Growth Parameter Dependence and Correlation of Native Point Defects and Dielectric Properties in Ba$_x$Sr$_{1-x}$TiO$_3$ Grown by Molecular Beam Epitaxy

DISSERTATION

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Abstract

Due to its large and tunable dielectric constant, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) is an attractive material for fabricating a myriad of radio frequency and microwave devices including tunable capacitors, phase shifters, voltage-controlled oscillators, tunable filters, and phased array antenna. A particularly advantageous feature of this material is the ability to tune the material properties by selecting a suitable Ba/Sr ratio. This allows the device engineer the ability to design the material to fit the device and intended use. However, to realize such devices, a high quality factor ($Q=1/\text{Tan(δ)}$) and high tunability are desired requiring not only precise control of the chemical composition, but of the material defects as well. Molecular beam epitaxy (MBE) offers an ideal means of BST fabrication satisfying both of these conditions.

Growth of BST films by MBE were carried out under a variety of oxidizing conditions and substrate temperatures. Typical oxygen pressures ranged from 0 Torr, with the substrate feeding atomic oxygen into the growing film, up to $1\times10^{-6}$ Torr with the oxygen either being introduced as an ambient oxygen background or as activated plasma. Films were characterized in-house by x-ray photoemission spectroscopy (XPS), depth resolved cathodoluminescence spectroscopy, and x-ray diffraction while the fabrication of interdigitated capacitor (IDC) structures and subsequent dielectric measurements were performed at Naval Research Laboratories. To facilitate XPS measurements of pristine
sample surfaces, an ultra-high vacuum transfer line was designed and built to transfer samples from the MBE growth chamber into the XPS analysis chamber without exposing the sample to air.

Depth resolved cathodoluminescence spectroscopy (DRCLS) measurements reveal a strong dependence of the material’s electrically active defects on the growth parameters and chemical compositions. In particular, we see a large increase in the 2.55 eV and 2.95 eV emission intensity from the STO substrate for films grown with low oxygen pressures. It is known that the 2.55 eV and 2.95 eV emissions are related to oxygen vacancies, and it is shown that these defects are generated deep within the substrate by out diffusion of oxygen into the substrate. As we increase the oxygen pressure, we see an increase in the intensity of the 2.1 eV and 2.3 eV emission intensities, and we can understand this as the depopulation of a state within the bandgap of the material at 0.6 eV above the valence band allowing transitions from the oxygen vacancy and conduction band into this new state respectively. We then go on to show how an excess of Sr in reduced strontium titanate (STO) films can behave as an acceptor, depopulating this state and again leading to an increase in the 2.1 eV and 2.3 eV emissions.

The utility of these defects is displayed by an observed strong positive correlation between the 2.3 eV emission and the Q of the material. By reducing carriers in the material we can reduce the dielectric loss and this is evident from our DRCLS spectra. We also see a strong dependence on the 1.9 eV emission intensity with the Ba/Sr which in turn depends on the oxygen background pressure (P(O2)) and shows a strong negative
correlation with the tunability of the material. Again, these results highlight the
dependence of dielectric properties on the material defects generated during growth and
the effectiveness of DRCLS to probe these defects. Control of material defects through
MBE opens an avenue for the engineering of materials through defect management at the
atomic level.
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Chapter 1: Introduction

1.1 Oxides

Oxides are an extremely important class of materials with an extensive list of physical properties that are at the focus of intense research presently. Roughly 2/3 of all elements are known to form an oxide\(^1\) and nearly half of those oxides take on the perovskite structure\(^2\). Strontium titanate, the prototypical perovskite, has been shown to exist as a quantum paraelectric\(^3\), a band insulator, and a high-k dielectric material, while slight modifications to the system can result in STO that can be an n-type conductor, ferroelectric, and even superconducting.

Even more striking are the phenomena on display in complex oxide heterostructures such as the LaAlO\(_3\) (LAO)-STO structures. Both LAO and STO are band insulators, but it has been shown that depositing more than 4 monolayers of LAO on TiO\(_2\) terminated STO will result in the formation of a 2-dimensional electron gas at the interface.\(^4\) The authors have suggested that charge transfer to the interface in order to avoid a “polar catastrophe” is the mechanism behind the formation of the 2-DEG, but it is still unclear what role native point defects such as oxygen vacancies play.
1.2 Ba$_x$Sr$_{1-x}$TiO$_3$

Barium strontium titanate exists in the perovskite crystal structure. BST is the solid solution of SrTiO$_3$ (STO) and BaTiO$_3$ (BTO) with the chemical formula A$_x$A$^\prime_{1-x}$BO$_3$ with the barium and strontium being distributed randomly on the A-site. Figure 1 shows the perovskite crystal structure. The A-site cations occupy the center of eight octahedra with oxygen anions at the vertices and B-site cations in their center. In BST the B-site is occupied by a Ti$^{4+}$ ion, and it is the easy displacement of the Ti$^{4+}$ ion from the center of the negatively charged oxygen cage that results in the polarization of the material leading to the large permittivity and tunability of the material.\textsuperscript{5}
At room temperature, BTO is a ferroelectric while STO is a quantum
paraelectric, and by changing the composition of Ba and Sr in BST one can tune the
Currie temperature of the material. It is desirable for microwave devices fabricated from
BST to operate near the Currie temperature to improve the tuning of the material. Figure
2a shows how the material will respond to an electric field in the ferroelectric state and
paraelectric state and Figure 2b shows how the Curie temperature will vary with Ba
concentration. While material in the ferroelectric state has found uses in memory
applications such as FeRAM, microwave devices are typically fabricated from material in the paraelectric phase to avoid hysteresis in the materials permittivity.

The large tunability and low dielectric loss of BST has made it attractive for a variety of RF and microwave devices including phase shifters, voltage controlled tunable capacitors, and phased array antenna. These key dielectric properties of the material depend intimately on the structural properties of the material which in turn depend sensitively on the growth conditions. It has been shown that in films grown by PLD, simply changing the oxygen background pressure during growth caused the strain in the film to move from in-plane compressive to in-plane tensile resulting in significant tetragonal distortion.\(^8\) It was also shown that in these films the one with the lowest tetragonal distortion had the lowest loss and largest tunability.
Structural distortions are not the only defects that can impact the dielectric properties of BST. Oxygen vacancies ($V_o$) are common defects that act as n-type donors.

Figure 2: (a) A schematic of the material’s response to an electric field in the ferroelectric state and paraelectric state. (b) Variation of the Curie temperature with Ba concentration.
generating two electrons per vacancy.\textsuperscript{10} These electrons easily hop between the Ti\textsuperscript{4+} ions which can lead to significant dielectric loss. However, it has been shown that substitution of Mg\textsuperscript{2+} on the Ti\textsuperscript{4+} site causes the Mg\textsuperscript{2+} to act as an acceptor, neutralizing some of the free electrons generated by V\textsubscript{o}’s.\textsuperscript{11} But the generation and concentration of these types of defects are complicated by their mobility and the need for charge neutrality.

BST is not a point compound and can take on a range of compositions extending from pure STO to pure BTO along with several impurity phases. Furthermore, an excess of A-site cations can result in the formation of Ruddlesden-Popper (RP) phases\textsuperscript{12,13}, or can be substituted on the B-site\textsuperscript{14}, and a deficiency of A-site cations are easily compensated for by the formation of vacancies. And while the oxygen vacancies are highly mobile through the material, cation vacancies are largely immobile at temperatures typically used for growth. MBE provides an extremely useful tool for the growth of BST under controlled conditions to study the effects of material defects on device properties.

1.3 MBE Growth and Characterization of Thin Films

MBE provides a unique platform for controlled growth of complex oxide films and heterostructures with unparalleled precision. The composition control and interface quality achievable by conventional oxide MBE rivals what is achievable in standard semiconductor growth such as the arsenides,\textsuperscript{15} and new advances in adsorption limited growth windows for the growth of the titanates promises the quality control and deposition rates needed to exploit oxides commercially.\textsuperscript{16,17} The utility of hybrid
molecular beam epitaxy to control the stoichiometry and dielectric properties in BST devices has been demonstrated with excellent results highlighting the need for precise stoichiometry control and low energy deposition.\textsuperscript{18}

Even in the absence of an adsorption controlled growth window, the level of control attainable in conventional MBE is at the atomic level and not only allows the growth of stoichiometric BST but also epitaxial STO on Si which is not possible by other growth methods. Integration of oxides with the standard semiconductor technology has long been a goal not only for improved tunnel barriers but also to add functionality to existing device structures.\textsuperscript{19} Even with this level of control material defects still exist in the grown films and in the film substrates.

Depth resolved cathodoluminescence spectroscopy (DRCLS) is a powerful, non-destructive method for studying the electrically active defects in BST films grown by MBE. Being a non-destructive technique, it enables us to measure the defects of a particular film and produce a device on the film to correlate the device properties with specific material defects. The depth resolved nature of this technique allows us to measure the defect levels through the film and into the substrate.

1.4 Thesis Outline

This thesis focuses on growth parameter dependence of native point defects in BST and how these defects influence the dielectric properties of the material. The effects of oxidizing environment, substrate temperature, and stoichiometry are explored.
Chapter 2 outlines the MBE growth process of shuttered deposition and the use of RHEED as a calibration tool. Chapter 3 reviews the analysis techniques brought to bear on the films: XPS, XRD, and DRCLS. Chapter 4 illustrates a novel UHV transfer mechanism designed to enable film transfer from the growth chamber into the XPS analysis chamber without air exposure. In chapter 5 we show DRCLS results from MBE grown films of $S_{(1-x)}TiO_{(3-δ)}$ films. Chapter 6 discusses the growth parameter dependence of native point defects and how they impact the dielectric properties of the material. Chapter 7 suggests new routes for improving material properties and suggests future work on BST thin films.
Chapter 2: Molecular Beam Epitaxy (MBE)

2.1 Introduction:

Molecular beam epitaxy is a material deposition process by which material is sublimated from a heated crucible forming an atomic beam and travels without interaction to a substrate where it reacts with other constituents forming a solid structure epitaxial to the substrate. MBE was pioneered in the late 1960’s by A. Y. Cho and J. R. Arthur at Bell Telephone Laboratories to grow GaAs epitaxial layers and since its inception the technique has been applied to a large array of materials. The first demonstration of MBE growth of oxide films was in the late 1970’s and was applied to the growth of a native oxide and an Al2O3 insulating layer on GaAs, while it wasn’t until half a decade later that the first examples of MBE applied to complex oxides began with the growth of Al2MgO4.

There are several key features that distinguish the MBE process from other crystal growth processes. A major advantage to the MBE growth process is that it is performed in UHV which allows the use of in-situ characterization techniques such as RHEED, x-ray photoemission spectroscopy, or Auger spectroscopy. Theses analysis techniques enable real time composition control in the growing film, and it has been demonstrated that by using RHEED coupled with shuttered growth one can create atomically abrupt
interfaces which can lead to novel phenomena. MBE’s level of deposition control is unmatched by other deposition techniques, but this control comes at the expense of deposition rate.

MBE’s slow rate of deposition (~1 ML/minute) can be a significant drawback for industrial scale applications requiring fast throughput but can also be a significant advantage in growing extremely high quality materials by allowing sufficient time for the adsorbed atomic species to migrate across the surface. Figure 3 shows the typical process impinging atomic species undergo of adsorption, surface migration, and either desorption or incorporation. Providing sufficient time for surface migration and incorporation into the material facilitates the epitaxial growth of the overlayer by allowing the incident material to redistribute itself at the crystal surface and find a position for incorporation.

In this chapter we will look at the system components and processes that enable such exquisite control of complex oxide growth by MBE.
Figure 3: The MBE growth process. Atoms incident on the sample surface can either desorb, diffuse along the surface, or be incorporated into the lattice. Once incorporated, interdiffusion can play a significant role in the degradation of interfaces.\textsuperscript{25}

2.2 MBE Process Equipment

The typical MBE growth chamber is shown in Figure 4 and displays several features that are typical of all MBE chambers. The system consists of the ultra-high vacuum chamber and associated vacuum pumps and gages, Knudsen effusion cells with mechanical shutters, a heated sample stage, a quartz crystal microbalance, and a reflection high energy electron diffraction system. These elements are essential for the growth of high quality epitaxial layers. For oxide systems, the oxygen can be supplied through a leak valve as either molecular oxygen or activated as an oxygen plasma. The
oxygen source is integrated with the system on the source flange directed toward the substrate in the growth position.

Figure 4: The typical MBE vacuum chamber showing effusion cells, RHEED system, heated sample stage, and cryo panels.\textsuperscript{26}
2.2.1 Ultrahigh Vacuum (UHV) Technology

The quality of the vacuum in MBE is particularly important for several reasons. First, in MBE the source material should not interact with any other materials, be they residual gases in the system or other constituent materials, while in transit to the substrate. This means the source materials should have a mean free path in excess of the distance from the effusion cell to the substrate which typically is around 20 cm. Second, residual gases in the system can incorporate into the growing films as impurities. At 1E-6 Torr background pressure a monolayer of material can adsorb onto the substrate surface every second while at 1E-10 Torr it takes almost 10 hours for a monolayer to build, assuming a sticking coefficient of one.27

Base pressures of modern MBE chambers are 1E-10 to 1E-11 Torr. To reach such high levels of vacuum a series of chambers with different pumping routines are required as well as careful maintenance of the vacuum. Figure 5 shows our Veeco Gen 930 MBE deposition system. It is composed of three chambers: a high vacuum introduction chamber, an ultra-high vacuum buffer chamber, and the ultra-high vacuum reactor chamber.
Figure 5: Brillson Group Veeco Gen 930 MBE system. The system is composed of three chambers with independent pumping systems designed to maintain the ultra high vacuum environment of the reactor chamber: the intro chamber, the buffer line, and the reactor chamber.

The introduction chamber is the smaller of the three chambers and serves as an insertion and outgas chamber for the substrates. Substrates are mounted onto specially designed holders and placed on a trolley that has 8 positions capable of holding 5 sample holders allowing the extra three spaces for transfer. Once loaded into the introduction chamber, a scroll pump capable of reaching 1E-3 Torr roughs down the chamber until a turbomolecular pump can turn on and bring the chamber down to its base pressure of 3E-8 Torr. The inside of the introduction chamber is lined with heater coils that heat the substrates typically to 200°C for 2 hours allowing them to outgas any surface adsorbates acquired from exposure to the atmosphere.
Once outgassed, the substrates are moved into the buffer line which is pumped by an ion pump capable of reaching 1E-10 Torr base pressure that is typical of the reactor chamber. The buffer line’s main purpose is, as the name implies, to buffer the very clean reactor chamber from the not so clean intro chamber. It also serves as a staging area for the substrates that are waiting to be inserted into the growth chamber. The ion pump has several advantages over conventional turbomolecular pumps. The first being the lower ultimate pressures achievable, and the second being no moving parts, hence no noise, no vibration, and less maintenance.

The reactor chamber is pumped to a base pressure of 1E-10 Torr by an extremely large turbomolecular pump capable of handling the high pumping loads generated by the oxygen source, and by a cryo-pump which uses a He cooled fin structure to freeze any ambient gasses. In addition to these two different pumps, there are two liquid nitrogen cooled cryo-shrouds at the front and back ends of the chamber which, when cooled, act as getter pumps by condensing ambient gasses onto their surfaces.

The front cryo-shroud, shown in Figure 6, also thermally isolates the effusion cells while at growth temperatures. Failure to cool the front cryo shroud while the sources are at growth temperatures will result in overheating of the sources and permanent damage is likely. From Figure 6a we see the circular arrangement of the source ports, all slightly angled to face the substrate which would be located in the center of the arrangement approximately 20 cm from the effusion cells. Figure 6b shows how the cryo shroud and source flange fit into the reactor chamber and the cutouts needed for
the mechanical shutters to pass through the shroud and block the atomic beams from the sources.

Figure 6: The cryo shroud used to thermally isolate the effusion cells and as a cryopump for the reactor chamber.

2.2.2 Effusion Cells

Effusion cells are like little ovens used to heat and sublimate the ultra high purity source material. Figure 7 shows an effusion cell used in our chamber. The source material sits inside of a ceramic or metallic crucible that is surrounded by a serpentine resistive heating coil, Figure 7b. A thermocouple provides temperature feedback to a PID controller which controls the power supplied to the heater coils. The source material is heated to the point of sublimation and a mechanical shutter placed in front of the source prevents material from escaping, allowing for precise control of deposition times.
The cells are arranged in a circular pattern, angled to face the heated growth stage and are thermally isolated from one another by a liquid nitrogen cooled panel.

![Image](image1.png)  ![Image](image2.png)

Figure 7: Effusion cells showing the electrical feed through and position of the source crucible with respect to the heating coil.

2.2.3 Heated Sample Stage

The heated sample stage, Figure 8, consists of a three inch diameter circular array of resistive heating wires that heat through radiation. Typical operating temperatures range from room temperature to 1000°C. The stage has two axes of motion, one about the normal axis of the sample and another that allows the sample to be rotated 90° from the transfer position into the growth position. Rotation about the axis normal to the
substrate is critical for several reasons. First, the source flux from the effusion cells incident on the substrate surface is not uniform across the surface and by rotating the substrate during growth a more spatially uniform film composition results. Second, rotating the film allows the RHEED pattern from different directions along the crystal surface to be imaged.

Figure 8: The heated sample stage is shown here in the growth position looking from the source flange. A sample holder and sample are mounted on the stage and the RHEED gun is visible in the top left-hand corner of the image.

2.2.4 Quartz crystal microbalance

Calibration of atomic fluxes in an oxide MBE system is a two part process. To achieve an atomic flux that is to within 5% of the desired flux, a quartz crystal microbalance (QCM) is employed. While not particularly accurate, it responds rapidly.
A small slab of quartz with gold electrical contacts is inserted into the chamber very near to the position at which the substrate will be mounted. This thin slab of quartz has a natural frequency of oscillation, and once the mechanical shutter blocking the atomic flux is opened, the material deposited onto the crystal causes its frequency to change. Knowing what the deposited material is and the change in frequency allows one to calculate the flux of material. Typically the flux from the cells is too small to measure directly and a time average flux is obtained by measuring the total thickness over an interval of several minutes.

There are several issues that are encountered when operating the QCM. Radiative heat transfer from the effusion cell to the QCM crystal plays a significant role in the QCM’s operation. Prior to opening the shutters to any source, the QCM crystal is at a much cooler temperature by virtue of the cooling water that is pumped through it. The shutter on the source serves two purposes: 1) it acts as a thermal barrier shielding the QCM crystal from radiative heating by the source and 2) it acts as an insulating layer for the source reflecting heat that would have otherwise escaped. Opening the source shutter changes both of these and the QCM crystal begins heating up while the source begins cooling down, both of which lead to such a drop in the measured flux that it appears negative. It takes around 15 minutes for the low temperature cells (<600°C), and 30 minutes for the high temperature cells (≈1400°C), and the QCM crystal to come to equilibrium where the source flux can be measured.

The QCM crystal’s position relative to the substrate’s actual position is also a source of error. Typically it is impractical to mount the QCM crystal at exactly the same
position as the substrate and this small difference in position leads to a small change in the flux measured by the QCM and that incident on the substrate. This can be accounted for by depositing material for a predetermined time on a substrate, measuring the actual thickness with a profilometer, and comparing that value to what was recorded by the QCM. The difference in the two can be used to determine the tooling factor of the QCM which is used to correct for the small differences in position of the components in the system.

It is noted here that the QCM is extremely useful when trying to find the sublimation point of a new source or material. These sublimation temperatures can be found in various tables or graphs in material handbooks, but the thermocouple measuring the temperature of the crucible either may not be calibrated in terms of emissivity or may be too far removed from the crucible to accurately measure the temperature of the source material. The general course of action is to get the values from tables and start at a low temperature and slowly increase the source temperature while monitoring the flux on the QCM allowing sufficient time for the source material to come into equilibrium with the heater coils and the QCM to come into equilibrium with the source.

2.2.5 Reflection High Energy Electron Diffraction

RHEED is an indispensible piece of equipment for achieving high quality oxide materials by MBE. In RHEED, 15-30 keV electrons are shown onto the substrate and film at glancing incidence ~1-3° and these electrons can reflect specularly or diffract in
the material onto a phosphorus screen on the opposite side of the reactor chamber. The shallow incidence of the electron beam causes only the topmost mono-layers to be probed making RHEED an extremely surface sensitive technique. The resulting diffraction pattern can give insight into the crystal quality, the in-plane lattice constant, and phase purity. Rotating the crystal through the crystal directions can tell us about how the crystal is ordered in-plane and with respect to the substrate. Monitoring the RHEED intensity of a given diffraction line or the specularly reflected spot allows us to monitor the growth of atomic layers at the surface of the material and is a common approach to calibrating the source flux which will be discussed below.

In addition to the intensity oscillations used during source flux calibration, the electron diffraction pattern can yield an indication of the overall crystal quality. The RHEED pattern from a 2-dimensional, i.e. flat, surface consists of narrow streaks the width of which mirror the full width at half maximum in XRD rocking curves. However, if the growth does not result in an atomically smooth surface and the over layers begin to form islands the diffraction pattern changes from streaks to spots, Figure 9. There are also instances, such as the deposition of the initial layers of STO on Si, where the film takes on an amorphous character and electron diffraction is incoherent, resulting in a diffuse green glow on the phosphorous screen.
RHEED patterns provide information on the stoichiometry in the outermost layers of the material as well. The three directions of diffraction for a (100) oriented perovskite substrate are along the [100], [110], and the [210] azimuths, and an excess of Sr (Ba) will
cause an intermediate diffraction line to emerge between the primary lines forming a 2X2 pattern along the [100] and [210] directions. If an excess of Ti is deposited a 2X1 pattern will form along the [110] direction. Once these lines have formed and have been identified they are easily compensated for and dissolved. Rotating the sample during growth sweeps through the three azimuths and one can monitor the stoichiometry in real time. By growing in this manner one can grow STO or BTO by manual shutter control.

In addition to the primary diffraction of electrons at the sample surface producing the prominent streaks and spots of the RHEED pattern, in samples that have a long range crystal order, secondary electron diffraction lines will be evident called Kikuchi lines. These appear to originate from the primary diffraction lines and sweep away. Appearance of Kikuchi lines is taken as a general indicator of high crystal quality.

2.3 MBE Process

The MBE growth process typically consists of three essential activities: substrate preparation, flux calibration, and growth.

2.3.1 Substrate Preparation

Substrate preparation is an extremely important step for growth of high quality complex oxide overlayers on STO substrates. Typical commercially available substrates come with a mixed termination layer composed of SrO and TiO₂ planes which is
undesirable when doing layer-by-layer deposition. Two methods of producing an atomically flat TiO$_2$ terminated surface layer have been developed by other research groups.

The first uses buffered hydrofluoric acid (BHF).$^{28}$ By this method, the substrates are first soaked in water to transform the surface SrO component into a Sr-hydroxide which is easily etched away by the BHF leaving a TiO$_2$ termination layer. A subsequent 1 hour anneal at 950 °C allows the remaining surface layers to recrystallize. The second method uses an almost identical method but substitutes aqua regia for the BHF acid.$^{29}$ However, DRCLS measurements have shown the aqua regia etch to generate far fewer defects in the material.$^{30}$ The aqua regia etch was adopted as the standard etch for all that follows and Figure 10 shows a typical atomic force microscopy (AFM) scan of the TiO$_2$ terminated surface. In Figure 10 we can clearly see the step edges of one unit cell height.

![Figure 10: TiO$_2$ terminated, commercially available STO substrate after aqua regia etch and subsequent anneal. Step edges of unit cell height are clearly visible.](image)

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Once the substrate is etched, it is mounted on the sample holder and inserted into the introduction chamber. Typically, it is then degassed for 2 hours at 200 °C before being moved into the buffer chamber.

2.3.2 Flux Calibration

One of the central challenges and most significant advantage of MBE is its ability to deliver a precise dose of atomic flux. The calibration of the source flux in an oxide MBE system is a two step process. The first step is to calibrate the source flux using the QCM, which will yield atomic beam fluxes to within 5% of stoichiometry, while the second step of calibration through RHEED intensity oscillations yields atomic beam fluxes to within 1% of stoichiometry. The typical procedure for calibration by QCM has been discussed above, but to illustrate flux calibration via RHEED intensity oscillations, consider the growth of homoepitaxial STO and Figure 11.
Starting from an atomically flat, TiO$_2$ terminated substrate, the specularly reflected portion of the incident electron beam would reflect perfectly and have a maximum intensity. Opening the Sr source shutter while flowing oxygen would begin to build the first monolayer of material and nucleation would begin as a series of islands increasing the roughness of the substrate. This would cause the specular reflection to become more diffuse resulting in a drop in its intensity until it reaches a minimum at half a monolayer where the surface begins to get smoother by the completion of the monolayer and the intensity begins to increase. At the minimum in the intensity the Sr source shutter is closed and the Ti shutter is opened and the cycle is completed by the
deposition of the TiO$_2$ layer when the first full monolayer is deposited bringing the intensity back to the maximum value. Measuring the deposition times of the Sr source and the Ti source over many cycles allows us to get the stoichiometry to within 1% of the expected values, but this method of calibration only works while growing films layer-by-layer in the Frank-van der Merwe growth regime. If we are growing in the Volmer-Weber regime of island growth or the film is grown by codeposition in the step-flow regime no oscillations will be observed. The different growth regimes are shown in figure 12.

Figure 12: Growth can happen in 3 different regimes: (a) Frank-van der Merwe is a layer-by-layer growth, (b) Volmer-Weber growth forms islands, and (c) Stranski-Krastanov is a mix of a and b with complete atomic layers beneath islands of material.$^{32}$

In this manner the source flux of Ba can be obtained by the growth of BaTiO$_3$ on STO substrates. Once the source flux of Ba, Sr, and Ti are known the shutter times for any composition of Ba$_x$Sr$_{1-x}$TiO$_3$ are calculated and fed into a computer program that
controls the shutters automatically. A fresh substrate is loaded into the chamber and

growth is commenced.

During the RHEED oscillation calibration process there are features in the
oscillations that can indicate an excess of A-site cations or B-site cations. We have noted
at the end of the Sr (Ba) deposition cycle and once the Ti shutter is opened a dramatic
increase in the RHEED intensity of the [00] reflection on the (110) azimuth if the Sr (Ba)
is in excess, Figure 13a. Similarly, we have noted a significant shoulder develops at the
end of the Ti deposition cycle if the Ti is in excess, Figure 13b. Other researchers in the
field have noted similar behavior and have demonstrated the introduction of a beat
frequency in the RHEED oscillations from an incomplete monolayer deposition,\textsuperscript{33} and we
show this in Figure 13 c.
Figure 13: RHEED oscillation features indicating (a) A-site rich growth, (b) B-site rich growth, and (c) incomplete monolayer coverage.\textsuperscript{34}
2.3.3 Growth

Once the source flux is calibrated, the deposition times are programmed into a software package designed to control the shutter states, and the calibration sample is replaced with a new substrate. The substrate is heated to the growth temperature while flowing oxygen to minimize the generation of oxygen vacancies in the substrate.

Once the substrate has reached growth temperature, the computer program is started and growth continues in a layer-by-layer manner. The substrate had previously been terminated with a TiO$_2$ layer thus growth begins by simultaneously opening the Ba and Sr shutters to deposit the first (Ba$_x$Sr$_{1-x}$)O layer. Once the time is up the Ba and Sr shutters close and the Ti shutter is opened to deposit the TiO$_2$ layer finishing the first unit cell. This cycle of opening and closing shutters is repeated, slowly building up the film one atomic layer at a time. Films are terminated with the TiO$_2$ layer. Each unit cell of material is $\approx$4 Å thick therefore the final film thickness can be determined by the number of cycles deposited.

It is no surprise that oxygen and its incorporation is an important aspect of growing complex oxides by MBE. There are limitations imposed by the MBE process and equipment to the amount of oxygen that can be flowed into the chamber. The typical distance between the effusion cell and substrate is about 20 cm limiting the maximum background pressure to 2E-4 Torr to ensure a mean free path of the atomic beams long enough to reach the substrate. A 20 cm mean free path for Ba and Sr can be maintained at an oxygen background pressure of 1.6E-4 and 1.9E-4 Torr respectively. However, the
MBE process equipment, especially the source heaters, is sensitive to oxidation and this places an even stricter limit on the oxygen pressures that can be used. For practical reasons the ultimate pressure of the MBE system is limited to $1 \times 10^{-5}$ Torr. To enhance the incorporation of oxygen while maintaining these relatively low pressures, we activate the oxygen to a plasma. The oxygen plasma is supplied via an RF plasma generator whose power can be varied from 50W to 300W. It was noticed early on the advantages to growing with an oxygen plasma. Figure 14a shows a film grown in oxygen ambient while Figure 14b shows a film grown with identical growth parameters but in a 200 W oxygen plasma. In these films we see the NBE emission intensity nearly triple by turning on the plasma.

![Figure 14: (a) Film grown in oxygen ambient. (b) Film grown in oxygen plasma (200 W).](image)

Once the film has reached the desired thickness, all shutters are closed and the film is cooled to room temperature while the oxygen is flowing to minimize the formation of oxygen vacancies. Before removal from the reactor chamber RHEED
images from along the [100], [110], and [210] azimuths are recorded. The film can then be transferred through UHV to our XPS analysis chamber for characterization.
Chapter 3: Analysis Techniques

3.1 X-ray Photoemission Spectroscopy

XPS is an invaluable tool for characterizing the electronic structure of material surfaces and near-surface interfaces. XPS provides detailed information on the local chemical environments, density of states, and material composition. This analysis technique uses monochromatic x-rays to eject electrons from the material being studied and counts them according to their energy. Due to the short inelastic mean free path of electrons in a solid, XPS is extremely surface sensitive and well suited to measuring surfaces and near surface interfaces.
A typical experimental setup is shown in Figure 15. The sample is mounted to a grounded sample stage and a monochromatic beam of x-rays excite electrons from core levels within the sample, Figure 16. These electrons are ejected from the sample with a kinetic energy equal to the difference between the photon energy and the sum of the spectrometer work function, $\Phi_s$, and the binding energy of the electron, Equation 1.

$$K.E. = h\nu - (\Phi_s + B.E.)$$  \hspace{1cm} (1)  

The electrons are collected and focused by a lens system and travel into the electron analyzer where they are sorted by kinetic energy. This information is transferred
to a data acquisition system for processing. Results are typically reported in terms of binding energy rather than kinetic energy.

Figure 16: The photoemission process. Incident photons eject electrons from deep core levels.  

There are several types of measurements that can be made using the simple setup described above. The first is a survey spectrum over a large energy range (0-1400 eV) with low energy resolution. From a survey spectrum we can quickly determine the chemical composition of the sample. To determine the chemical state of the sample, a detailed scan must be performed. By zooming in on a specific, smaller energy range, we can increase the energy resolution of the measurement by decreasing the pass energy of
the analyzer, decreasing the energy step, and increasing the duration of the measurement. This allows us to determine the peak position with much better accuracy and also see the detailed line shape of the emission peak to perform peak fitting.

The stoichiometry of the samples can be calculated from the areas bounded by the core level peaks according to equation 2 where C is the composition, A is the area, and S is the XPS sensitivity to a given element.

\[
C_X = \frac{A_X S_X}{\sum A_i S_i} \quad (2)
\]

We can change the surface sensitivity of the measurement by performing angle resolved x-ray photoemission spectroscopy (ARXPS) measurements. Figure 17 shows the universal curve of inelastic mean free paths of electrons in a solid determined by Seah and Dench in 1979\textsuperscript{39}. What this curve shows is that electrons from only the top few nanometers of the sample escape without scattering and can contribute to photoemission lines with the rest contributing to the background. However, this assumes a 90° takeoff angle to the analyzer. By tilting the sample surface away from the analyzer we can increase the surface sensitivity of the measurement by forcing electrons from deeper in the sample to travel a larger distance through the sample increasing the probability of scattering. This measurement is very useful for determining the thickness of thin overlayers or obtaining information on the depth distribution of atomic concentrations or different charge states.
Figure 17: Electron scattering length versus energy. The red area shows the typical energies of photoelectrons indicating a scattering length of 10-20 Å.39

With either of these measurement techniques, for an insulating sample special attention must be given to surface charging. If the sample surface begins to charge (either positively or negatively) this will cause a rigid shift in the binding energy of all measured spectral features which can present significant challenges when trying to determine the chemical state of the material. There are several methods to compensate surface charging, the first of which uses a low energy electron gun to replace electrons lost to the photoemission process. However, the x-ray beam causes only a small area of the surface to charge positively by ejecting electrons, the rest of the sample surface
charges negatively which will repel the electrons from the neutralizer. Using an Ar$^+$
flood gun can effectively reduce the negative surface charging allowing the electron flood
gun to operate optimally.

Another method to address surface charging, albeit indirectly, is to use adsorbed
carbon from the atmosphere. Since any shift in the spectrum from surface charging
would be a rigid shift affecting the entire spectra, the C-1s core level can be used as a
reference. It is generally accepted that the adventitious carbon 1s core level peaks at
284.8 eV.

There are several spectral features that can be seen in a given spectrum, and the
main features in any XPS spectrum are the photoemission lines. Photoemission lines are
the direct result of the photoelectric effect, an x-ray is absorbed and an electron is ejected.
There are several final states that the atom can be left in and this can affect the position of
the photoemission lines. The simplest situation is when the atom is left ionized in its
ground state, resulting in intense photoemission lines at the characteristic binding energy,
but it can happen that the atom is left in an excited final state which is usually a few
electron-volts above the ground state and this results in a photoemission line that is
shifted to higher binding energy called a shake-up or satellite line.

Photoemission lines can have an energy shift associated with the chemical state of
the element and this shift can be either to higher binding energy or lower binding energy
depending on whether the element is the cation or the anion. As an example we can
consider carbon in one of three forms; elemental carbon, carbon in carbonates, and
carbon in carbides. The 1s orbital binding energy from elemental carbon is generally
accepted to be 284.8 eV, but if the carbon is bound in a carbide such as silicon carbide where it receives electrons from the Si, the C1s binding energy decreases to 282.8 eV. On the other hand, if carbon is bound in a carbonate, electrons are transferred from the carbon to the oxygen atoms shifting the C1s binding energy to a higher binding energy of about 290 eV.

Photoemission lines can also have an energy shift due to band bending at the surface of the material. If there is an overlayer of deposited metal, or of contamination, charge will transfer between the layers and accumulate at the surface. The opposite amount of charge will distribute through the material, and due to this dipole, the bands can bend significantly changing the distance from the conduction band to Fermi level and the valence band to Fermi level. Band bending will cause a rigid shift of all binding energies as well. By subtracting the energy separation between the valence band edge and a core level peak for the clean surface, noting this value will be the same after metal deposition, from the energy separation between the same core level and the Fermi level after metal deposition, we can determine the new energy of the valence band edge. The Schottky barrier height is then simply the difference between the band gap of the semiconductor material and the new position of the valence band edge.

The valence band electrons are typically considered to have binding energies ranging from 0-20 eV. By definition the Fermi level is 0 eV binding energy, and to calibrate the system, we can measure the valence band of gold to obtain both the Fermi level of the system with respect to ground and the energy resolution of the system by measuring the width of the valence band edge, Figure 18. Once the Fermi level of the
system is known, placing a sample on the stage will cause the Fermi levels to line up and we can measure the energy separation from valence band edge to the Fermi level of the sample.

![Figure 18: Valence band scan of gold. From this we can determine the energy resolution of the system by measuring the width of the valence band edge and the Fermi level position at the center of the sloping region.](image)

Besides the core levels, another obvious spectral feature is the splitting of core level peaks due to spin orbit coupling. The energy shift between two spin orbit split peaks is well known and can be obtained from reference data. The ratio of the areas of the peaks is also well known and for the $p_{1/2}$-$p_{3/2}$, $d_{3/2}$-$d_{5/2}$, and $f_{5/2}$-$f_{7/2}$ core level peaks is 1:2, 2:3 and 3:4 respectively\textsuperscript{40}. This can be determined directly from the degeneracy of the states with angular momentum $\ell$, that is $2(\ell+1/2)$.

Auger lines are also common features in XPS spectra. These features are the result of a two step process where a deep core level electron is excited by a photon leaving a hole. A shallow level electron decays into this hole and gives up its energy to
another electron ejecting it from the sample as an Auger electron. These features can be very helpful in determining the composition of an unknown material.

XPS can also be used to determine the atomic composition of a thick film by using an \( \text{Ar}^+ \) ion source to ablate away thin layers of material. By measuring the composition between rounds of ablation a composition profile can be compiled one slice at a time. However, the ablation process disrupts the lattice and causes information on the chemical state to be lost. Another potential issue with depth profiling is the preferential removal of certain atomic species over another which can lead to spurious results. \( \text{Ar}^+ \) ion bombardment can also be used to clean a surface having a contaminating overlayer on it. Our method of gentle cleaning using 500 eV \( \text{Ar}^+ \) ions is detailed here.\(^{41}\)

![Figure 19: \( \text{Ar}^+ \) ablation of the surface can be used to determine the composition at depths not accessible by angular resolved measurements.\(^{42}\)](image)

XPS is a very surface sensitive technique allowing for rapid, non-destructive determination of quantities and positions of elemental species as well as their chemical state within a sample making it ideal for studying complex oxide heterojunctions.
Furthermore, by measuring the precise positions of the core level peaks with respect to the Fermi level and valence band, one is able to determine the Schottky barrier height or band offsets in a given heterojunction.

3.2 Cathodoluminescence Spectroscopy

Cathodoluminescence spectroscopy (CLS) provides a nondestructive complimentary technique to XPS but unlike XPS can probe structures on the nanometer scale at the surface as well as into the bulk. CLS uses a beam of electrons to create electron-hole pairs that recombine and emit light at energies characteristic of the bandgap and defect states within the material. By changing the energy of the incident electrons we can probe interfaces and structures at varying depths within the material, depth resolved cathodoluminescence spectroscopy (DRCLS).

The standard CLS system is shown in Figure 20 and consists of an electron gun, a cooled sample stage, an optical lens system to collect light, a monochromator, a detector, and data acquisition system. The measurements must be done in ultra high vacuum for several reasons. First and foremost is to prevent oxidation of the electron gun filament. Other reasons include preventing ice from forming on the sample as well as to keep the electron beam from breaking up carbon based molecules and depositing a carbon overlayer on the surface making the data difficult to interpret.
Figure 20: The typical CLS system. Incident electrons excite electron-hole pairs in the material that emit light after recombination. The light is gathered, sent through a monochromator and detector, then on the data acquisition system.43

Figure 21 details the processes which lead to the features observed in CLS spectra. The incident electrons excite electrons within the material from the valence band into the conduction band leaving a hole in the valence band, but the electrons are typically excited to energies well above the conduction band minimum and relax thermally to the conduction band minima. From the conduction band minimum these electrons can recombine with holes through several processes. The first is by direct recombination with holes in the valence band releasing light with energy that is characteristic of the bandgap of the material. The electrons could also decay into a defect state before decaying into the valence band giving off light with a lower energy than band-to-band recombination. There could also be multiple defect levels within the
bandgap of the material that the electron could transition between again emitting light with a characteristic energy lower than band-to-band recombination.

![Diagram](image)

Figure 21: Excitation of electron hole pairs by an incident high energy electron beam and the possible routes of recombination.

The main type of measurement that is made is with constant current but changing the beam energy. By changing the accelerating voltage one can change the depth at which the sample is probed. We can model this through Monte Carlo simulations by allowing the electron to take a random walk through the material having random collisions and giving up energy in the collision to create electron hole pairs. Doing this for tens or hundreds of thousands of electrons, it is possible to simulate the electron cascades and determine the depth at which they excite the electron-hole pairs and also the volume over which the cascade spreads. The results of the Monte Carlo simulations for an infinite slab of STO are shown in Figure 22. From the Monte Carlo simulation we can read off two values of interest: the maximum energy loss per unit depth, \( U_0 \), and the Bohr-Bethe range, \( R_B \), which is the maximum range over which excitation occurs.
Cathodoluminescence provides a non-destructive means of determining the bandgap and defect concentration as a function of depth with nanometer spatial resolution. Performing constant beam energy, varying current measurements can provide information on the origin of spectral features. Central to this technique is the use of Monte Carlo simulations to determine the probing depth in the material.
3.3 X-ray Diffraction

X-ray diffraction is a powerful, non-destructive technique used to determine the structural properties of a crystalline material. XRD can be used to measure the lattice parameters, phase purity, chemical composition and stress in thin films.

XRD uses a monochromatic beam of x-rays incident on a crystalline material and a detector to measure the intensity of diffracted x-rays from the material. In order to have diffraction from the material the wavelength of the monochromatic x-rays needs to be on the same order of size as the atomic spacing in the material, and in SrTiO$_3$ the atomic spacing is 3.905 Å indicating the x-ray wavelength needs to be on the order of an angstrom. In this work we utilize a Bruker D8 Discover with x-rays generated from a Cu K$_\alpha$ source (λ=1.5404 Å) which are collimated by a GOBEL reflecting mirror.

![Figure 23: The geometry of Bragg diffraction showing the incident and reflected waves.](image)

Figure 23: The geometry of Bragg diffraction showing the incident and reflected waves.
The geometry of the measurement is shown in Figure 23 with the x-rays incident on the sample surface at some angle, $\theta$, and reflecting from the first and second atomic planes. The reflected x-rays will arrive at the detector and will interfere constructively if the plane separation and angle $\theta$ satisfies the Bragg equation, equation 1, where $d$ is the path length difference from the first to second plane, $\theta$ is the incident angle, and $\lambda$ is the x-ray wavelength:

$$2d \sin \theta = n\lambda \quad (1)$$

This expression can be written in a slightly more general form by noting that the atomic plane spacing, $d$, can be generalized to any atomic planes represented by the Miller indices $(h, k, l)$. For an orthorhombic crystal system with lattice parameters $a$, $b$, $c$ where $a \neq b \neq c$, the atomic plane spacing can be written as:

$$d_{hkl} = \left[\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2\right]^{-1/2} \quad (2)$$

From Equations 1 and 2 and XRD measurements of in-plane and out-of-plane reflections it is possible to calculate the in and out of plane lattice parameters for thin films. At room temperature STO is cubic ($a=b=c$) with a lattice parameter of 3.905 Å while BTO is tetragonal ($a=b\neq c$) with an $a$ lattice parameter of 3.992 Å and a $c$ lattice parameter of 4.036 Å. Using Vegard’s law and lattice parameters determined from XRD measurements, it is possible to determine the chemical composition from relaxed samples. For $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ the $a$-axis lattice parameter should be 3.949 Å while the $c$-axis lattice parameter should be 3.971 Å.

In addition to determining the atomic plane spacing by the $\omega$-20 scans, rocking curve scans are typically acquired and provide information on the crystal planes.
alignment to one another. In a rocking curve measurement the detector and x-ray source are fixed and the crystal is rotated. In a perfect crystal the rocking curve should be extremely narrow, however, in real crystals defects such as mosaic spread, dislocations, and curvature will cause the rocking curve to broaden. Rocking curves provide a general gauge of crystal quality.

Finally, from the XRD measurements typically performed we can extract an estimation of the film thickness which can then be used to confirm the thickness of our films determined from the number of deposition cycles during MBE growth. By noting the spacing between the thickness fringes on either side of the Bragg peak and using equation 3 to determine the sample thickness $D$:

$$D = \frac{(n_1-n_2)\lambda}{2(\sin \theta_1-\sin \theta_2)}$$  \hspace{1cm} (3)

Figure 24 shows a typical $\omega$-2$\theta$ scan of a BST film, and in it we can see three distinct features: the STO substrate (002) reflection, the BST film (002) reflection, and the thickness fringes surrounding the film peak. Taking the peak positions of the first thickness fringe before and after the (002) film reflection and using equation 3, we can calculate the film thickness to be 49.84 nm. This film was grown for 125 cycles with a c-axis parameter measured by XRD of 4.019 Å yielding a total thickness of 50.23 nm which is in very good agreement with the thickness calculated from the thickness fringes.
Figure 24: XRD $\omega$-2$\theta$ scan showing the (002) reflections from the STO substrate and BST film. The film thickness can be determined from the thickness fringes surrounding the BST film peak. Fitting multiple peaks and taking the separation between them improves the accuracy of the measurement.
4.1 Introduction

Due to advances in molecular beam epitaxy (MBE), laser-MBE, and sputtering, it is now possible to grow atomically thin and atomically flat complex oxide heterostructures. These complex oxides demonstrate a range of phenomena including superconductivity\textsuperscript{47}, ferroelectricity\textsuperscript{48}, ferromagnetism\textsuperscript{49}, and piezoelectricity\textsuperscript{50}, while complex oxide heterojunctions have generated surprising results due to emergent phenomena at their interfaces, leading to novel functionality not possessed by either constituent.\textsuperscript{51,52,53,54} Many of these phenomena rely on the exchange of charge and XPS is a very surface sensitive analysis technique that is well suited for studying the atomic valence states of thin films and heterostructures.

Due to this surface sensitivity however, exposure to the atmosphere will introduce surface contaminants that will result in spurious XPS data. It has been shown that oxide thin films can react with the atmosphere forming over layers not representative of the film.\textsuperscript{55} Thus, it is desirable to transfer films directly from the growth chamber to the analysis chamber under UHV conditions eliminating atmosphere exposure. Whitman et
al. have developed a UHV compatible device to transfer MBE grown samples to a scanning tunneling microscopy (STM) analysis chamber, but this design required modification to their STM sample stage. We designed a UHV transfer line capable of transferring a sample from our MBE growth chamber into our XPS analysis chamber and back again or into any number of additional chambers without the need to modify the existing systems. Smathers et al. have also eliminated the need for modifying the sample stage. However, their design appears to be limited to transfer between their MBE and an STM.

This chapter details a mechanism and the accompanying sample holders we designed to transfer between our VEECO 930 oxide MBE and our PHI Versa Probe X-ray photoemission spectroscopy (XPS) chamber within a multiple station growth, processing, and analysis system through ultra high vacuum (UHV). The mechanism consists of four parts: (1) a platen compatible with the MBE growth stage, (2) a platen compatible with the XPS analysis stage, (3) a sample coupon that is transferred between the two platens, and (4) the accompanying UHV transfer line. The mechanism offers a robust design that enables transfer back and forth between the growth chamber and analysis chamber, and yet is flexible enough to allow transfer between standard sample holders for thin film growth and masked sample holders for making electrical contacts and Schottky junctions, all without breaking vacuum. We used this mechanism to transfer barium strontium titanate (BST) thin films into the XPS analysis chamber through ultra-high vacuum and have found a barium excess at the surface.
4.2 Sample Coupon and Platens

The sample platens consist of three parts machined from heat-resistant stainless steel; a platen that fits the specimen manipulator’s sample heater stage of the Veeco 930 MBE chamber, a smaller platen that fits into the sample holder stage in the PHI Versa Probe XPS chamber, and a substrate coupon on which the sample is mounted that can be transferred between the two platens using a pincer on a z-translator.

The MBE platen, shown in Figure 25, is a 3.5 inch diameter circular holder with six slotted holes on the periphery to accommodate a 3 prong bayonet style transfer system. The peripheral edge is 0.1” while the center of the platen is 3/16” thick. The sample coupon interfaces the MBE platen through a tongue and groove joint in the center that reaches just past the center so that the substrate can sit at the center of the heater during growth. The corners of the tongue and grooves on all pieces have been chamfered to accommodate for small misalignments during transfer.
Figure 25: MBE Platen a) Front, b) Edge, c) Back, d) 3D view. The MBE platen is a circular heat-resistant stainless steel platen with six slotted holes at the outer edges to allow the platen to be manipulated and held using bayonets. Through the center of the platen is a grooved, rectangular cutout for the sample coupon to slide into. If rotation of the sample during growth is desired, a clip can be fitted over the tongue of the sample coupon to prevent it from sliding out of the MBE platen.

The sample coupon is shown in Figure 26 and can accept substrates up to one square cm. It is a rectangular piece with grooves machined on the edges to slide into tongues on the MBE and XPS platens. The top edge is machined to a 0.1” thickness to match the MBE platen peripheral thickness and has a square through hole for the pincer to engage during transfer. 1/16” of material was machined from the backside, bottom half of the coupon creating a step shown in Figure 24c. The XPS platen is oriented vertically during transfer between different heights, and this step mates to a step machined in the XPS platen to act as a mechanical stop during insertion, preventing the sample coupon from sliding out of its new holder. It also aligns the sample coupon in the center of the UHV transfer line.
Figure 26: Sample Coupon a) Front, b) Edge, c) Back, d) 3D view. The sample coupon has a tongue on both long sides for the coupon to slide into the grooves in the MBE and XPS platens. There is a step on the back side of the coupon (shown in lower left panel) to mate with a similar step on the XPS platen to align it in the center of the transfer line and prevent it from sliding through the XPS Platen. At the top of the coupon there is a square cutout for the pincer to engage during transfer between platens. The substrate can be affixed to the front surface using silver or platinum paint or by a mechanical fastener.

The XPS platen, shown in Figure 27, is a 1” diameter cylinder with a grooved, cutaway at the top for the sample coupon, the opening of which has been flared to funnel the sample coupon into the proper position. Furthermore, the mating step for the sample coupon has been machined into the opening. Two rings have also been machined out of the cylinder wall to accommodate the fork style transfer system of the XPS. Having two rings allows the XPS platen to be transferred by horizontal, perpendicular forks from one chamber to another linked to the main transfer line.
Figure 27: XPS Platen a) Front, b) Edge, c) Back, d) 3D view. The XPS platen is a cylinder with two rings machined into the side to accommodate a fork style transfer mechanism. Having two rings allows the platen to be transferred between two perpendicular forks within the transfer line. The opening for the sample coupon is flared to funnel the coupon into the proper position and a step is machined at the bottom of the flare to stop the coupon.

4.3 The Transfer Line

Figure 28 shows the transfer line with the motion of the sample through the transfer line shown by red, numbered arrows, and the different transfer rods shown by blue, lettered arrows, and Figure 29 shows the MBE platen, sample coupon, and XPS platen at the various points along the transfer line. A sample grown on the sample coupon mounted in the MBE platen is transferred into a vertical buffer line by a bayoneted transfer rod and onto a magnet-manipulated trolley which is then moved horizontally to the next bayoneted transfer rod (Figure 28 movement 1, Figure 29a). Next, the sample coupon and MBE platen is removed from the trolley, by transfer rod b, and transferred into a 6” 6-way cross (Figure 28 movement 2, Figure 29b). A rotatable pincer on a z-
translator, transfer rod a, is used to remove the vertically-oriented sample coupon from the MBE platen (Figure 29c). The pincer had to be rotatable since the axis of movement 1 is rotated from the axis of movement 2 by 10° in order for the 48” transfer rod c to avoid interference with the superstructure of the MBE and the sample coupon could not be inserted into the XPS platen with this much misalignment.

Figure 28: UHV transfer line. The red arrows show the direction of travel from the MBE chamber to the XPS analysis chamber. The blue arrows show the transfer rods enabling transfer between the various parts of the system.
Figure 29: Sample and holders at various points along the transfer line.  a) Sample coupon in the MBE platen on the trolley in the buffer line coming from the MBE (Figure 22, movement 1). b) Rear view of the sample coupon in the MBE platen on transfer rod b in the 6” 6-way cross with the pincer engaged (Figure 22, movement 2). c) The MBE platen with the the sample coupon removed. d) The sample coupon lowered to the 4.5” 6-way cross where the XPS platen is waiting in the vertical position on the end of transfer rod c (Figure 22, movement 3). e) The sample coupon inserted into the XPS platen. e) The sample coupon inserted into the XPS platen rotated into the horizontal position ready to be transferred into the XPS (Figure 22, movement 4).

After the sample coupon is removed from the MBE platen, the MBE platen is moved back into the buffer line, clearing the way for the sample coupon to be lowered 26” into a 4.5” 6-way cross and inserted into the XPS platen which is on a fork attached to
a 48” transfer rod c (Figure 28 movement 3, Figure 29d). The 26” travel distance depends only on the difference in vertical height between the MBE transfer line and the XPS sample stage. This height will depend on vertical distance for any arbitrary growth and analysis chamber combination.

Once the step of the sample coupon is mated to the step of the XPS platen, the pincer is disengaged and moved out of the way (Figure 29e). Transfer rod c now rotates the sample coupon in the XPS platen 90° about the axis of travel from a vertical to horizontal orientation (Figure 29f). The XPS platen can then be moved into the XPS chamber directly (Figure 28 movement 4) or transferred onto another fork and moved into one of the side chambers along transfer rods d and e.

The transfer line is separated from the XPS chamber, MBE buffer line, and all side chambers by gate valves. In order to minimize vibrations transferred to the XPS chamber, flexible bellows were used at the attachment points, and an ion pump is used to maintain the UHV environment in the transfer line.

4.4 General MBE Platen Remarks

The additional thickness of the heated MBE platen and sample coupon compared to the thinner factory supplied growth platens has advantages as well as drawbacks. With the additional thickness, it is possible to drill and tap holes for screws in either the MBE platen or the sample coupon. One can then use a low profile, mechanical fastener such as a mask, clips, or screws to hold the substrate to the sample coupon eliminating the need
for silver or platinum paint. Tapped holes on the MBE platen provide a convenient attachment point for a shadow mask to pattern simple contacts or devices. However, the additional thickness does lead to a longer time required to stabilize the growth temperature measured by an optical pyrometer. We also have drilled and tapped holes in the XPS platen to attach a shadow mask for use in our metals deposition chamber.

By keeping the same shape and a similar thickness profile to the sample holders provided by VEECO we were able to use the existing transfer mechanisms and growth stage. Furthermore, no adjustment to the reflection high energy electron diffraction (RHEED) gun or sample stage was necessary since the substrate sits at the same position in the growth chamber when using the factory supplied platens or our own. Similarly, transferring a small coupon has allowed us to retain the existing XPS stage without any modification.

4.5 Growth and Transfer of Ba$_x$Sr$_{1-x}$TiO$_3$

Utilizing our UHV interconnect mechanism, we grew BST and analyzed its surface composition using XPS without breaking vacuum and after exposure to air. We grew 20 nm BST (x=0.5) films on TiO$_2$–terminated SrTiO$_3$ (STO) (100) substrates prepared by etching in aqua regia and a subsequent anneal.$^{58,59}$ The treated substrates were baked in an introduction chamber at 200 °C for two hours and then transferred into the growth chamber and brought up to 800 °C at an oxygen background pressure of 1E-6 Torr. Ba, Sr, and Ti base metals were evaporated from Knudsen effusion cells whose
source flux was calibrated using a quartz crystal microbalance (QCM) and RHEED oscillations from a calibration sample grown at 1E-6 Torr background oxygen pressure and 800 °C substrate temperature. The films were grown by codeposition of Ba and Sr and alternating deposition of Ti at a temperature of 800 °C. Films were cooled to room temperature at growth pressure.

After MBE growth, we transferred this film through our UHV transfer line mechanism into the PHI Versa Probe XPS analysis chamber. After the analysis was performed, we removed the sample from UHV and repeated the XPS measurements after an hour and four hours of exposure to the atmosphere. XPS measurements were performed using a monochromatic Al Kα (1486 eV) X-ray source, a pass energy of 23.5 eV, and a 0.05 eV energy step. Under these conditions the ultimate energy resolution of the system is 0.48 eV. To minimize the effects of sample charging, the system is equipped with a 2 stage sample neutralization scheme consisting of a 10 eV electron flood gun and a 10 eV Ar+ ion beam. Photoemission measurements were taken at a 45° takeoff angle to the analyzer.

Figure 30 shows the Ba 3d$_{5/2}$, Sr 3d$_{5/2}$ and 3d$_{3/2}$, Ti 2p$_{3/2}$ and 2p$_{1/2}$, O 1s, and the C 1s emission lines before and after air exposure. The Ba 3d$_{5/2}$ is composed of two chemical states with a binding energy separation of 1.73 eV. For measurements performed after UHV transfer, the binding energies of the two components of the Ba 3d$_{5/2}$ emission were found to be 779.41 eV and 777.68 eV. We see the Sr and Ti are in a single chemical state with the Sr 3d$_{5/2}$ emission at 132.11 eV, the Sr 3d$_{3/2}$ emission at 133.85 eV, the Ti 2p$_{3/2}$ emission at 457.46 eV and the Ti 2p$_{1/2}$ emission at 463.15 eV.
The O 1s is at 528.70 eV. There was no trace of C at the surface of the UHV transferred film. There is very little change in these binding energies for the measurement taken after 1 hour of air exposure but after 4 hours of air exposure we see a clear shift towards higher binding energy of all peaks by about 1 eV.
Figure 30: XPS spectra taken at a 45° take-off angle to the analyzer of the Ba 3d$_{5/2}$, Sr 3d$_{5/2}$ and 3d$_{3/2}$, Ti 2p$_{3/2}$ and 2p$_{1/2}$, O 1s, and the C 1s emission lines. The high binding energy Ba 3d$_{5/2}$ component dominates the signal at shallow take-off angles indicating an additional surface Ba component. Likewise, there is a high binding energy shoulder to the oxygen that indicates an additional O component.

Two chemical states of Ba have been observed in BaTiO$_3$ that has been cleaved in UHV by L.T. Hudson et al. and the higher binding energy component has been attributed
to undercoordinated Ba at the free surface while the lower binding energy component has
been attributed to Ba in a 12-fold configuration representative of the bulk. \(^{60}\) Angle
resolved XPS measurements of pristine BST surfaces confirm this by indicating the high
binding energy Ba component dominates the spectra at shallow take-off angles
demonstrating it is a surface component of the Ba. Using our transfer mechanism we
have observed the presence of this undercoordinated component of Ba without cleaving
the sample.

<table>
<thead>
<tr>
<th>% Comp.</th>
<th>UHV</th>
<th>1 Hour</th>
<th>4 Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>9.6</td>
<td>9.5</td>
<td>6.9</td>
</tr>
<tr>
<td>Sr</td>
<td>10.5</td>
<td>10</td>
<td>9.2</td>
</tr>
<tr>
<td>Ti</td>
<td>19.9</td>
<td>19.7</td>
<td>17.2</td>
</tr>
<tr>
<td>O</td>
<td>59.9</td>
<td>60.1</td>
<td>65.1</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
<td>0.7</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 1: Atomic concentrations determined after UHV transfer, 1 hour air exposure and 4 hours of air exposure.

Table 1 shows the atomic concentrations from the three measurements: UHV
transfer, 1 hour air exposure, and 4 hours air exposure. After 1 hour of air exposure there
is a slight shift higher binding energies as well as a small amount of adsorbed carbon.
We see that there is a significant amount of absorbed oxygen on the surface after 4 hours
of air exposure. This adsorbed oxygen is readily observed as shoulder to the BST O1s
line and is shifted by 2.51 eV to higher binding energy. We also see a significant amount
of carbon adsorbed on the surface as well. This adventitious carbon overlayer is
generally used to adjust for energy shifts induced by sample charging, but we see that the

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binding energy of the C 1s peak is at 284.7 eV while the standard is 284.8 eV indicating the dual charge neutralization system is working well.

Our transfer mechanism provided us with the capability to observe the surface chemical composition and bonding of the MBE-grown surface termination, completely free of air adsorbates and any rebonding. With exposure to air and resulting adsorption of carbon, precise determination of core level binding energy and sample composition is compromised leaving the user to make corrections to their data. Similarly, one can employ this mechanism to observe heterojunction band offsets between, e.g., BST and STO as a function of interface growth conditions.\textsuperscript{61}

4.6 Conclusions

In summary, we have developed a UHV compatible transfer mechanism capable of transferring between an oxide MBE chamber and an XPS analysis chamber or a variety of post processing chambers. To accomplish this, we needed to remove the substrate from a MBE compatible platen and lower it vertically to a platen compatible with our XPS system. Our ability to transfer into the XPS platen, which is small enough to be transferred into the side chambers, adds versatility to this system in that additional chambers can accommodate this small size holder. In addition, we show a significant shift, \(~1\) eV, of the core level binding energies after exposure to air.
Chapter 5: Depth Resolved Cathodoluminescence Spectroscopy Analysis of Highly Reduced BST-STO Heterojunctions Grown by Plasma Assisted MBE

5.1 Introduction

A central challenge in growing high quality oxide films by molecular beam epitaxy is incorporation of sufficient oxygen into the growing film to prevent the formation of oxygen vacancies. Due to the high temperatures required to evaporate transition metal oxides the oxygen background pressures that can be realized is limited to the $10^{-5}$ Torr in most cases to extend the lifetime of the source filaments. Since there is a limit to the maximum P(O2) that can be used, several methods to increase the reactivity of the oxygen have been developed. Instead of using molecular oxygen, some researchers have opted to used distilled ozone. Ozone has the disadvantages of being both explosive and toxic.

In order to understand the incorporation of oxygen in Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) films grown by plasma assisted molecular beam epitaxy (MBE), we grew BST thin films in a 200W oxygen plasma at oxygen background pressures (P(O2)) of 0, 3E-8, 1E-7, and 5E-7 Torr. Subsequent depth resolved cathodoluminescence spectroscopy (DRCLS) measurements reveal strong features at 1.9eV, 2.55eV, 2.9eV, and 3.1eV in the films.
prepared under the most reducing conditions while the film grown at 5E-7 Torr showed additional features at 2.1eV and 2.3eV. Overall, we found the emission intensity of the 2.9eV, blue luminescence, feature drops dramatically with increasing oxygen pressure. Probing these features as a function of depth through the film, at the interface, and into the substrate we see the 2.9eV feature extends well into the substrate indicating oxygen out-diffusion from the substrate. We also report direct observation of an interband transition between the Ti 3d t2g and O 2p bands by DRCLS at 4.2 eV.

Here we describe the preparation and characterization of BST thin films under various P(O2)’s by plasma assisted MBE in a 200 W oxygen plasma and demonstrate the utility of DRCLS in characterizing oxygen deficient thin films of BST.

5.2 Experiment/Results

BST thin films were grown in a VEECO Gen 930 molecular beam epitaxy system with a base pressure of 1E-10 Torr. Films were grown layer-by-layer by alternate deposition of co-deposited Sr and Ba, and Ti base metals onto TiO$_2$-terminated STO (100) substrates treated with the standard aqua regia etch.$^{64,65}$ All films were prepared at 800°C substrate temperature. The source flux was calibrated using a quartz crystal microbalance (QCM) and in situ reflection high energy electron diffraction (RHEED) oscillations from a calibration sample. Three 100nm thick films were then grown in a 200W oxygen plasma at 3E-8Torr, 1E-7Torr, and 5E-7Torr. One 20nm thick film was
grown in the absence of externally supplied oxygen. The film grown at $P(O_2)=5 \times 10^{-7}$ Torr was clear while all other films were dark blue/black.

In all films the RHEED patterns consisted of well defined streaks indicating a smooth 2-dimensional surface with some secondary diffraction lines. The sample grown without externally supplied oxygen had the best RHEED patterns in terms of the main diffraction line width and secondary diffraction lines, and these RHEED patterns from along the [100], [110], and [210] azimuths are shown in Figure 31.

![Figure 31](image)

Figure 31: RHEED patterns from (a) along the substrate [110] azimuth, (b) along the film [100] azimuth, (c) along the film [110] azimuth, and (d) along the film [210] azimuth. The RHEED patterns show sharp diffraction lines indicative of a well ordered 2-dimensional surface. Furthermore, there is strong secondary diffraction, Kikuchi lines, indicating a high degree of long range crystal order. In panel (c) the arrows point to 2X patterns due to a Ba excess at the surface.
The streaky RHEED patterns indicate an atomically smooth surface which is confirmed by AFM scans of the 100 nm films shown in Figure 32. In the AFM scans step edges are clearly visible in all three films with large dislocations intersecting at 90° angles.
Figure 32: 10 μm X 10μm AFM topography scans of the 100 nm BST films grown at (a) 3E-8 Torr, (b) 1E-7 Torr, and (c) 5E-7 Torr oxygen background pressure. Step edges and dislocations are visible in all three films.
Figure 33: Large angle XRD ω-2θ scans of the 100 nm BST films grown at (a) 3E-8 Torr, (b) 1E-7 Torr, and (c) 5E-7 Torr oxygen background pressure. We see no evidence of secondary phase formation.
Large angle x-ray diffraction (XRD) measurements of the 100nm films show our films to be single crystal, phase-pure BST, Figure 33. High resolution x-ray diffraction (HRXRD) measurements of the (002) and (101) reflections were performed for all samples to determine the c and a-axis parameters and are listed in table 2.

<table>
<thead>
<tr>
<th>Film P(O2)</th>
<th>Thickness (nm)</th>
<th>c (Å)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Torr</td>
<td>20</td>
<td>3.9979</td>
<td>3.9080</td>
</tr>
<tr>
<td>3E-8 Torr</td>
<td>100</td>
<td>4.0169</td>
<td>3.9067</td>
</tr>
<tr>
<td>1E-7 Torr</td>
<td>100</td>
<td>4.0157</td>
<td>3.9050</td>
</tr>
<tr>
<td>5E-7 Torr</td>
<td>100</td>
<td>4.0248</td>
<td>3.9064</td>
</tr>
</tbody>
</table>

Table 2: O-series film lattice parameters.

To probe electrically active defects in the material we used depth resolved cathodoluminescence spectroscopy (DRCLS). The measurements were performed at 80 K in UHV with a constant 2 μA emission current while the beam energy was increased from 1 kV to 5 kV in 1 kV steps. Monte Carlo simulations yield maximum excitation depths of ~20, 45, 75, 115 and 170nm for electron beam energies of 1, 2, 3, 4, and 5 kV, respectively.

Figure 34 shows DRCLS spectra from 100nm films grown at a P(O2) of 3E-8 Torr, 1E-7Torr and 5E-7 Torr. Figure 35a shows the DRCLS spectra of the 20 nm film. The films grown at less than 5E-7 Torr P(O2) all displayed the same DRCLS features. Fitting these spectra with four Gaussian curves yielded nice fits with the Gaussians centered at 1.9 eV, 2.55 eV, 2.95 eV, and another peak whose center varied from 3.1 eV to 3.27 eV. The film grown at 5E-7 Torr P(O2) however had a more intense green band emission with features at 1.9 eV, 2.1 eV, and 2.3 eV, as well as the feature at 2.9 eV and
the varying feature at 3.1 eV to 3.27 eV. Low intensity, higher energy features at 3.55 eV and 4.2 eV were also observed in several films.

![Diagram](image)

Figure 34: DRCLS spectra from the 100nm films grown at (a) P(O2)=3E-8 Torr, (b) P(O2)=1E-7 Torr, and (C) P(O2)=5E-7 Torr. All films show a strong 2.9 eV emission.

Figure 35a shows the normalized DRCLS spectra for the 20 nm film grown without externally supplied oxygen. We see a clear transition from the film spectra to the substrate spectra at 2 kV. Deconvolving the spectra and plotting the center of the NBE peak versus beam energy we see a clear transition from a NBE of 3.1 eV in the film to 3.2 eV NBE in the substrate, Figure 35b. Plotting the integrated area of the 2.55 eV and 2.95 eV emissions versus beam energy we see that they both have the same areas through the film and into the substrate Figure 35c.
Figure 35: DRCLS spectra from a 20 nm thick BST film grown without externally supplied oxygen by feeding of atomic oxygen from the substrate. (a) Spectra normalized to the NBE. (b) NBE peak position as a function of beam energy. (c) The integrated area of the 2.55 eV and 2.95 eV emissions versus beam energy.
5.3 Discussion

Figure 33 shows the wide angle XRD scans of the 100 nm thick films. We can see well defined diffraction peaks for the (001), (002), (003), and (004) reflections from both the substrates and the film. We do not see any evidence of other reflection which would indicate the presence of secondary phases. From the lattice parameters listed in table 1, we see that all films show a significant tetragonal distortion being nearly perfectly strained to the substrate in-plane lattice parameter (3.905Å) and the unit cell volume of the BST being conserved to within 1%. The 100 nm films’ XRD patterns had well defined Laue oscillations in both the (002) and (101) reflections indicating sharp interfaces and a high degree of uniformity.

All films grown with a P(O2) less than 5E-7 Torr were blue/black in appearance, and with this in mind, it is no surprise that the dominant feature in these films is the 2.95eV blue band emission. Recently, the 2.95eV blue luminescence has attracted a lot of attention and has been reported for Ar+ irradiated and n-type doped SrTiO$_3$.\textsuperscript{66,67} Owing to the similarity in band structure of BST and STO one would expect a similar mechanism for 2.95eV emission in BST, and the effect of a reducing growth environment on our DRCLS spectra supports this. In the case of BST, the oxygen vacancies form a state just below the conduction band edge while doping two electrons per vacancy into the conduction band. Excitation of electrons from the valence band into the conduction band by the high energy DRCLS electron beam leaves holes in the valence band which
pair to electrons thermalized into the in-gap state created by the $V_o$. Subsequent radiative recombination of the electron-hole pair produces the 2.95eV emission.

Plotting the 2.95eV emission intensity normalized to the beam energy as a function of depth for the 100 nm films, Figure 36, we see at high beam energies the intensity of the 2.95 eV emission increases with decreasing P(O2). We also see that the intensity is low at the free surface and rapidly rises and levels off past 1kV. The low intensity at the free surface could be due to surface adsorbates creating pathways for non-radiative recombination, but is most likely due to oxidation of the surface layers from exposure to air. That the intensity past the free surface is uniform through the surface and into the substrate indicates a redistribution of $V_o$ between the film and substrate. This redistribution is not surprising given the high mobility of $V_o$ in STO.
Figure 36: 2.95eV emission VS depth for the films grown at P(O2) equal to 3E-8 Torr, 1E-7 Torr, and 5E-7 Torr.

It has been previously demonstrated that it is possible to grow BTO-STO superlattices and BTO-STO heterojunctions without an external source of oxygen via the feeding of atomic oxygen from the substrate, and in order to push the reducing conditions to the limit and see what DRCLS features resulted, we grew 20 nm’s of BST without introducing any oxygen into the reactor chamber. We transferred one of these BST samples through UHV from the growth chamber into an x-ray photoemission spectroscopy system via the transfer system described in chapter 4 and determined that the oxygen content at the surface and through the depth of the film, determined by an Ar+ bombardment depth profile, was nearly stoichiometric. The concentration of oxygen at the surface shows the oxygen in the film out diffused from the substrate rather than in
from the free surface from air exposure. Figure 37 shows the atomic concentrations versus sputter time for the BST sample grown without oxygen.

Looking at Figure 37, the first thing that is evident is an excess of Ba at the free surface. From the 2X pattern visible in the RHEED images of this BST sample it was evident that there was an A-site excess and the uptick of the Ba atomic concentration confirms that it is an excess of Ba. Under typical deposition conditions with P(O2)≠0, an A-site excess would be incorporated into the lattice as a Ruddlesden-Popper phase\textsuperscript{70,71,72}, but here, with P(O2)=0, we see evidence of an A-site excess forming a Ba rich overlayer. Since the Ba\textsuperscript{2+} ions are \textasciitilde22\% bigger than Sr\textsuperscript{2+} ions and the film is perfectly strained to the substrate, the energetics for the segregation of Ba atoms to the surface could be satisfied solely through strain if there were an excess of A-site atoms being deposited.\textsuperscript{73} If however the atomic source flux was stoichiometric, the surface segregation of Ba ions in this extremely reduced film could be evidence of cation vacancies forming to compensate for the excessive oxygen vacancies to form a Schottky like defect with the Ba again being the cation of choice due to its larger radius and the strain in the film.
Figure 37: XPS measurements of the 20nm film grown without an externally supplied source of oxygen show a nearly 60% concentration of oxygen at the surface. The film was transferred from the growth chamber to the XPS chamber through UHV.

The DRCLS measurements from the films grown at P(O2)’s less than 5E-7 Torr show features at 1.9eV and 2.55eV as well. The reducing growth conditions producing a 2.55 eV DRCLS emission is expected and in good agreement with previous reports of an oxygen vacancy to valence band transition with an emission of 2.6 eV. The 1.9 eV emission feature, however slight, is still a significant feature in the highly reduced BST samples.

Previous DRCLS measurements by Chen et al. on Ba0.6Sr0.4TiO3 show features at 1.9 eV, 2.1 eV and 2.3 eV and citing similar results from BTO samples, the authors have attributed them to oxygen and cation vacancies. Figure 38 shows the defect levels in BTO assigned by Koschek and Kubalek. A 1.8 eV feature in particular has been
attributed to a transition of an electron in the conduction band to doubly ionized Ba vacancy 1.2 eV above the valence band. Extending this model to BST we can generalize this transition to doubly ionized A-site vacancies.

Considering the position in the band gap of these two transitions and their possible relation to the singly and doubly ionized A-site vacancies, there are two possible explanations as to why the 1.9 eV transition would be observed in the highly reduced samples and not the 2.1 eV and 2.3 eV transitions. The first explanation is that the 2.1 eV and 2.3 eV features involve a transition into the state 0.6 eV above the valence band, and at low temperatures, electrons doped into the system by Vo’s would fill this state leaving transitions into it unlikely. The second would be that any A-site vacancies present would be doubly ionized due to the extra electrons from the oxygen vacancies causing that defect level to move higher in the gap.

Whether electrons from Vo’s are filling the state 0.6 eV above the valence band or electrons are localizing on the site changing it from a singly to doubly ionized vacancy remains unclear, but that these electrons are preventing transitions into this state is apparent. Hence, the 2.1 eV and 2.3 eV emissions are absent in the reduced BST.
Chen et al. also report an indirect near band emission at 3.07 eV and another transition at 3.50 eV for which two possible mechanisms were proposed. The first developed by Capizzi and Frova claims that this transition results from the direct transition at the $X$ point.\textsuperscript{76} The second proposed by Redfield and Burke says that this feature is due to the saturation of the phonon assisted indirect transition.\textsuperscript{77} While Chen et al. were inclined to agree with the process proposed by Redfield and Burke based on their observation of the 3.50 eV feature only existing as a shoulder to the 3.07 eV feature, we see the 3.6 eV feature as a well defined feature in the film grown at 5E-7 Torr suggesting
it is a separate, high energy, transition. We also see evidence of another high energy transition at 4.2eV.

The 4.2eV feature we see has an energy larger than either the direct or indirect transitions between valence and conduction bands. Bentham et al. report a transition energy of 4.2eV for the interband transition between the upper O 2p level and lower Ti 3d t2g level in STO. Using higher electron beam excitation energies (~kV), it is possible to access these higher energy transitions. We see that the film grown with P(O2)=5E-7 Torr shows a well defined 4.2 eV feature while films grown at lower pressures have a slight shoulder that has been shifted to lower energy by about 0.2 eV. This is not surprising since the films grown at lower P(O2) should have a larger concentration of V_o’s and thus a larger number of recombination pathways through them thus lowering the number of interband transitions.

5.4 Conclusions

Several samples of highly reduced BST were grown by MBE on STO substrates in a 200 W oxygen plasma with varying P(O2)’s. The resulting films were phase pure and showed a large degree of tetragonal distortion.

DRCLS analysis shows that the dominant spectral features in highly reduced BST are at 1.9 eV, 2.55 eV, and 2.95 eV. The 2.9 eV transition is attributed to the recombination of an electron localized on a V_o state just below the conduction band with a hole from the valence band. The 2.55 eV transition is due to clustering of V_o’s while
the 1.9 eV emission is due to the transition of electrons from the conduction band to doubly ionized a-site vacancies just above the valence band. The DRCLS data indicates that films grow at P(O2)’s less than 5E-7 Torr in a 200 W oxygen plasma are all highly reduced and reduce the substrate as well.

The ability of oxygen vacancies to migrate from the film into the substrate allowing oxygen to escape is evident from the growth of BST without an external supply of oxygen. By transferring through a UHV transfer line into an XPS analysis chamber, we have confirmed the substrate as the source of oxygen for the grown film. Subsequent DRCLS measurements of a similar sample have shown DRCLS features identical to the highly reduced films.

At P(O2)=5E-7 Torr the film became clear in appearance with a significant decrease in the 2.9 eV DRCLS emission intensity. We see a dramatic shift in the spectra from the 2.9 eV blue band luminescence to the 1.9 eV-2.1 eV-2.3 eV green band luminescence. These defects are reported to be related to oxygen and cation vacancies. It is believed that by incorporating more oxygen into the film the number of doped electrons decreases which depopulates the state at 0.6 eV above the valence band allowing transitions into that state. Since both the 2.1 eV and 2.3 eV features result from transitions through this state, depopulation results in a significant increase in the intensities of these features at the higher growth pressure.
Chapter 6: MBE Growth and DRCLS Characterization of High Quality Sr\(_{(1-x)}\text{TiO}_{(3-\delta)}\)

6.1 Introduction:

In the last chapter we saw how it was possible to grow high quality BST films by feeding atomic oxygen from the substrate, and how the DRCLS spectra from reduced BST and the STO substrate was composed of the 1.9 eV, 2.55 eV and 2.95 eV features, but it is unclear how small changes in the stoichiometry would affect these features.

In this study we show how RHEED, DRCLS, and XRD are used to assess film quality and how stoichiometry influences the DRCLS spectra. We see RHEED patterns change as a function of stoichiometry from broad streaks with little secondary diffraction for films grown with a severe Sr deficiency to sharp steaks with intense secondary diffraction lines for films grown near stoichiometry. Furthermore, we see half order peaks along the [100] and [210] azimuths for films grown with a Sr deficiency. We also show an excess Sr can behave as an acceptor and depopulate the state 0.6 eV above the valence band allowing the 2.1 eV and 2.3 eV DRCLS transitions and how DRCLS is a sensitive indicator of stoichiometry.
6.2 Experiment/Results

20 nm’s of Sr\((1-x)\)TiO\((3-\delta)\) was deposited on TiO\(_2\) terminated STO(100) treated with the standard aqua regia etch by molecular beam epitaxy using a VEECO Gen 930 system. The source flux was calibrated using the standard method of QCM calibration followed by RHEED oscillation calibration. The RHEED oscillation calibrations were performed without oxygen. Once the shutter times were determined from the RHEED oscillations the Ti shutter time was fixed to 18.66 s and the Sr shutter time was varied to grow films both Sr deficient and Sr rich with \(T_{Sr}/T_{Ti}\) ranging from 1.5 to 2.3. The substrate temperature was 800 °C and no oxygen was supplied. After growth, images of the RHEED diffraction patterns were captured and are shown in Figure 39. The RHEED diffraction patterns are streaky indicating a 2-dimensional surface with strong Kikuchi lines in several films indicating a high degree of crystallinity.

HRXRD measurements of the (002) reflections shown in Figure 40 reveal a well defined film peak at extreme Sr deficiency while it develops into a low angle shoulder on the substrate peak as stoichiometry is approached. At \(T_{Sr}/T_{Ti}=2.2\) the film peak is observed as broad peak superimposed on the substrate peak with thickness fringes present. Increasing \(T_{Sr}/T_{Ti}\) to 2.3 resulted in the film peak moving to lower angles and the thickness fringes disappearing.
Figure 39: RHEED patterns showing the progression from Sr deficient to Sr rich. (Continued)
Figure 39 Continued: RHEED patterns showing progression from Sr deficient to Sr rich.
Figure 40: XRD of the (002) reflection showing the progression from Sr deficient to Sr rich.

DRCLS measurements were performed at 80 K in UHV with a constant 2 μA emission current while the beam energy was increased from 0.5 kV to 5 kV in 0.5 kV
Monte Carlo simulations yield maximum excitation depths of ~20, 54, 97, 149 and 211 nm for electron beam energies of 1, 2, 3, 4, and 5 kV, respectively. The normalized DRCLS spectra are shown in Figure 41 and we see several features at 1.9 eV, 2.1 eV, 2.3 eV, 2.55 eV, 2.95 eV, and 3.2 eV. Spectra could be obtained at 0.5 kV beam energy only for the films with T_{Sr}/T_{Ti} = 2.1, 2.2, and 2.3 but increasing the beam energy allowed DRCLS spectra to be obtained from the other films. Due to the low intensity of the spectra and to increase the signal to noise ratio of the spectra taken at 0.5 kV and 0.75 kV, several measurements 2 seconds in duration averaged for 2 scans were averaged together with long pauses between them. Figure 42 shows the normalized DRCLS spectra taken by averaging several short duration scans with pauses between them and taken using a single long duration scan. We see that the 3.23 eV NBE is dramatically reduced from the electron beam exposure while all other features remain constant.
Figure 41: DRCLS spectra from the STO films.
6.3 Discussion

In the last chapter it was shown that BST films can be grown on STO substrates by atomic feeding of oxygen from the substrate. Our oxygen supply is controlled through a mechanical leak valve that is extremely unreliable at delivering precise pressures of oxygen, and we will see in the next chapter how the films’ composition is sensitive to oxygen background pressure. Thus, the reducing environment with no externally supplied oxygen was chosen for consistency between films.

RHEED images from along the [100], [110], and [210] azimuths are shown in Figure 39. We can see that the films with a large Sr deficiency have RHEED patterns with broad streaks and almost no secondary diffraction lines. As the Sr concentration in the films increase there is an apparent sharpening of the RHEED streaks and the secondary diffraction lines begin to emerge. In the Sr deficient films we can see strong half order streaks in the [100] and [210] directions and we see these peaks disappear in the Sr rich film where $T_{Sr}/T_{Ti}=2.3$ which is consistent with what we saw in the last chapter with the film with a Ba excess at the surface displaying half order peaks in the [110] direction.

The XRD results from these films, shown in Figure 40, is consistent with previous studies showing an expanding lattice constant for both Sr deficient and Sr rich films. It was shown in these studies that the XRD peak position is a sensitive indicator of film stoichiometry. Starting with a Sr deficient film which has a well defined and separated film peak from the substrate peak and increasing the Sr deposition time
cause the film peak to approach the substrate peak until $T_{Sr}/T_{Ti}=2.2$ when the film and substrate lattice parameters are the same. At $T_{Sr}/T_{Ti}=2.3$ there is clear separation of the film and substrate peaks once again indicating an excess of Sr in the film. However, there is an expansion in the lattice parameter between $T_{Sr}/T_{Ti}=2.0$ and $T_{Sr}/T_{Ti}=2.1$ which we believe is due to an instability in the Sr flux.

Figure 41 shows DRCLS spectra from these films. All spectra with $T_{Sr}/T_{Ti}<1.9$ are qualitatively similar to what is shown for $T_{Sr}/T_{Ti}=1.9$ and are not shown. DRCLS results from the near surface, Figure 41a, of the $T_{Sr}/T_{Ti} = 2.1, 2.2$ and $2.3$ are the most dramatic showing a very intense NBE at $3.23$ eV for the $T_{Sr}/T_{Ti} = 2.2$ film. This film shows very narrow streaks with intense secondary diffraction in its RHEED pattern and a lattice constant that is nearly identical to that of the substrate from the XRD measurement. In terms of the RHEED characteristics, XRD peak position, and NBE intensity from DRCLS, the film with $T_{Sr}/T_{Ti}=2.2$ is the highest quality film in the series. This result demonstrates the power of these tools to assess film quality and stoichiometry.

As we probe with higher energies further into the film we see that the Sr rich films have large defect emissions at $1.9$ eV, $2.1$ eV, $2.3$ eV, and $2.95$ eV while the Sr deficient films show transitions only at $1.9$ eV, $2.55$ eV, and $2.95$ eV. According to Koshek and Kubalek the $2.1$ eV and $2.3$ eV transitions both involve a singly ionized A-site vacancy $0.6$ eV above the valence band. In the case of Sr deficient films all Sr vacancies would be doubly ionized as a result of the reducing conditions used during growth, and thus the singly ionized vacancy state would not exist. As the Sr content in the film is increased, the $Sr^{2+}$ may begin to substitute on the $Ti^{4+}$ site compensating for
electrons doped into the system by oxygen vacancies opening the singly ionized state and allowing the 2.1 eV and 2.3 eV transitions.

Finally we see a strong decrease in the NBE intensity when exposed to the electron beam for long periods of time (>4s). However, we also see that this is not permanent damage and by allowing the material to rest between shorter data acquisition cycles, and averaging several of those shorter cycles, we can increase the signal to noise ratio and still have an intense NBE emission. The mechanism behind the decrease in NBE intensity is unclear and it appears to be the only transition affected by exposure to the electron beam. We show in Figure 42 a set of averaged, short duration scans with a pronounced NBE emission and a single long duration scan with a low intensity NBE peak. The short duration scan has been multiplied by 5 to adjust for the different accumulation times in each experiment, but once adjusted, the defect peaks are nearly identical in intensity with only the 3.23 eV NBE emission being affected.
6.4 Conclusions

We see that the RHEED pattern characteristics, DRCLS NBE emission intensity, and XRD peak position are all sensitive indicators of film quality of STO films. The RHEED patterns for Sr deficient films is streaky indicating a 2-dimensional surface but are very diffuse, lacking Kikuchi lines, and have strong half order lines in the [100] and [210] directions. As the films approached a stoichiometric concentration of Sr, the diffraction lines sharpened, the Kikuchi lines became well defined and intense, and the half order lines disappeared.
The XRD $\omega$-20 scans showed a systematic progression of the (002) film peak position that indicated an expanded c-axis parameter for films grown Sr deficient and Sr rich. This is consistent with other work regarding MBE growth of STO films. However, thickness fringes were present in the stoichiometric film with a broad film peak superimposed over the narrow substrate peak which indicates a film with the same lattice parameter as the substrate but fundamentally different from the substrate, possibly due to a deficiency in Ti, but this remains unclear.

DRCLS measurements showed several features that increased or decreased in intensity depending on whether the film was grown Sr deficient or rich. The film grown with a stoichiometric composition of Sr had a very intense NBE at the very surface of the film. The intensity of the NBE was found to dramatically decrease with prolonged exposure to the electron beam but that this change was reversible by letting the sample rest between short intervals of exposure. The Sr deficient films showed transitions at 1.9 eV, 2.55 eV, and 2.95 eV which is consistent with reduced STO while the film grown Sr rich showed an additional features at 2.1 eV and 2.3 eV and a reduced intensity of the 2.95 eV feature. It is believed that the additional Sr can act as an acceptor depopulating the state 0.6 eV above the valence band and allowing transitions into and out of this state.
Chapter 7: Native Point Defects and Correlation with Growth Parameters of Barium Strontium Titanate

7.1 Introduction

Barium strontium titanate is an attractive material for RF components due to its low dielectric loss, large permittivity, and high tunability. However, the native point defects that we have seen in our films can have a significant impact on these material properties. It is well known that oxygen vacancies, $V_{o}$, are responsible for n-type conductivity observed in STO and is known to cause the same behavior in BST which leads to conduction loss and break down in electronic devices. In BST a deficiency in either Ba or Sr can be a accommodated through vacancies while an excess is either incorporated either as extra layers of SrO and BaO leading to the formation of Ruddlesden-Popper (RP) phases, or can be substituted on the B-site. It has been previously reported that formation of RP phases causes a decrease in the dielectric constant. The first 5 members of the homologous series of $\text{Sr}_n \text{Ti}_n \text{O}_{3n+1}$ were grown by MBE and it was reported that the dielectric constant of the material was a minimum for the $n=1$ film ($\text{Sr}_2 \text{TiO}_4$) and a maximum for the $n=\infty$ film ($\text{SrTiO}_3$) without additional SrO layers.
As we have seen, the positions and densities of native point defects are complicated by their mobility and the need for charge neutrality leading to compensating defects. The mobility of oxygen vacancies under an externally applied electric field plays a leading role in devices such as memristors made from TiO$_2$\textsuperscript{87}, and it is well known that oxygen vacancies are highly mobile in both STO\textsuperscript{88} and BST\textsuperscript{89}. The movement of these defects at growth temperatures can lead to the generation of defects deep within the substrate material, which in turn can lead to significant dielectric loss due to fringe fields at RF frequencies penetrating the various layers of the capacitor-film-substrate structure. DRCLS provides a unique approach to measuring the positions of these defects within the film and into the substrate.

In this chapter we correlate the growth conditions of as-grown BST thin films with the native point defects and dielectric properties. X-ray photoemission spectroscopy measurements revealed the A-site composition that is sensitive to the P(O2) and we see a strong correlation between the tunability of the material with the A-site composition indicating a direct link between the growth process and the dielectric properties of the material. Native point defect concentrations of the BST films were measured using depth resolved cathodoluminescence spectroscopy (DRCLS) and we see again the 1.9 eV and 2.95 eV defects have a strong dependence on the P(O2) used during growth. The 2.3 eV emission intensity had a more complicated dependence on the substrate temperature and oxygen pressure. Interdigitated capacitors (IDC) were then deposited on the as grown material, and from measurements of the quality (Q=1/Tan(δ)) and tunability, we see that Q increases significantly as the 2.3 eV emission rises at the BST-STO interface and the
tunability increases as the 1.9eV emission intensity decreases. By controlling the growth process and using a combination of in-situ XPS, DRCLS, and conformal mapping techniques applied to IDC devices, we show how native point defects depend on the growth parameters and how these defects affect device performance. This work suggests a route for engineering material properties to suit specific applications through an appropriate choice of growth parameters.

7.2 Growth and Analysis

100nm Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) thin films were grown in a VEECO Gen 930 molecular beam epitaxy system by alternate deposition of Sr and Ba, and Ti base metals. BST was deposited onto TiO$_2$-terminated STO(100) substrates treated with the standard aqua regia etch.$^{90,91}$ The source flux was calibrated using a quartz crystal microbalance (QCM) and then by measuring in situ reflection high energy electron diffraction (RHEED) oscillations from a calibration sample grown in a 200 W, 5E-7 Torr oxygen plasma atmosphere at 800°C substrate temperature. Five films were then grown using the shutter times from the calibration sample in a 200 W oxygen plasma at nominal P(O2)’s and substrate temperatures of 3E-7 Torr at 800 °C, 5E-7Torr at 800 °C, 1E-6 Torr at 800 °C, 1E-6 Torr at 700 °C, and 1E-6Torr at 900 °C. RHEED patterns along the [100], [110], and [210] azimuths were sharp streaks indicating two-dimensional growth and an ordered BST epitaxial film.
Large angle x-ray diffraction measurements show our films to be single crystal, phase-pure BST. High resolution x-ray diffraction measurements of the (002) and (101) reflections show strong Laue oscillations for the film grown at the calibration sample parameters with their intensity diminishing as the growth parameters are changed. From the HRXRD we were able to determine the c and a-axis parameters, listed in table 3. The films show a significant tetragonal distortion with all but one being strained to the substrate in-plane lattice parameter. The film grown at high oxygen pressure and low substrate temperature was nearly relaxed.

<table>
<thead>
<tr>
<th>Film</th>
<th>c (Å)</th>
<th>a (Å)</th>
<th>Ba (%)</th>
<th>Sr (%)</th>
<th>Ti (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3E-7Torr, 800°C</td>
<td>4.0282</td>
<td>3.9178</td>
<td>7.5</td>
<td>9.7</td>
<td>21.5</td>
<td>61.4</td>
</tr>
<tr>
<td>5E-7Torr, 800°C</td>
<td>4.0403</td>
<td>3.9129</td>
<td>8.3</td>
<td>9.3</td>
<td>21.4</td>
<td>61</td>
</tr>
<tr>
<td>1E-6Torr, 800°C</td>
<td>4.0535</td>
<td>3.9177</td>
<td>8.1</td>
<td>7.9</td>
<td>21.6</td>
<td>62.3</td>
</tr>
<tr>
<td>1E-6Torr, 700°C</td>
<td>3.9953</td>
<td>3.9774</td>
<td>8.8</td>
<td>8</td>
<td>22.2</td>
<td>61.1</td>
</tr>
<tr>
<td>1E-6Torr, 900°C</td>
<td>4.0722</td>
<td>3.9087</td>
<td>9.6</td>
<td>7.9</td>
<td>23.2</td>
<td>59.2</td>
</tr>
</tbody>
</table>

Table 3: Film lattice parameters and atomic compositions.

After growth, samples were transferred without air exposure through ultra high vacuum to a PHI Versaprobe x-ray photoemission (XPS) analysis chamber with a monochromatic Al Kα source (hν= 1486.6 eV), pass energy of 23.5 eV and an energy resolution of 0.48 eV. Calibrated intensities of the Ba 3d_{5/2}, Sr 3d, Ti 2p, O 1s yielded surface and subsurface atomic compositions. The absence of C1s emission confirmed the quality if the UHV environment. Spectra to determine the atomic concentrations of the films were acquired with the sample surfaces tilted 90° relative to the analyzer, which has a 40° total angle of acceptance that minimizes any photoemission diffraction effects.
Sample surface charging was minimized using an electron neutralization flood gun at 20 μA emission current and a low energy (≈ 10 eV) Ar\(^+\) ion beam. The atomic concentrations determined from XPS measurements are listed in Table 3.

To probe electrically active defects in the material we used depth resolved cathodoluminescence spectroscopy (DRCLS). The measurements were performed at 80 K in UHV with a constant 2 μA emission current while the beam energy was increased from 0.5 kV to 5 kV in 0.5 kV steps. Monte Carlo simulations\(^{92}\) yield maximum excitation depths (\(U_0\)) of ~20, 45, 75, 115 and 170 nm for electron beam energies of 1, 2, 3, 4, and 5 kV, respectively.

Figure 43 shows DRCLS spectra representing the film (1 kV), interface (3 kV), and substrate (5 kV). These measurements revealed several defect states within the bandgap of the material at 1.9 eV, 2.1 eV, 2.3 eV, 2.55 eV and 2.95 eV whose intensities differ significantly in the film, at the film-substrate interface, and in the substrate. The energies of these features do not change significantly in the film versus the substrate.
Figure 43: DRCLS spectra representative of the (a) film, (b) the interface, and (c) the substrate vs. P(O2). The pronounced 2.95 eV feature attributed to oxygen vacancies increases from BST surface (a) to STO bulk (c) and decreases with increasing oxygen pressure. The 1.9 eV feature attributed to BST A-site vacancies in (a) decreases with increasing oxygen pressure along with the 2.1 and 2.3 eV oxygen vacancy-related features. This A-site feature also decreases with proximity to the substrates in (b) and (c).
IDC structures were then patterned on the surface of the film for microwave characterization. The measurements were performed as a function of frequency from 1-20 GHz and DC bias from -40 to 40 V. Values are reported from measurements at 10 GHz and shown in table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tuning (%)</th>
<th>( \varepsilon ) at 0V</th>
<th>Q at 0V</th>
</tr>
</thead>
<tbody>
<tr>
<td>3E-7Torr, 800°C</td>
<td>9.73</td>
<td>2878.3</td>
<td>1.50</td>
</tr>
<tr>
<td>5E-7Torr, 800°C</td>
<td>5.05</td>
<td>2931.5</td>
<td>7.35</td>
</tr>
<tr>
<td>1E-6Torr, 800°C</td>
<td>3.93</td>
<td>3724.7</td>
<td>6.77</td>
</tr>
<tr>
<td>1E-6Torr, 700°C</td>
<td>2.33</td>
<td>3762.0</td>
<td>7.77</td>
</tr>
<tr>
<td>1E-6Torr, 900°C</td>
<td>1.73</td>
<td>3488.7</td>
<td>5.70</td>
</tr>
</tbody>
</table>

Table 4: Dielectric properties measured at 10 GHz.

7.3 Discussion

Figure 44 shows the A-A’ site occupancy versus the measured P(O2). We can see that while the shutter times remained constant for all films, the Ba to Sr ratio increases with an increasing oxygen pressure. It is has been shown in high energy deposition techniques such as PLD\(^{93}\) and sputtering\(^{94}\) that film stoichiometry can be controlled by the background pressures. Here we show that the stoichiometry, given fixed atomic flux and deposition times, can be controlled in MBE by varying the background growth pressure. In PLD and sputtering the higher oxygen growth pressure causes gas scattering which is the dominant process affecting the stoichiometry, but the low growth pressure of MBE leaves this an unlikely mechanism. More likely the change in stoichiometry is the result of desorption of underoxidized Ba.
Figure 44: (a) XPS Ba:Sr ratio vs. P(O2) and (b) corresponding RF tunability. Increasing oxygen pressure increases Ba:Sr ratio from <0.8 to >1.2 and decreases corresponding tunability from >9% to <2%.

This change in Ba/Sr composition should have a well known effect on the material properties. At room temperature, BaTiO₃ is ferroelectric while SrTiO₃ is paraelectric and by changing the Ba to Sr ratio in BaₓSr₁₋ₓTiO₃ one can modify the Curie temperature.⁹⁵ Thus, increasing the P(O2), and the associated increase in Ba relative to Sr, should move the Curie temperature towards room temperature, which in turn should lead to an increase in the tunability of the material, but this is not what we see. We see a decrease in the tunability of the material as the Ba to Sr ratio increases, Figure 44b, and believe this to be due to material defects. In particular, we see a negative correlation between the 1.9 eV emission intensity and the tunability of the material, Figure 47a.

The electronic structure of BST is very similar to that of BaTiO₃ with the conduction bands composed of empty Ti 3d orbitals and the valence bands composed of filled O 2p orbitals. It is logical to believe the electrically active defects probed by DRCLS would be similar as well and has been shown by Chen et. al.⁹⁶ The defect
structure of BTO has been studied theoretically\textsuperscript{97} and experimentally\textsuperscript{98,99,100} in detail with the 1.9 eV, 2.1 eV, 2.3 eV, and 2.6 eV defects being assigned to \( \text{CB} \rightarrow V_{\text{Ba}^-} \), \( V_{\text{O}^+} \rightarrow V_{\text{Ba}^-} \), \( \text{C} \rightarrow V_{\text{Ba}^-} \), and \( V_{\text{O}^+} \rightarrow \text{VB} \) transitions respectively where CB represents the conduction band and VB represents the valence band. The charged barium vacancies can be generalized to A-site vacancies for BST\textsuperscript{101}, and the 2.95 eV emission has been observed in electron doped and Ar\textsuperscript{+} irradiated STO and is thought to be the result of oxygen vacancies\textsuperscript{102}.

With this in mind and looking again at Figure 43, we see a clear progression in the line shapes from the film to the substrate with the 1.9, 2.1, and 2.3 eV defects dominating in the film and the 2.95 eV defect dominating in the substrate. That we see a significant drop in the 1.9 eV, 2.1 eV, and 2.3 eV emissions compared to the 2.95 eV emission as we probe into the substrate is not surprising. The 1.9 eV, 2.1 eV and 2.3 eV defects are related to A-site vacancies which have a very small mobility through the lattice at the temperatures used for growth which would effectively confine them to the film.\textsuperscript{103} The 2.95 eV emission, however, is related to oxygen vacancies which are compensated for by the ionized A-site vacancies leading to a significant decrease in the 2.95 eV emission in the film. The concentration of A-site vacancies in the substrate however is not large enough to compensate for the oxygen vacancies leading to a much larger 2.95 eV intensity. The 2.95 eV emission from the substrate is further enhanced in films grown at low P(O2)’s by out-diffusion of oxygen from the substrate into the film.

Figure 45a shows the dramatic increase of the 2.95 eV emission in the substrate for films grown under low P(O2)’s, and this is likely due to the high mobility of oxygen.
vacancies through the lattice at the growth temperatures. Looking at the 2.95 eV intensity at the maximum depth, 70 nm into the substrate, there is a drop in the intensity with increasing P(O2), Figure 45b. There have been several studies indicating that the amount of oxygen that can diffuse out of the substrate is sufficient to grow BTO and STO overlayers on STO substrates without an externally supplied source of oxygen\textsuperscript{104,105} and this same mechanism of oxidation could be responsible for the formation of BST at the extremely low P(O2) used for our films grown at 3E-7 and 5E-7 Torr which is confirmed by the increase in the $V_o$ related defects in the substrate for these two films.

![Figure 45](image)

(a) The 2.95 eV emission intensity versus electron beam energy increasing with increasing excitation depth into the STO substrate. (b) As P(O2) increases the 2.95 eV substrate emission at $E_B = 5$ keV decreases.

The 1.9 eV and 2.3 eV emissions have been assigned as transitions from the conduction band to the doubly ionized A-site vacancy and singly ionized A-site vacancy respectively. In Figure 46 we plot the average intensity of these defects through the film and see that they both have a power law dependence on P(O2). The 1.9 eV intensity
shows a much stronger dependence on the P(O2) than the 2.3eV intensity indicating the
generation of the doubly ionized Ba vacancy is preferred in this pressure range. It has
been reported that the A-site vacancy concentration increases with increasing P(O2) in
sintered pellets of BTO\textsuperscript{7} and our DRCLS measurements confirm this in thin films.

Figure 46: Intensities of the 1.9 eV and 2.3 eV defects increase as the P(O2) increases.

Comparing the defect emission in the DRCLS spectra to the dielectric properties
of the materials revealed a correlation between the 1.9eV defect emission and the
tunability of the material leading us to believe decrease in tunability is related to material
defects. Figure 47a shows a strong decrease in the tunability of the material with an
increasing 1.9 eV emission intensity with the tunability dropping an order of magnitude
for a doubling of the 1.9 eV emission intensity. The 1.9 eV emission feature is believed
to be related to the doubly ionized A-site vacancy. Thus, the total concentration of A-site
vacancies has a larger influence on the tunability of the material than the Ba/Sr
composition.
Figure 47: We see strong correlations between the defects and dielectric properties of the materials. (a) The tunability drops off as the 1.9 eV defect intensity increases and (b) a rapid increase in the $Q$ of the material with an increase in the 2.3 eV emission near and at the interface.

We also see a rapid increase in the quality factor, $Q=1/\tan(\delta)$, with the intensity of the 2.3 eV emission intensity near the interface. Figure 47b shows the 2.3 eV emission intensity for the 2.0 kV, 2.5 kV and 3.0 kV beam energies versus $Q$. The 2.3 eV emission involves a transition from the conduction band into a singly ionized A-site vacancy, 0.6 eV above the valence band, which is the lowest electrically active defect level in the band gap. Films grown with less than optimal oxygen form oxygen vacancies donating electron to the system, and at the cooler temperatures used to perform DRCLS, these electrons may localize on the A-site vacancy site filling these states, preventing subsequent transition into them. So, that we see an increase in the quality factor of the films with an increase in the intensity of this defect may indicate an overall lower free carrier concentration in the film.
By using a layer-by-layer growth of BST with fixed shutter times and controlling the P(O2), one can change the A-site vacancy content and the A-site atomic composition of the film. At typical growth temperatures the mobility of these vacancies is limited, effectively freezing them into the overlying film. Due to the mobility of the oxygen vacancy, however, the change in P(O2) will lead to significant changes in the oxygen vacancy content extending beyond the film and well into the substrate.

Using DRCLS we are able to detect these defects and determine their relative concentrations as a function of depth within the material. We were then able to correlate specific defects with both the growth parameters and the dielectric properties. We see a high concentration of A-site vacancies in the film while we see a large concentration of oxygen vacancies in the substrate. Comparing the 1.9 eV and 2.3 eV defects to the dielectric properties of the as-grown films, we see that the tunability of the material decreases with increasing 1.9 eV intensity while Q increases rapidly with increasing 2.3 eV emission intensity. These results demonstrate the first order effect of defects on dielectric properties of complex oxide heterojunctions and the ability to control them by MBE growth conditions.
Chapter 8: Conclusions and Future Work

8.1 Conclusions

During this work we have developed a growth method for growing high quality BST thin films by molecular beam epitaxy for analyzing the electronic and structural properties of the material, and for understanding the nature of defects related to these structural properties. Beginning with commercially supplied STO(100) substrates and using the standard aqua regia etch, we were able to produce substrates with an atomically flat, TiO₂ termination layer necessary for growth. This step dramatically improved our ability to calibrate the atomic flux via reflection high energy electron diffraction intensity oscillations. With the substrates properly terminated and the source flux properly calibrated we were able to grow high quality Ba₀.₅Sr₀.₅TiO₃ films under a variety of conditions.

In order to analyze pristine sample surfaces with our x-ray photoemission spectroscopy system, we developed a novel method of ultrahigh vacuum transfer. This required the design of platens compatible with our MBE and XPS stages and a sample coupon that could be transferred between them in UHV. Utilizing this transfer system, we showed the effects of air exposure to BST films and were able to see the
undercoordinated Ba 3d\textsubscript{5/2} component without the need for UHV fracturing of the sample. This system also allowed us to demonstrate the atomic feeding of oxygen from the substrate into films grown without an external supply of oxygen. If we would have been forced to transfer these samples through the air this result would have been questioned, and whether the oxygen came from the substrate or was a result of oxidation due to air exposure would not have been certain.

Once we were able to produce high quality BST films, we proceeded to study the effects of the background oxygen pressure on the films’ defects probed by depth resolved cathodoluminescence spectroscopy. We saw that in severely reduced samples the 1.9 eV, 2.55 eV and 2.95 eV transitions were the only features represented in the spectra with the 2.55 eV and 2.95 eV being the most intense emissions. It is believed that the 2.55 eV and 2.95 eV features are related to oxygen vacancies. Knowing this we were able to confirm that oxygen was migrating from the substrate and into the film using DRCLS. We show that the 2.55 eV and 2.95 eV emission profiles from several films grown at low or no oxygen pressure had very intense emissions at these energies and the intensity increased as the beam voltage was increased to probe below the interface, into the substrate. We also showed that the intensity of the 2.95 eV emission dramatically decreases with increasing oxygen pressure.

It has been previously reported that the 1.9 eV feature is related to a doubly ionized A-site vacancy, and while it is beyond the scope of this work to confirm or deny the origin of this feature, a simple model relying on this defect state (1.2 eV above the valence band edge) and another, the singly ionized A-site vacancy (0.6 eV above the
valence band edge), is proposed to explain the behavior of our DRCLS features from a variety of growth conditions.

It is believed that electrons donated from oxygen vacancies populate the singly ionized A-site vacancy state preventing transitions into it. According to the defect model proposed by Koschek and Kubalek, the 2.1 eV and 2.3 eV features result from transitions from the oxygen vacancy and conduction band to the singly ionized A-site vacancy respectively. Therefore, filling the singly ionized A-site vacancy state would prevent these transitions. This is demonstrated by the absence of 2.1 eV and 2.3 eV transitions in the highly reduced films where there is an abundance of oxygen vacancies. We showed that at a background oxygen pressure of 5E-7 Torr (200 W) there was a dramatic decrease in the 2.95 eV emission and 2.1 eV and 2.3 eV features were present presumably from the reduction of donated electrons through filling oxygen vacancies by the higher growth pressure. It is also noted that the film appearance changed at this pressure as well to clear from dark black/blue.

We then went on to show how excess A-site cations could act as acceptors in highly reduce films opening the singly ionized state and allowing the 2.1 eV and 2.3 eV transitions. By growing STO under controlled conditions and varying the deposition time of just the Sr, we saw how the RHEED, DRCLS, and XRD measurements are sensitive to the stoichiometry and crystal quality.

Our model was confirmed again with IDC structures fabricated on 100 nm BST films that showed a dramatic increase in the quality factor of the device with an increasing 2.3 eV emission. We can explain this once again via an increased 2.3 eV
emission due to less free carriers from oxygen vacancies which would lead to less conduction loss, and thus the observed increase in the quality factor of the devices.

We also saw in this series a strong correlation between the tunability of the BST, the 1.9 eV emission intensity, and the background oxygen pressure used during growth. With increasing oxygen background pressure we saw an increase in the Ba/Sr ratio which should have resulted in an increasing tunability but we saw a decreasing tunability. This result highlighted the importance of defect management in the growth of high quality material for IDC devices.

Between the 2.3 eV emission’s relation to the quality factor and the 1.9 eV emission’s relation to the tunability, we demonstrated the utility of DRCLS to effectively probe the two most important qualities of BST IDC devices. That DRCLS is a rapid, non-destructive form of testing makes this characterization technique that much more desirable from an industrial standpoint.

8.2 Future Work

By coupling our oxide MBE chamber to our XPS analysis chamber, and a slew of peripheral chambers with the capabilities of depositing simple devices or annealing using remote oxygen plasma, we are presented with a nearly limitless list of possibilities. But a central challenge of conventional oxide MBE that still remains is stoichiometry control. There is some evidence that suggests a desorption controlled growth window for BTO in the ultra-low oxygen pressure growth regime; however, we have seen no evidence of this
in STO films. Exploiting this growth window and using intermittent oxygen anneals during growth could lead to dramatic improvements in material quality.

Another factor that should be addressed is the relatively low quality factor of these films. In the films discussed, we wanted to look at the growth parameter dependence of the material properties and how DRCL features correlated to those properties. So, the samples were sent as-grown meaning we did not subject the films to any post growth oxygen anneals. But in this study it became clear that oxygen vacancies are playing a large role in the quality factor of these films. Subsequent studies should address the effects of oxygen anneals on the material properties and the redistribution of defects within the material. Another avenue of approach that these studies pointed to is the use of compensating defects to reduce the free carriers and thus reduce the dielectric loss. We saw that a slight excess of A-site cations in STO caused a dramatic increase in the 2.3 eV emission which would imply an associated increase in the quality factor of the material.

Finally, in the immediate future a DRCLS system will be installed coupled to the transfer line for rapid characterization of grown film surfaces. The system will be capable of 100 μA beam currents, which is 50X what is available to us now, and spot sizes of 0.5 mm. While the spot size is larger than what we use now, the uniformity of our MBE grown films should render this a non-issue. The system will also have a liquid nitrogen cooled sample stage. The cooled sample stage will do two things. First, we have seen that the increased beam current causes the sample holder to heat and outgas.
significantly and having a low temperature thermal reservoir should prevent this.

Second, reducing thermal vibrations will lead to sharper spectral features.

Coupling the MBE, RHEED, XPS, metals evaporator, ROP chamber, and a DRCLS system all in one UHV super-system presents unique opportunities for future graduate students interested in studying complex oxide surfaces and heterostructures. I believe there is a tremendous amount of opportunity available and that the new students are set to build on the lessons we have learned and what was presented here.

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