical dipper. It is important to note that several LB trials were done at different times with similar parameters. The description of LB film deposition that follows is for a typical trial.

The LB trough was thoroughly cleaned with chloroform and then filled with deionized water of 18.2MO-cm resistivity. The water was left to sit for a few minutes while the Wilhelmy plate is submerged and able to equilibrate. Drop by drop, the nanoparticle solution is spread on the subphase with a syringe and the hexane is allowed to evaporate. Solution is added until the particle surface pressure after the hexane has evaporated is 1mN/m. This is equivalent to about 500µL of solution, though the solution volume varies depending on how dilute it is. When the desired surface pressure is reached, the barriers are slowly brought together to compress the monolayer. The typical barrier speed is 25cm²/min. It is important to use a slow barrier speed to let the particles continually re-order and prevent the monolayer from collapsing. The barriers compress until an ideal surface pressure has been reached. For the oleic acid-coated Fe₃O₄ particles, the ideal surface pressure is 25mN/m, though on occasion it was difficult to reach this surface pressure before the barriers were too closed for a deposition.

The software connected to the LB trough creates an isotherm while the monolayer is compressing. An isotherm representative of most trials is presented in figure 5.6. In this isotherm, the gas-liquid transition is clearly visible around 27Å². However, the liquid-solid transition is not as clear, but there does seem to be a change in slope between 5 and 7Å².
When the barrier is sufficiently closed, the monolayer is ready to be deposited. Besides using the BSTO/BaF multilayers as substrates for the nanoparticle films, monolayers were also deposited on bare Si/SiO$_2$ and formvar-coated TEM grids. The substrates were attached to plastic straws by double-sided tape. Depositions of single layers were done by manually touching the straws to the monolayer surface. When multiple layers were deposited, the substrates were mounted (via double-sided tape) to a glass slide, which was clipped onto the mechanical dipper. The substrates with monolayers were used for TEM and AFM imaging.

Figure 5.6. Pressure/area isotherm for Fe$_3$O$_4$ nanoparticle LB film.
5.3 Structural Characterization of LB Films

Two methods were used to characterize the LB films. TEM is traditionally the best method for imaging LB films as it has such high resolution. However, in order to use TEM, the films should be deposited onto TEM grids. While this technique will provide a good idea of the small-scale ordering of the particles, it will not give any indication how the LB films will interact with different substrates. Since we deposited LB films on bare Si/SiO$_2$ as well as our BSTO/BaF multilayers, we had to find another way to image these films. Atomic force microscopy (AFM) provides enough resolution to determine where LB films are deposited and any large-scale ordering present.

An ideal LB film of nanoparticles will be composed of particles with a single layer of surfactant (monolayer forming material, in this case oleic acid) coating them. The size distribution of particles will be minimal and such that the particles can be arranged in a hexagonal close-packed fashion. This occurs when the monolayer is in the solid phase, at high surface pressure but below the collapse point. Achieving these conditions is a major task, involving much time and patience. With this in mind, it is no surprise that the LB films we deposited on TEM grids did not show these characteristics given the brief amount of time that we spent optimizing conditions and practicing the LB technique. Figure 5.7 is a TEM image of an LB film deposited on a TEM grid. One noticeable feature of figure 5.7 is the gaps where there are no particles. This could be due to the particles failing to form a sufficient solid phase. This failure could be due to a
Figure 5.7. TEM image of an LB film.
deficiency in particle number, resulting in the particles not being able to form a continuous monolayer over the subphase. Another possibility is barrier speed. While this film was compressed at 25 cm²/min (in accordance with other literature), a slower speed may give the particles more time to fill in voids as the monolayer is being compressed.

The film in figure 5.7 also seems to have a spread in particle size. We believe that most if this is due to particle aggregation. While measures were taken to discard clumps of particles by means of centrifugation, there appear to still be small clusters present. These are indicated by the much darker particles and the particles lacking circular symmetry. This happens over time to nanoparticles in solution even if they are coated with surfactant. One aspect of making an LB film is determining how much surfactant should be present in the solution. While the particles were initially coated to prevent aggregation, too much surfactant results in an oily appearing monolayer and the particles cannot interact enough to go through the phase transitions. Too little, and the particles will adhere and not form a monolayer. This may have happened to the film in figure 5.7. A delicate balance of surfactant and particles must be achieved to successfully form a monolayer. As stated earlier, optimizing parameters for LB deposition is an ongoing project which will continue to be refined in the future.

It seems as though there is little difference between the TEM image of the nanoparticles drop-cast onto the grid and the TEM image of the nanoparticles deposited by LB onto the grid. This begs the question: what are the advantages of our present LB technique over drop-casting? It turns out that substrate material plays a larger role than
we had previously assumed. Figure 5.8a is an AFM image of nanoparticles deposited on bare Si/SiO$_2$ by LB. The image is 10µm on each side. This scale is too large to distinguish individual particles, but it is large enough to see some large-scale ordering. We believe that there are aggregated particles in the middle of the circles around which the single, smaller particles have gathered. Voids are still clearly visible on this scale. It is likely though that these voids are not created by the same mechanism as the voids in the TEM image. While the nature of the voids in the TEM image seems to be due to not enough packing, these larger voids seem to be due to poor adhesion. We are just learning that lack of adhesion of LB films to Silicon is a common problem. It is solved by pre-treating the Silicon with dichlorodimethylsilane, which makes the surface very hydrophobic [5.2]. Future LB depositions onto bare Si/SiO$_2$ will incorporate this pre-treatment. Although the ordering does not seem to be hexagonal close-packed on this scale, the presence of ordering is encouraging, even if it is not clearly seen on the nanometer scale.

Figure 5.8b is an AFM image of nanoparticles from the same solution drop-cast onto Si/SiO$_2$. This time there is a clear difference between the two different deposition methods. While the drop-cast sample does appear to be spread uniformly over the substrate, there is no noticeable ordering of the particles. In both cases, we are unable to verify that the particles have formed monolayers, though the color contrast in the drop-cast image suggests that there is either significant aggregation or multiple layering in some areas.
Figure 5.8. AFM images of nanoparticles on Si/SiO$_2$. In a) the particles are deposited by LB method. In b) they are deposited by drop-casting.
Figure 5.9 shows AFM data for the Fe$_3$O$_4$ nanoparticles deposited on BSTO/BaF multilayers. In all images, the top layer of the multilayer structure is BaF, as we are particularly interested in the interaction between the two magnetic materials. All images are also of films deposited on Si/SiO$_2$. This is not because we saw a significant difference in structures deposited on Si/SiO$_2$ or Al$_2$O$_3$. Rather, the best quality images we obtained were those on Si/SiO$_2$. All multilayer films were those grown at Oak Ridge National Laboratory due to their overall superior quality over the films grown at the University of Central Florida thus far.

Panels (a) and (b) are nanoparticles that were drop-cast onto multilayer films. The image in (a) is 10µm on each side. In this scale, BaF particles are seen as large bright areas. In panel (a), a BaF particle is in the center of the image. Large islands of particles are visible in bw areas on the upper half of the image. Features near the lower right side of the BaF particle could be groups of nanoparticles, but it difficult to be sure. Even though we want to study the interaction between the nanoparticles and the BaF, there are no visible nanoparticles directly on top of the BaF.

Figure 5.9b is another image on a smaller scale, 2.5µm. Here the BaF particles can be easily seen as the large, bright features and spherical clusters of nanoparticles can be seen as well. Here, as in panel (a), the particles appear to group along the edges of the BaF particles and in the crevices between particles. Based on these images, we can conclude that depositing nanoparticles on top of multilayer films by drop-casting does not allow the particles to uniformly coat the area. In areas where the surface is relatively
smooth the particles form large islands. In areas where BaF appears to be especially textured, the particles gather into crevices, failing to coat the entire BaF particle.

In panels (c) and (d) we present AFM images of multilayer films coated with Fe₃O₄ nanoparticles by LB deposition. In figure 5.9c, as with the TEM image, the LB film is not entirely continuous as there seems to be small voids where the particle network is not present. This is a 2.5µm scale, so while individual particles can not be seen, groups and clusters are visible. Even though the highest areas are bright white (indicating tops of BaF particles), the particles seem to be distributed over them as well as the underlying structure in yellow (note particularly the small white island in the center and the top of the elongated BaF particle).

Figure 5.9d is the most convincing evidence that nanoparticles of Fe₃O₄ are forming networks on top of the BSTO/BaF multilayer films. As in the other images, there are some voids, but they do not appear to preferentially form around the highest points of the BaF particles. The BaF particles appear to be completely coated as well as the underlying structures. Clustering of the nanoparticles is apparent from the photo but it is not clear if it is due to the deposition method or a different mechanism. We could not resolve to what extent the nanoparticles were ordered as higher magnification led to instrument artifacts.

From figures 5.9 (c) and (d) we are convinced that LB is an appropriate method for depositing these Fe₃O₄ nanoparticles. LB allows the films to deposit more uniformly over surface features such as those present in BaF films. Drop-casting, on the other hand, results in particles gathering in cracks and crevices, which is not ideal for films with
Figure 5.9. AFM images of Fe$_3$O$_4$ nanoparticles on BSTO/BaF multilayers. Particles in a) and b) were deposited by drop-cast. Particles in c) and d) were deposited by LB.
surface features. This difference in coating could be due to the particles being deposited while they are suspended in hexane. Hexane’s lack of viscosity could enable the particles to quickly flow and end up in lower areas while not being able to stay on the highest points of the BaF particles. Another explanation is when the particles are compressed in the LB trough, their transition to a two-dimensional solid involves stronger interactions between the particles, making them stay in a more or less uniform array while they are being deposited onto the textured surface of the BaF. Whatever the reason, future trials will still include depositions onto multilayers using the LB technique.

It is discouraging that there are still voids present in the AFM images of nanoparticles on the multilayers deposited by LB. Voids on a small scale (< 50nm, such as we saw in figure 5.7) indicate insufficient surface pressure or a barrier speed that is too fast. Voids on a larger scale (> 2µm, such as in figure 5.8a) can mean lack of proper adhesion. It is not immediately clear what caused the voids in figures 5.9 (c) and (d). Further investigation and practice with the LB method needs to be done to answer this question and to improve overall quality of the monolayers.

5.4 Magnetic Properties of LB Films

In order to detect a magnetic signal, depositions of several layers of Fe$_3$O$_4$ nanoparticles onto Si/SiO$_2$ were done using the LB method. Plots of magnetization versus applied magnetic field (M-H) were done at 10K and 300K using our Physical Properties Measurement System (PPMS). Figure 5.10 shows M-H loops for one LB films consisting of 40 layers of Fe$_3$O$_4$ nanoparticles. The results are summarized in table 5.1.
Figure 5.10 (a-d). M-H Loops for LB films of Fe₃O₄.

![M-H Loops](image)

**Table 5.1. Magnetic properties of LB films on Si/SiO₂.**

<table>
<thead>
<tr>
<th>40 layers of Fe₃O₄</th>
<th>10K</th>
<th>300K</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_r (emu/cc)</td>
<td>160</td>
<td>~0</td>
</tr>
<tr>
<td>M_s (emu/cc)</td>
<td>800</td>
<td>480</td>
</tr>
<tr>
<td>H_c (Oe)</td>
<td>210</td>
<td>~0</td>
</tr>
</tbody>
</table>
At 300K, there is a strong diamagnetic background due to the Si/SiO$_2$ substrate (figure 5.10a). When the background is removed, the loop appears consistent with superparamagnetic particles (5.10b). There is no measurable remnant magnetization or coercivity. At 10K (figures 5.10c and d), the superparamagnetism is no longer present and a small hysteresis can be seen. Since this effect is small compared to the span of both of the axes, a close-up graph of the coercivity and remnant magnetization is presented in figure 5.10d.

The superparamagnetism seen at 300K and the hysteresis seen at 10K is consistent with other data taken of Fe$_3$O$_4$ nanoparticles of similar dimensions [5.4]. The transition from superparamagnetic to ferromagnetic behavior occurs at the blocking temperature. Though the blocking temperature has been show to differ depending on conditions of particle synthesis, the accepted value for surfactant-coated Fe$_3$O$_4$ nanoparticles is around 150K [5.6].

It is important to note that the saturation magnetization, remnant magnetization and coercivity for the LB film at both 300K and 10K are a full order of magnitude smaller than the values seen for the BSTO/BaF multilayers. When we deposited the same amount of Fe$_3$O$_4$ nanoparticles (40 layers) on a BSTO/BaF multilayer sample and took the same M-H measurements, the presence of the nanoparticles could not be detected over the strong signal from the BaF. However, we are confident that the Fe$_3$O$_4$ particles on the tunable oxide multilayers will be detected in RF measurements and possible magnetic coupling between the BaF and the Fe$_3$O$_4$ may be seen.
5.5 Conclusion

In this chapter, we have presented the Langmuir-Blodgett technique as a powerful tool for depositing monolayers or stacks of monolayers of amphiphilic particles. Fe$_3$O$_4$ nanoparticles synthesized in our lab and coated with oleic acid were deposited using this method, as well as drop-casting, onto TEM grids, bare Si/SiO$_2$ and most importantly, our BSTO/BaF multilayers. TEM images showed little difference between the methods in regards to organization of particles. Currently we attribute this to our inexperience with LB films compared to what is necessary to produce ideal monolayers of nanoparticles.

Using AFM we saw that LB films deposited on bare Si/SiO$_2$ had much better organization on a large scale than films deposited by drop-casting. We were unable to see any small-scale ordering due to instrument limitations. Large voids could be seen on the Si/SiO$_2$ sample that we now believe is a result of poor adhesion of the LB film to the Si/SiO$_2$. Further LB depositions onto bare Si/SiO$_2$ will first involve pre-treating the substrate with dichlorodimethylsilane, producing a more hydrophobic surface.

The most important of the images obtained with AFM were of the BSTO/BaF multilayers with nanoparticles on the surface. Particles deposited by drop-casting tended to fall into crevices and lower areas of film. Whether this is due to the hexane in the drop-cast solutions or particle interactions is not known. Particles deposited using LB gave a much smoother, uniform distribution of nanoparticles that covered entire BaF particles as well as the areas in between. Unfortunately there were still voids present of unknown origin. This problem, as well as better ordering, packing and reproducibility of LB films are priorities for future depositions.
Magnetic measurements of 40 layers of Fe₃O₄ nanoparticles deposited on Si/SiO₂ using the LB method revealed magnetic properties consistent with Fe₃O₄ particles of comparable size. Though our Physical Properties Measurement System (PPMS) is not sensitive enough to pick up a magnetic signal from the Fe₃O₄ when deposited on the BSTO/BaF multilayers, we are confident that we can explore the interaction between the Fe₃O₄ and both multilayer components. Testing the RF properties of these systems varying several parameters (substrate material, whether the top layer is BSTO or BaF, Fe₃O₄ thickness, etc) is of paramount importance for their integration into the next generation of technology.
Chapter Six

Summary and Future Plans

We have grown two sets of films consisting of multilayers of Barium Strontium Titanate (BSTO) and Barium Hexaferrite (BaF) using magnetron sputtering. The first set was grown using the facilities at Oak Ridge National Laboratory (ORNL) which were available to us through our long standing collaboration with Dr. Nancy Dudney's thin film group and also supplemented by a SURA summer fellowship. The films grown at ORNL were deposited on Al$_2$O$_3$ and Si/SiO$_2$. We attempted to grow multilayers on kapton, but deposition and annealing conditions were not compatible with the material. Initial deposition trials yielded films that flaked off, which led us to build and integrate a substrate heater into the sputtering system. Subsequent films grown at 300°C adhered to the substrates and remained intact after annealing at 1000°C.

The second set of films was grown through collaboration with Professor Kevin Coffey at the University of Central Florida. Due to the geometry of the sputtering system, an aluminum substrate holder had to be designed and machined specifically for the chamber to meet our deposition needs. The four-armed design of the substrate holder
provided us with the opportunity to grow four different types of films during one deposition run. These were pure BSTO, pure BaF, BSTO/BaF/BSTO multilayers and BaF/BSTO/BaF multilayers. They were all grown on Al₂O₃ substrates; though some films had Platinum buffer layers underneath so that capacitance and ferroelectric measurements could be made at a later time.

As with the films grown at ORNL, adhesion was once again a problem. BaF on Platinum flaked off immediately after deposition and BSTO/BaF/BSTO multilayers did not adhere after low temperature. All other films have been successfully annealed and characterized.

Thickness measurements done with a profilometer showed that the films made at ORNL were between 1.0 and 1.3 µm, which was less than our intended thickness of 2µm. Profilometry done on the films made at UCF again indicated thinner films that we had hoped: about .7µm for the multilayers and .5µm for the single layers. Intended thicknesses for the multilayers and the single layers were .9µm and .6µm respectively.

X-ray diffraction (XRD) analysis on all of the films revealed peaks consistent with crystalline phases of both BSTO and BaF. However, there was variation in the specific peaks seen depending on the substrate and whether the films were part of the first set or the second. Films grown on Si/SiO₂ showed strong peaks consistent with Sr₃Si₃O₉, indicating that a chemical reaction between the SiO₂ and the BSTO could have been responsible for the lack of adhesion exhibited in some of the films.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to image both sets of films. The films grown at ORNL with BaF as the top layer showed the elongated, needlelike BaF grains that are typical of this material. We also
imaged BSTO which crystallizes into more symmetric particles that were clearly visible as well. The films grown at UCF were shown to be discontinuous due to pores in the Al₂O₃ which were deeper than the films’ thickness. We were also able to produce the first known cross-sectional images of BSTO/BaF multilayers using SEM. These images revealed clear interfaces between the two materials even after post-annealing, our most encouraging data.

Using the Physical Properties Measurement System (PPMS) in our lab, we measured magnetization versus applied magnetic field (M-H) loops for the pure BaF films and the multilayers. The remnant magnetization and saturation magnetization for the pure BaF films were consistent with other data published on BaF thin films [6.1]. We also saw the familiar trend of decreasing coercivity with temperature.

Due to our inability to precisely know the thicknesses of each layer of the multilayers, we were not able to normalize the remnant magnetization and saturation magnetization of these films to compare them to previous work. We did however see an increase in coercivity (a parameter associated with the types of material, not the amount of material present) with temperature. We believe that the presence of the BSTO is affecting the growth of the BaF grains, an occurrence also observed by Huang et al [6.2]. Usually, the competition of shape and magnetocrystalline anisotropies leads to a decrease in coercivity with increase in temperature as seen in the pure BaF sample. We believe that the effect that the BSTO has on the crystal anisotropy is enough to produce the opposite effect.

We also showed that there was little difference between the magnetic properties of films grown at room temperature and those grown at 300°C. While other groups have
observed a difference in the magnetic properties of BaF with substrate temperature [6.3], the temperatures we achieved during deposition are evidently not high enough for these differences to be present.

There were differences in the magnetic properties between the multilayers grown on Al₂O₃ and those grown on Si/SiO₂. Overall, the films on Si/SiO₂ showed better magnetic properties, consistent with Capraro et al’s assessment of substrates for BaF growth [6.1]. We saw smaller coercivities, implying larger particle size and the increase in coercivity with temperature was present again. There was also a distinct difference of coercivity with applied magnetic field orientation which is evidence for magnetic anisotropy. Analysis of the M-H loops implies that the effective easy axis of magnetization for these samples is parallel to the film plane.

Lastly, in order to combine the advantages of ferroelectric-ferrite multilayers with those of nanoparticles, we used the Langmuir-Blodgett (LB) method to deposit Fe₃O₄ nanoparticles on top of the multilayers. We used transmission electron microscopy (TEM) and AFM to characterize the LB films. TEM images of particles deposited onto TEM grids did not differ significantly from those simply drop-cast onto TEM grids. However, large differences were observed in images of the nanoparticles deposited onto Si/SiO₂ and the multilayers compared to particles drop-cast onto the same substrates. There seems to be large-scale ordering present in those films deposited on Si/SiO₂ by LB, unlike the random distribution of particles seen by the drop-cast method. The most important difference was seen in the particles deposited on the multilayers. While the nanoparticles deposited by drop-casting spread into the area between the BaF particles (most likely due to the hexane in which the particles were suspended), the LB film was
evenly distributed over and in between the BaF particles. This leads us to believe that LB is the preferred method for depositing nanoparticles onto our textured multilayers.

The goal of this thesis was to grow and characterize ferroelectric-ferrite multilayers, correlate their magnetic properties with their observed microstructure and deposit nanoparticles on top of the multilayers using the LB method. While each of these tasks was accomplished, we are still left with many questions and avenues of exploration. We are eagerly awaiting capacitance and ferroelectric measurements on some of the films grown at ORNL. This will greatly round out our study, adding the ferroelectric data to our analogous ferromagnetic data.

We are still faced with adhesion problems with some of the films grown at UCF. Future depositions will include different metals on which to deposit layers beginning with the BaF and ways to eliminate the lack of adhesion between multilayers with the BSTO as the bottom layer. Some of our ideas have been to grow a buffer layer of BSTO with a heated substrate holder, and then switch to our original arrangement to grow the multilayers. Other buffer layers are possible as well.

The thicknesses of the multilayers and the porosity of the Al₂O₃ also need to be addressed when we grow films at UCF. By adding another buffer layer to fill in the pores or greatly expanding our deposition time we hope to grow films with comparable quality to those grown at ORNL. Lastly, careful deposition of buffer layers of Titanium and/or Platinum should be used to try deposition onto Si/SiO₂ substrates at room temperature, since our work has shown Si/SiO₂ substrates to be superior to Al₂O₃ with regards to magnetic properties of BaF.
We also hope to greatly improve our current LB technique. While we have identified why we must use LB, we still need to produce the small-scale, close packed ordering characteristic of LB films. The equipment and skill present in our own Materials Physics Lab make it possible for us to synthesize and deposit other magnetic nanoparticles such as CoFe$_2$O$_4$ and even BaF using the LB method.

Only after these deposition improvements have been achieved can we take careful and consistent RF measurements of the multilayers. It is with RF data that we hope to provide the most convincing evidence that ferroelectric-ferrite multilayers will be useful in future devices by exhibiting simultaneous electric and magnetic tuning. We will also try to identify effects such as the magnetoelectric effect, and dielectric (magnetic) anomalies at magnetic (dielectric) transition temperatures to determine if there is coupling between the ferroelectricity and magnetism present in these materials. Multiferroism exhibited by composites or multilayers not only has promise for technology but also contains exciting new physics. Most importantly, it is our hope that the structures we have made and continue to improve will be multifunctional and versatile in the next generation of electronic devices.
References

Chapter 1


Chapter 2


Chapter 3


Chapter 4


Chapter Five


**Chapter Six**


Bibliography


Appendix
Appendix: Journal Publications and Conference Abstracts


