Characterization of Native Point Defects in Barium Strontium Titanate / Strontium Titanate Heterostructures

THESIS

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By

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Abstract

In this study Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) thin films were grown on (100) oriented SrTiO$_3$ (STO) substrates using molecular beam epitaxy. The BST films were produced under varying conditions with substrate temperature ranging from 700 °C to 900 °C, nominal oxygen background pressures ranging from ~0 Torr to 1E-6 Torr, and with an oxygen environment ranging from a 200 W plasma to an ambient O$_2$ atmosphere. The films were analyzed using a multitude of techniques including depth resolved cathodoluminescence spectroscopy (DRCLS) surface photovoltage spectroscopy (SPS), atomic force microscopy (AFM), and x-ray diffraction (XRD). The DRCLS spectra obtained from the films display well-resolved emissions at 1.9 eV, 2.1 eV, 2.26 eV, 2.95 eV and 3.5 eV. Surface photovoltage spectroscopy results correlate well with the emissions observed in the DRCLS and allow for the assignment of the positions of these defect states within the BST band gap. Furthermore, several trends are observed correlating the nature of the 2.9 eV emission to an oxygen related defect.
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1.1 Introduction

Perovskite structured complex oxides, previously studied in bulk, have received renewed attention recently after the observation of a number of phenomena in thin film samples of the various materials. The perovskites have proven to be one of the most versatile ceramic structures exhibiting properties including high-k dielectric constants, ferroelectricity, superconductivity, ferromagnetism, and multiferroic behavior. The multitude of properties observed in this material system makes the perovskites suitable for a number of technical applications ranging from improved gate dielectrics in modern CMOS technology, to novel microwave communication devices. The perovskite crystal structure ABO3 is shown below in Figure 1. Here the octahedra formed by O atoms and centered on the B site cations (blue) share corners in all 3 directions and the A sites (orange) cations occupy the middle of the cell formed by the octahedra.
Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) is one such material that has been investigated recently in thin film form for several applications. BST exhibits a phase change at a critical temperature (the Curie temperature, $T_c$) from a paraelectric state to a ferroelectric state. In its ferroelectric state the material exhibits a spontaneous polarization, which can be switched with application of an external field yielding hysteretic behavior. The critical temperature and the dielectric constant of the material have been shown to vary with differing Ba/Sr ratios affording customization of the material properties for different applications. The ferroelectric properties of BST show promise for the development of non-volatile memory technologies (FeRAM), and the its high relative dielectric constant makes it a strong candidate for next generation dynamic memories (DRAM) for which it has been thoroughly investigated. In addition, the relative dielectric constant of BST is
well known to vary with the application of an electric field affording tunability of its dielectric properties in upwards of 50% with small DC biases.\textsuperscript{8,9} The voltage-controlled tunability of BST’s dielectric constant makes it a strong candidate for the fabrication of voltage variable capacitors (varactors). Such devices are employed in the construction of several tunable microwave devices including filters, phase-shifters, and voltage controlled oscillators. These BST varactors offer an edge over conventional junction varactor diodes in that they do not produce the junction noise observed in varactors diodes and they are exhibit less loss in the RF and microwave frequency ranges.\textsuperscript{9} Additionally the low cost, and high tunability at low voltages make BST varactors a sensible alternative to conventional devices. However, before BST varactors can be deployed on a large scale, a significant understanding of the frequency and field dependence of the materials permittivity and dielectric loss tangent are required. Ideal BST varactors would yield high tunability with small dielectric losses in the RF and microwave frequency range.

1.2 Defects in Barium Strontium Titanate

Theoretical calculations predict a number defect states within the BST band gap. The formation of these defects are attributed primarily attributed to vacancies on the Ba and Sr as well as the O site of the BST lattice.\textsuperscript{10} Oxygen vacancies have been shown to have a particularly large influence on the electrical properties of BST and other titanate perovskites. Oxygen related defects have also been attributed to distortions observed in
the BST lattice which, as previously described, can have a significant impact on the dielectric properties of the material.\textsuperscript{2,11}

Oxygen vacancies are well established dopants in the titanates and reduce the titanium from Ti\textsuperscript{4+} to Ti\textsuperscript{3+} and dope the material n-type.\textsuperscript{12} These oxygen vacancies have been shown to be mobile in STO, diffusing along edge dislocations and grain boundaries, and are thought to give rise to the resistive switching mechanism observed in the material.\textsuperscript{13}

A number of studies have been undertaken to investigate the impact of film properties on the microwave performance of BST thin films. Unsurprisingly, conduction via electron doping has been shown to increase the loss tangent in BST thin films.\textsuperscript{12} Intentional doping of epilayers has also proven to affect the dielectric properties of BST, specifically the addition acceptor ions, thought to compensate native donor type defects have been shown to improve the loss tangent of BST varactors.\textsuperscript{12} Despite the impact that defects can have on the electrical properties of BST, a complete understanding of the properties contributing to their formation has yet to be well established.

Strain has proven to be a critical property with regard to device performance. Theoretical models of strain effects derived from dielectric measurements on stoichiometric BST thin films and earlier models of ferroelectric phenomena in bulk BaTiO\textsubscript{3} predict significant changes in the dielectric properties of strained BST thin films.\textsuperscript{10} Experimental analysis of the dielectric properties of differently strained BST thin films has demonstrated significant changes in both the tunability and dielectric loss for differing strain conditions.\textsuperscript{14} Strain engineering undertaken through light doping and
buffer layer lattice matching of BST thin films has similarly demonstrated strain dependent changes in the dielectric properties of the material.\textsuperscript{14,15}

1.4 Experimental Goals and Research Approach

In this work an investigation is undertaken to determine how variations in the crystal growth process affect the quality of the grown films, most specifically the formation and incorporation of point defects within the BST film and at the film interfaces. Understanding and controlling the formation of these defects is of significant importance in the development of high quality BST based devices, as defects can have a significant impact on the dielectric properties of BST thin films.

Molecular beam epitaxy (MBE) offers an edge over many crystal growth techniques often used in the literature because of the precise monolayer level control over the growth process afforded by the technique. Layer by layer precision engineering of complex oxide heterostructures and superlattices has been demonstrated using MBE making it a suitable technique for investigations into the nature of the formation of defects and custom engineering BST’s electrical properties.\textsuperscript{16} By fully understanding the nature of defects observed in BST thin films and their corresponding impact on the dielectric properties of the material, high-quality BST thin films may be able to provide a true alternative to conventional varactor technologies.

Following this introduction, Chapter 2 provides a description of the techniques employed in this work for the growth and characterization of Ba\textsubscript{0.5}Sr\textsubscript{0.5}TiO\textsubscript{3} thin films. Chapter 3 provides a detailed overview of the MBE growth process used in this work for
the fabrication of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ thin films. Chapter 4 examines the results obtained from
the characterization of several films. Lastly Chapter 5 provides a brief recap of the work
presented in this thesis and presents future directions of this work.
Chapter 2: Experimental Techniques

2.1 Introduction

The fabrication and analysis of the BaSrTiO3/SrTiO heterojunctions investigated in this thesis was undertaken through the use of several growth and analysis techniques, which are discussed in the section in order to introduce the reader to the results presented in later chapters of this document. The growth of all of the heterostructures presented in this document was performed using the molecular beam epitaxy growth technique. Analysis of the grown heterojunctions was undertaken using a variety of characterization techniques including x-ray photoelectron spectroscopy (XPS), x-ray diffractometry (XRD), atomic force microscopy (AFM), Kelvin probe force microscopy, surface photovoltage spectroscopy (SPS) and depth-resolved cathodoluminescence spectroscopy (DRCLS).

2.2 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is a technique, which allows for epitaxial growth of thin film structures. Epitaxial growth requires that the thin films maintain the crystalline order of the substrate crystal on which growth occurs to form a single crystal layer. Epitaxial growth is achieved using MBE in a layer-by-layer fashion on top of a heated substrate crystal. As a consequence of the relatively slow deposition rates which allow for surface diffusion and nucleation of the deposited atomic species, MBE is distinguished from other film growth techniques by the relatively slow deposition rates, the precise control of atomic fluxes, and the ultra-high vacuum conditions under which
growth takes place MBE growth has in the past, been predominately used for the fabrication of III-V based semiconductor devices. More recently, MBE has been utilized in the fabrication of oxide thin films with only minor adjustments to the process. A typical oxide MBE system is shown in Figure 2.

Figure 2. Schematic of a typical oxide MBE chamber

In the MBE growth chamber, several quasi-Knudsen effusion cells are arranged symmetrically on a source flange so that they are directed to a central point in the growth chamber where crystal growth occurs. The effusion cells are loaded with ultra-pure sources of the atomic species used in growth (e.g. Sr, Ba, Ti) and heated independently to temperatures sufficient to induce sublimation of the ultra pure materials. Precise control of the effusion cell temperature affords equally precise control of the sublimation and
subsequently deposition rates of the atomic species contained within the cells. Externally operated pneumatic shutters, positioned in front of the effusion cells, allow the operator to control the exposure of the substrate crystal to the various atomic fluxes.

2.2.1 Oxide Molecular Beam Epitaxy

The molecular beam epitaxy system used in the Oxide Molecular Beam Epitaxy Lab at The Ohio State University is a recently acquired Veeco Gen930 system designed for the growth of oxide materials. The growth chamber of the system is outfitted both a turbo and cryo-pump to maintain the ultra high vacuum conditions necessary for MBE growth. Additionally, the main chamber features both a source and a main cryopanel, which are cooled using liquid nitrogen prior to and during growth. The source cryopanel is attached to the growth chamber’s source flange and surrounds the effusion cells providing thermal isolation of the various sources form one another, even at the high (T > 1000°C) temperatures necessary for the sublimation of some source materials. The main cryopanel is mounted in the rear of the chamber in close proximity to the substrate heating block. The main cryopanel provides cold wall pumping in the area near the substrate-heating block, which serves to trap stray atomic species and prevent incorporation of impurities into the film during growth.

The effusion cell heating filaments are powered by DC PID controlled power supplies. The PID controllers allow for accurate control of effusion cell temperature via a closed-loop temperature feedback system. The substrate-heating block is powered by a DC PID controlled power supply equipped with a closed-loop temperature feedback
system to maintain stable substrate temperature during crystal growth. Ultra-pure oxygen is supplied to the chamber from an external tank and an RF plasma generator is used to ionize the O\textsubscript{2} gas during growth.

2.2.2 \textit{Reflection High Energy Electron Diffraction (RHEED)}

The oxide MBE system is equipped with a Staib Instruments RH 30RHEED system comprised of a high-energy electron gun and a phosphorus-coated screen as depicted in Figure 2. A CCD, used to digitize the RHEED diffraction pattern allows for computer aided monitoring of the RHEED features.

RHEED is an extremely surface sensitive technique that allows for direct measurement of the surface structure of a crystalline film during growth. The high-energy beam of the electron gun is directed at the surface of the substrate crystal at glancing incidence (typically \(\sim 1^\circ-3^\circ\)). The electrons, having a de Broglie wavelength on the order of tenths of an angstrom, undergo transmission reflection diffraction as they are scattered by the atomic species of the crystal. The glancing incidence of the electron beam limits penetration to the top most monolayers of the crystal yielding surface sensitivity. The reflected electrons strike a phosphor screen opposite the chamber from the electron gun and form a diffraction pattern.\textsuperscript{17} The intensity of the diffraction pattern streaks is proportional to the surface roughness and is maximal for an atomically flat, ordered surface. As a monolayer of material is deposited, growth (ideally) evolves through the formation of small islands of material on the surface of the substrate. As these islands nucleate and spread, the surface roughness of the film is increased resulting in a more
diffuse diffraction pattern. As the clusters fill in to form one monolayer, the surface roughness of the film decreases resulting in, ideally, an atomically flat surface once again. As shown in Figure 3, the RHEED diffraction streaks reach a minimum intensity at some percent surface coverage and then increase as the clusters combine to form one monolayer of material. Thus, by observing oscillations in the intensity of the RHEED diffraction streaks, crystal growth can be monitored in real time.

Figure 3. The evolution of RHEED intensity oscillations corresponding to two monolayers of deposition.
By monitoring the oscillation of the RHEED streak intensity during deposition on a fresh substrate, one is able to calibrate the shutter times so that they provide a sufficient dose for one monolayer of material growth. Additionally, by observing the RHEED oscillations and diffraction patterns during growth, one is able to monitor the film growth progress and quality.

2.3 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy is a photoemission technique, which is used to characterize the chemical properties of a material. XPS involves the measurement of the kinetic energies of electrons that are ejected from a material via the photoelectric effect. The X-ray photons used to excite electrons from the material in XPS have sufficient energy (typically $h\nu > 1000 \text{ eV}$) to excite electrons from the core shells of most atomic species. The kinetic energy, $E_k$, of an electron ejected from a material via the photoelectric effect is governed by the following equation:

$$E_k = h\nu - E_b - (E_{\text{vac}} - E_f)$$

Where $h\nu$ is the energy of the incident photon, $E_b$ is the binding energy of the bound electron before excitation, and $E_{\text{vac}} - E_f$ is the work function of the sample. In XPS electrons are excited from a sample by a monochromatic x-ray source that produces
photons with energy $h\nu$ the ejected electrons are collected by a hemispherical analyzer, which is used to determine the electron’s kinetic energy. The sample, in equilibrium with the XPS system has a known work function leaving the binding energy as a solvable unknown. Known binding energies and cross sections allow one to identify the chemical species comprising a sample. Shifts in the kinetic energy of characteristic electrons, termed “chemical shifts”, are representative of the local bonding environment of an atomic species and can be used determine its chemical bonding environment. While XPS analysis is limited to the outermost atomic layers because of the attenuation length of the x-rays used in the technique, depth dependent analysis can be achieved through the use of ion-sputtering techniques, which are used to remove layers of material during acquisition allowing for a more significant depth profiling of chemical species.

The XPS system used in the Oxide MBE lab at Ohio State is a Phi Versa-probe 2000 system manufactured by Physical Electronics. The system uses a monochromatic aluminum-$k\alpha$ alpha source with energy $h\nu = 1486.6$ eV. The system has an energy resolution of 0.046eV allowing precise identification of species with comparable binding energy as well as differentiation between different bonding environments.

A vacuum coupled transfer system between the MBE growth chamber and the XPS analysis chamber allows for the characterization of grown films without exposure to air. XPS analysis of the samples transferred under vacuum allows for much more accurate characterization of chemical species at the film free surface as the samples are free of adsorbents that tend coat the surface with even limited air exposure.\textsuperscript{20}
2.4 X-Ray Diffraction (XRD)

X-Ray diffraction is a technique used to characterize the crystalline structure of materials. In XRD, monochromatic, collimated x-rays impinge on the surface of a solid material. The high energy of the x-rays gives them a wavelength that is on the order of angstroms, or comparable to the interatomic spacing of atoms in a crystal lattice. When an x-ray impinges on a sample it is scattered by the electrons associated with the atoms or ions that lie within the path of the incident wave. In a periodic arrangement of atoms, such as that of a crystalline structure, diffraction occurs when x-rays are scattered by the scatter sites of adjacent atomic planes. When a monochromatic, parallel, coherent beam
of x-rays with wavelength $\lambda$ is incident at an angle, $\theta$, upon two parallel planes of atoms that have the same miller indices $(h,k,l)$ and are separated by a distance $d_{hkl}$, the x-rays are scattered at scattering sites in the two adjacent planes. Constructive interference of the scattered waves also occurs and an angle, $\theta$, and is governed by Bragg’s Law, that is:

$$2d_{hkl} \sin \theta = n\lambda$$

Bragg’s Law dictates that the path difference of the scattered waves, $2d_{hkl} \sin \theta$, is equal to an integer number, $n$, of wave lengths $\lambda$. This condition is illustrated below in Figure 5.

Figure 5. Conditions for Bragg diffraction between two crystal planes\textsuperscript{22}
In a standard XRD system the sample $S$, is mounted onto the sample holder, which is free to rotate about its axis, $O$. The sample is positioned such that its atomic planes form an angle $\theta$ with the incident x-ray source. The x-ray detector, which is also free to rotate about the axis $O$, is positioned so that it forms an angles $2\theta$, relative to the incident x-ray source and $\theta$ with relative to the atomic planes. During measurement, the sample and the detector are mechanically coupled so that a rotation through $\theta$ by the sample is accompanied by a $2\theta$ rotation of the photodetector. As the sample and the detector are rotated about the axis $O$, x-rays are detected at angles $\theta_n$, which satisfy the Bragg condition for constructive interference. A schematic of this set up is presented below in Figure 6. Using Bragg’s equation and the equation governing the interplaner distance for the crystal structure being studied, the lattice parameters of crystal structure can be calculated. Similar scans can be performed by rotation of the sample about the $\omega$ axis (into plane in the provided diagram) allowing for the calculation of in-plane lattice constants.
XRD is a highly valuable tool for the characterization of epitaxial films as it allows one to calculate the lattice parameters of the grown epilayers and determine, among other things, the strain induced by substrate lattice matching of the epilayer and the incorporation of defects into the film. More advanced system geometries and analysis can yield much more information about the properties of the grown epilayer however even the explanation of these techniques is beyond the scope of this discussion.

A Bruker D8 Discover high-Resolution triple axis X-Ray diffractometer with a Cu kα X-Ray source was used for XRD analysis in this study.
2.5 Depth Resolved Cathodoluminescence Spectroscopy (DRCLS)

Depth resolved cathodoluminescence spectroscopy (DRCLS) is a powerful technique that combines optical spectroscopy and electron excitation to probe the electronic properties of materials and novel material structures. Cathodoluminescence is one of several processes resulting from the irradiation of solids with an electron beam. When a material is irradiated with electrons, secondary and backscattered electrons, among other things, are generated as a result of the ionization of impacted atoms within the solid and the random collisions of electrons that have lost significant energy, respectively.\textsuperscript{23} Cathodoluminescence is the optical emission that results from the recombination of the electron-hole pairs excited by the electron beam-solid interactions. Electron hole pairs may recombine directly, emitting photons at the energy of the material’s band gap, or indirectly through defect states within the band, emitting photons at a fraction of the material band gap. By measuring the number of photons emitted at different energies one can characterize among other things, the phase of a material, the type of defects present in a material.\textsuperscript{23} A schematic of the DRCLS process is provided in Figure 7.
Figure 7. a) Recombination of excited electrons through a defect state (black) and direct recombination (blue) b) Depths $d_1 < d_2 < d_3$ probed at electron beam energies $E_{b1} < E_{b2} < E_{b3}$

At low electron beam energies (less than 1kV) cathodoluminescence occurs only in the top few nanometers of the materials, however by increasing the energy of the incident electron beam, the phenomena can be extended microns into the material. Depth resolution of material properties is achieved by taking emission spectra from a sample at increasing beam energies, which probe further into the material (Figure 7 (b)). Using DRCLS defect distributions can be characterized through the bulk of a sample and at interfaces between epilayers. The depth resolution afforded by DRCLS makes it a
powerful tool for the characterization of interfacial and film properties in material heterojunctions. While it is challenging to quantify absolutely the number of defects present in a sample using DRCLS, the technique is useful for qualitative analysis of samples prepared under different conditions and the defects that arise as a result of those differences.

Monte Carlo simulations based on the random collisions of secondary electrons generated by electron radiation can accurately model the creation of electron-hole pairs vs. depth as a function of electron beam energy. Using these simulations one is able correlate the features in DRCLS spectra with known interfaces within a heterostructure. An example of a Monte Carlo simulation for a 100nm Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ film grown on a SrTiO$_3$ substrate is presented in Figure 8.
Figure 8. Monte Carlo simulations of electron excitation depth for a 100nm Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ grown on a SrTiO$_3$ substrate.

The DRCLS system used in The Electronic Materials and Nanoscale Devices Laboratory at Ohio State is a custom built system, which features a Physical Electronics electron gun capable producing an electron beam accelerated at voltages of up to 5kV. Deflector plates on the gun allow for translation of the electron beam across a sample surface so that spectra can be taken from multiple points on a sample. A sapphire lens collects the emitted light and couples it into a fiber optical cable. The fiber optic cable is then coupled into a monochromator with a diffraction grating, which separates the collected light by wavelength and directs it onto a CCD camera used for spectral acquisition. The system has a spectral resolution of ~0.1eV system can measure photons
with energy ranging from 1.6 to 6.1 eV allowing for characterization of even wide band gap materials. A schematic of the DRCLS system is presented below in Figure 9.

![Figure 9. Schematic of depth resolved cathodoluminescence experimental setup](image)

2.6 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a non-destructive technique used to image the topographical features of a surface on the nanometer scale. In one standard AFM system configuration, a laser beam is reflected off of the top of a force sensitive cantilever and directed onto a photodetector array. Forces between the surface features and cantilever tip cause the cantilever to deflect, changing the position of the reflected laser on the photodetector array. In this way, the deflection of the tip is measured in real time as the
tip is scanned across the surface that is being imaged. A schematic of a typical AFM system is shown in Figure 10.

The force, $F$, exerted on the tip of the cantilever in proximity to the surface is governed by Hooke’s law $F = k \cdot d$, where $d$ is the deflection of the cantilever and $k$ is the cantilever’s spring constant. Two modes of contact are often employed in AFM; contact and non-contact operation modes. When operated in non-contact mode, as in these experiments, distances of 10 to 100 nm separate the cantilever tip and the sample surface. At these distances the cantilever is subjected to a number of forces including van der Waals, and electrostatic forces yielding information about surface topology and charge distribution.

The AFM system used in the EMN Lab is a modified Park Systems XE-70 AFM/KPFM.
2.7 Kelvin Probe Force Microscopy (KPFM)

Kelvin Probe Force Microscopy (KPFM) is a technique used to measure the electrostatic potential of a sample surface. Charged trapped in spatially localized states at the free surface of a semiconductor sample induce band bending in the near surface region. This band bending causes localized changes in the semiconductor work function in the near surface region as dictated by the continuity of the vacuum level through space. KPFM measures the potential of the sample surface by modulating a capacitor probe near a semiconductor sample surface. As the probe is modulated, a displacement current is generated by the difference in the work function between the probe and the sample.
surface. Figure 11 (a) illustrates the difference in work function between the reference probe and the sample surface with the Fermi levels aligned.\textsuperscript{20}

![Diagram of metal and semiconductor work functions]

Figure 11. Illustration of metal and semiconductor work functions relative to vacuum levels with a) fermi levels aligned b) compensating voltage $eU_{sm}$\textsuperscript{20}

The work function of a material is by definition, $E_{vac} - E_F$, using this, the work function, $\Phi$, of the probe and the sample surface are defined as: as $e\Phi^{M} = E^{M}_{vac} - E^{M}_{F}$ and $e\Phi^{S} = E^{S}_{vac} - E^{S}_{F}$, respectively. If the Fermi levels of the sample and the probe are aligned then the difference in the work function is defined as the contact potential $U^{SM}$ as follows:

$$e(\Phi^{S} - \Phi^{M}) = E^{S}_{vac} - E^{S}_{F} - E^{M}_{vac} + E^{M}_{F} = eU^{SM}\textsuperscript{20}$$
A typical KPFM setup resembles that of an AFM system however, in KPFM a metalized cantilever tip is employed as a capacitor plate, which is then modulated over the sample surface to induce a displacement current. The contact potential is measured by applying a bias sufficient to nullify the displacement current induced in the capacitor probe (Figure 11 (b)). Translating the probe across the sample surface and measuring the local contact potential allows for a mapping of the potential at the sample surface. KPFM coupled with AFM offers the ability to correlate topographical features with changes in the contact potential. The KPFM system used in the EMN Lab is a modified Park Systems XE-70 AFM/KPFM.

2.8 Surface Photovoltage Spectroscopy (SPS)

Surface photo-voltage spectroscopy is a technique which can be used to identify specific defect states at the free surface of a semiconductor material. SPS measurements are performed in the same manner as KPFM measurements. A capacitor probe, here a metalized AFM cantilever, is modulated in proximity to the sample surface and a displacement current is generated by the difference in work function between the probe and the sample surface. While modulating the capacitor probe, the surface of the sample is optically excited by monochromatic light to induce charge transitions in the near surface region. A schematic of a typical SPS system is shown below in Figure 12.
Figure 12. Schematic of modified atomic force microscopy/Kelvin probe microscopy system for surface photovoltage spectroscopy

The optically excited electrons can make a number of transitions as shown below in Figure 13. Transitions at the surface may occur between the material’s valence band edge and a defect state within the band gap, or between a defect state within the band gap and the conduction band edge. As mentioned previously, the occupation of localized defect states at a semiconductor surface induces band bending in the near surface region. Promoting a valence electron to a defect state fills the defect state at the surface and results in increased band bending in the near surface region. Electrons promoted from a surface defect state are swept away in the conduction band and result in decreased band bending in the surface. If the contact potential of the surface is monitored while monochromatic light of different wavelengths is incident upon the sample, transitions into and out of defect states can be observed as changes in the contact potential.
Figure 13. a) Photo-excited transitions emptying (a) and filling (b) surface states and their corresponding effect on the contact potential observed in surface photo voltage spectra (c)

Using SPS it is possible to identify complementary transitions at the surface of a material that is, promotion into and out of a defect state, by pairing transitions that affect the contact potential in opposite ways, and who’s energies sum to the band gap energy. Performing SPS measurements at different points on the sample allows for identification
of localized defect states. The SPS system used in the EMN Lab is a modified Park Systems XE-70 AFM/KPFM system with a fiber optic coupled monochromator for optical excitation.
Chapter 3: Growth of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$/SrTiO$_3$ Heterojunctions

3.1 Introduction

This chapter provides a detailed description of the growth processed used in this work for the production of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ thin films. Substrate preparation, and relevant growth parameters are discussed in detail.

3.2 Substrate Preparation

The substrates used in this investigation were 10mm x 10mm 0.5mm (100) oriented SrTiO$_3$ (STO) single crystals with a $\sim$0.5° miscut produced by MTI corporation. Before preparation the substrates were cut into 4 equal 5mm x 5mm by inscribing a line into the unpolished surface using a diamond tipped scribing tool and applying pressure across the scribed region causing the sample to split. The quartering of the as received substrates is necessary for mounting of the substrates on the custom designed vacuum transfer sample holders used in the oxide MBE chamber. The surface of the STO substrates is ‘EPI’ polished for crystal growth, however the substrates arrive with a mixed SrO/TiO$_2$ surface termination layer$^{25}$, which is undesirable for layer-by-layer epitaxial growth techniques such as MBE. The SrO layers of the STO substrates are highly reactive and can be removed through a wet chemical etching process. Two techniques have been demonstrated to produce atomically abrupt surfaces, one conventional technique employing buffered hydrofluoric acid (HF), and a more recently developed technique employing a mix of hydrochloric acid (HCl) and nitric acid (HNO$_3$) or aqua regia.$^{25}$

$^{25}$
Previous studies of the surface characteristics of STO substrates prepared using the two techniques have demonstrated that the aqua regia etch technique leaves considerably fewer defects at the film substrate surface making it more suitable for high quality epitaxial growth.\textsuperscript{26}

As prescribed by the aqua regia etch recipe, the substrates were soaked in deionized water for 25 minutes to create soluble hydroxide complexes. The substrates were then wet etched in an aqua regia solution for 10 minutes to remove the surface SrO layer. After etching the substrates were ultrasonically cleaned with acetone, methanol and deionized water to remove residual contaminants and then annealed at 1000°C in flowing oxygen for 1 hour to further reduce the etch induced defects at the surface of the crystal.

After preparation, the samples were mounted to the MBE growth platen using silver paint to insure sufficient heat transfer between the platen and the substrate crystal, and loaded into the intro chamber of the MBE system.

3.3 Source Flux Calibration

The deposition rates of the effusion cell sources of the MBE chamber were calibrated using both a quartz crystal microbalance (QCM) and the RHEED system in the MBE chamber. After cooling the cryo panels of the MBE main chamber, the effusion cells were heated to temperatures sufficient to induce sublimation of their respective atomic species. The QCM, positioned at the substrate growth location, was exposed to the individual atomic fluxes of Ba, Sr, and Ti individually and in the absence of oxygen no fewer than three times for durations of 15 minutes. The temperature of the effusion cells
were adjusted based upon the deposition rates observed from the QCM to obtain, roughly, the desired deposition times for the three atomic species.

After QCM calibrations were performed, a freshly prepared substrate was introduced into the growth chamber for further refinement of the atomic deposition times. The heating of the sample platen to the desired growth temperature and the introduction of oxygen typical of growth conditions into the chamber brought the substrate to growth conditions. The BST lattice in the (100) direction can be viewed as alternating layers of Ba$_{0.5}$Sr$_{0.5}$O and TiO$_2$. With this in mind, the oscillations of the specularly reflected spot in the RHEED pattern were timed for the alternate, manually controlled, deposition of Ba, Ti, and Sr, to determine the deposition duration necessary for the formation of one half monolayer (BaO, TiO2 or SrO) of BaTiO$_3$ and SrTiO$_3$. The average of the half monolayer deposition times was calculated and entered into the software used for control of the pneumatic shutters during extended (actual) crystal growth.

3.4 Crystal Growth

For this investigation the growth of multiple BST thin films was undertaken under a variety of different growth conditions. Among the growth parameters, substrate temperature, oxygen partial pressure, and oxygen plasma power are expected to have most significant impact.

Substrate temperature has a significant impact on the series of processes occurring at the substrate surface during crystal growth. The sticking coefficient, defined at the ratio of atoms adsorbing to a surface to the number that impinge on a surface varies with
the temperature of the surface. As the substrate temperature is varied, a change in the probability of an atom overcoming the attractive forces and desorbing from the substrate surface occurs.\textsuperscript{17} It is expected that substrate surface temperature are will impact the incorporation of atomic species into the growing epilayer producing different defects within the films.

Similarly, the amount (pressure) of oxygen in the MBE growth chamber is expected to have a significant impact on the stoichiometry and defect concentrations of the grown BST epilayers. Lower oxygen pressures during growth result fewer oxygen atoms available for incorporation into the epilayer lattice. Limited incorporation of oxygen into the epilayer lattice leads to the formation of oxygen vacancies in the film, which have been demonstrated to have a significant impact on the electronic properties of BST.

An oxygen plasma, produced using the MBE chambers RF oxygen plasma source is also expected to have an impact on the incorporation of oxygen within the BST epilayer. Ionized oxygen species are more chemically reactive than their stable constituents allowing them to incorporate into the growing epilayer more easily than stable $O_2$ gas. The extent of the ionization of the oxygen in the growth chamber is controlled by the power of the RF plasma source and higher powers are expected to produce more ionized oxygen in the chamber.\textsuperscript{27}

The following describes the growth process used for all films grown in this investigation. After calibration of the source fluxes was completed, a substrate prepared in the manner previously described was introduced in the growth chamber. The substrate
was brought to the desired growth temperature with the chamber at the oxygen pressure intended for the specific growth. Intensity oscillations in the specularly reflected spot of the (100) RHEED pattern were observed and recorded during the growth process to monitor the deposition of the film. During growth, the shuttered depositions of the atomic species (Ba, Sr, Ti) were controlled automatically by the Molly growth software provided with the system. Each film was grown to a thickness of 100nm as observed in the RHEED intensity oscillations. Observations of the post growth RHEED diffraction patterns indicated ordered crystalline growth of the BST thin films.

3.5 Experimental Parameters for Grown BST Films

Two series of 100nm BST thin films were grown for this investigation. Growth of the first series, hereafter referred to as the plasma series, was undertaken to investigate the impact of substrate temperature and oxygen plasma power on the formation of defects within the material. Three films were grown in a 200W oxygen plasma atmosphere with a nominal oxygen background pressure of 1E-6 Torr at substrate temperatures of 700°C, 800°C, and 900°C. An additional film was grown in a 150W oxygen plasma atmosphere with a nominal oxygen background pressure of 1E-6 Torr at 800°C. Two additional films were grown in an ambient O₂ atmosphere at nominal background pressure of 1E-6 Torr and a substrate temperature of 900°C. The last two films in the series were intentionally grown with slightly differing Ba and Sr shutter times. Flux deposition durations were calibrated from the observation of RHEED intensity oscillations on a calibration sample. The durations of the Ba and Sr doses corresponding to the formation of one layer of BaO
and SrO, respectively were calibrated so that the required Ba deposition time was 3.3 seconds longer (29.96 seconds) than that of the Sr (26.33 seconds). One film was grown with equal deposition durations of Ba and Sr and was anticipated to be slightly A/A’ cation deficient, with a Ba/Sr ratio less than 1. The second was grown with the calibrated Ba and Sr shutter times and was expected have a Ba/Sr ratio of ~1.

The second series of films, hereafter referred to as the oxygen series, were grown to investigate the impact oxygen pressure and substrate temperature on the formation of defects within the material. All of the films in this series were grown in a 200W oxygen plasma atmosphere with co-deposition of Ba and Sr. Three films were grown at a substrate temperature of 800°C with nominal oxygen background pressures of 1E-7 Torr, 4E-7 Torr and 9.2E-6 Torr. Two other samples were grown under nominal oxygen background pressures of 1.3E-6 Torr and 1.2E-6 Torr with substrate temperatures of 700°C and 900°C, respectively.

One additional film was grown in the absence of an external oxygen supply at a substrate temperature of 800°C to a thickness of 20nm.
Chapter 4: Characterization of the GrownBa$_{0.5}$Sr$_{0.5}$TiO$_3$/SrTiO$_3$ Heterojunctions

4.1 Introduction

Analysis of the heterojunctions grown under the conditions described in the previous chapter were undertaken to determine the impact of growth parameter on the formation of defects within the BST thin films. The Films were characterized using X-ray photoelectron spectroscopy, X-ray diffraction, atomic force microscopy, depth resolved cathodoluminescence, kelvin probe force microscopy, and surface photovoltage spectroscopy.

4.2 Characterization of the 1.9 eV Defect

No significant trends were observed over the characterization of the entire plasma series. However, two films from the series showed significant differences that provide insight into the nature of the formation of defects during crystal growth. These two films, grown under identical conditions, but with slight differences in the cation deposition durations, exhibit dramatic differences throughout all of the techniques used in their characterization.

RHEED diffraction patterns (Figure 14) observed at the conclusion of growth indicate that the growth of both films was epitaxial.
Figure 14. RHEED diffractions patterns at the conclusion of crystal growth for (a) calibrated Ba and Sr deposition time ($T_{Ba}>T_{Sr}$) (b) equal Ba and Sr deposition time

XPS measurements show variation in the Ba/Sr ratio between the two films as expected from the adjustments to the Ba and Sr deposition durations. The film grown with the calibrated shutter times shows a Ba/Sr ratio of 1.2, the film grown with reduced barium deposition time shows a Ba/Sr ratio of 0.83.

XRD data obtained from the barium rich BST film show high intensity (100) and (200) diffraction peaks. The (300) diffraction peak exists weakly in the spectra and the (400) diffraction peak is not observed. XRD data from the stoichiometric BST film show high intensity (100), (200), (300), and (400) diffraction peaks.
The c-axis parameters for the two films, calculated from the second order diffraction peak observed in high resolution theta-2 theta XRD scans and the bulk BST lattice constant reported in literature\textsuperscript{28}, show a slight difference. The barium rich film is calculated to have a smaller c-axis parameter than the stoichiometric film. The larger c-axis parameter of the stoichiometric film indicates an increased tensile strain.

Figure 15. Theta-2Theta XRD scans for Ba\textsubscript{x}Sr\textsubscript{1-x}TiO\textsubscript{3} grown with (a) equal Ba and Sr deposition times and (b) reduced Ba deposition time.
<table>
<thead>
<tr>
<th>Film</th>
<th>C-axis lattice parameter (Å)</th>
<th>Strain (Relative to bulk BST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Ba/Sr Deposition</td>
<td>4.02</td>
<td>1.85 %</td>
</tr>
<tr>
<td>Reduced Ba Deposition</td>
<td>4.03</td>
<td>2.1 %</td>
</tr>
</tbody>
</table>

Table 1. C-axis parameters and strain values calculated for Ba$_x$Sr$_{1-x}$TiO$_3$ films

Dramatic differences are observed in the surface morphology of the two films. In good agreement with the strain values calculated from the XRD data, AFM scans reveal edge dislocations appearing orthogonally at the surface of the barium rich BST film. Line scans of the surface morphology show the dislocation heights at approximately 200pm. No dislocations are observed in the BST film grown with equal Ba and Sr deposition times however features resembling step edges are observed in line scans taken over the surface with a height of roughly 0.4nm, corresponding to the unit cell c-dimension. The difference in the c-axis parameters between the two films is attributed to a relaxation of the film grown with full Ba and Sr deposition times as indicated by the dislocations observed in the AFM topography scans.
Figure 16. AFM topography scans (left) of and line scans showing surface features (right) for partially relaxed (a) and strained (b) BST films.

Both the stoichiometric and the barium rich films exhibit resolved emission in the cathodoluminescence spectra at 1.6 eV, 1.89 eV, 2.22 eV, 2.95 eV and a shoulder at 3.1 eV (the band gap). In both cases the 2.9 eV emission is the dominant feature of the spectra (Figure 17).
In the barium rich film the 1.9 eV emission intensity is observed to increase as the electron beam probes away from the film free surface and into the bulk of the BST film. Correlating the change in intensity with the peak electron excitation depth simulated via Monte Carlo simulations it is observed that the emission intensity reaches a maximum within the thickness of the film and decreases into the film-substrate interface. These observations are a stark contrast to the trend in emission intensity of the 1.9 eV effect in the non-stoichiometric film. Here the 1.9 eV defect demonstrates a consistent decline away from the film free surface reaching a minimum at the film substrate interface. A plot of the 1.9 eV emission intensity, normalized to the 2.9 eV emission intensity as a comparative reference, is shown below in Figure 18.
SPS spectra obtained from the two BST films show good agreement with the emissions observed in the DRCLS spectra. Transitions are observed at photon energies of ~1.6 eV, ~1.89 eV, ~2.22 eV, and ~3.1 eV for both films (Figure 19). A number of other transitions are observed in the SPS spectra, which are not present in the DRCLS spectra corresponding to the population of defect states at the surface. Observations of the change in the contact potential difference associated with these transitions allows for the assignment of complementary transitions to and from defect states within the BST band gap as shown in Figure 20.
Figure 19. SPS spectra taken from partially relaxed (left) and strained (right) BST films

Figure 20. Defect transitions assigned from SPS spectra

Previous theoretical calculations have attempted to predict defect energies in bulk BaTiO$_3$ (BTO). Theory predicts singly charged oxygen vacancy states ($V_o^+$) at an energy just below the conduction band minimum, doubly charged oxygen vacancy states ($V_o^{++}$) at 1.3 eV below the conduction band minimum, singly charged barium vacancy states at 1.4 eV below the conduction band minimum ($V_{Ba}^-$), and doubly charged barium vacancy states at $V_{Ba}^{++}$.
states at 2.2 eV below the conduction band minimum ($V_{Ba^-}$). These predicted defect state energies are presented in Figure 20 (a). It is expected that similar defects would be observed in BST, and such transitions are observed in the literature in cathodoluminescence (CL) spectra from BST films. Experimental Transitions observed in CL studies of BTO have been compared to those CL and a number of transitions predicted in theory were observed. The authors used theory to assign the emissions observed in their CL spectra as shown below in Figure 21 (b)

![Figure 21](image-url)

Figure 21. (a) Defect energies predicted in BaTiO$_3$ by theoretical calculations, (b) defect transitions observed experimentally in CL spectra taken from BaTiO$_3$.

The assignment of the 1.9 eV and 1.1 eV complimentary transitions observed in the SPS spectra show good agreement with those predicted and observed in literature for BTO. Here the 1.9 eV transition is associated with the depopulation of a double charged barium vacancy and the complementary 1.1 eV transition is associated with the population of this state. This assignment agrees well with the changes in growth conditions of the two films and the trends in the 1.9 eV emission intensity observed in the
DRCLS. The reduction in the A site cation dose is presumed to result in an increase in the formation of A site vacancies resulting in an increase in 1.9 eV emission intensity.

4.3 Characterization of the 2.9 eV Defect

Interestingly a transition at 2.9 eV is present only in the relaxed BST film and is not shown in SPS spectra obtained from the strained film. The absence of the 2.9 eV defect transition from the strained sample merits further investigation as the transition is observed to be the primary feature in the DRCLS spectra obtained from both samples.

To further probe the nature of the 2.9 eV transition, SPS spectra were taken at various points across the surface of the barium rich BST film. A plot of several of the BST films is shown below in Figure 22.
Here is observed that the 2.9 eV transition is not present in all SPS scans taken across the film surface. From the initial value of the contact potential difference a separation criteria is observed which differentiates the spectra containing the 2.9 eV transitions from those that do not. Spectra containing the 2.9 eV transition are observed to have an initial contact potential difference of greater than 0.225 eV (dotted line, Figure 22). This upward shift in contact potential demonstrates a decrease in the local work function of the material and an increase in the Fermi level of the sample. It observed that the 2.9 eV transition presents the only notable difference in the spectra taken in areas with different contact potential which leads to the conclusion that the 2.9 eV defect state is electrically active and acts as an n-type dopant in the BST film.
KPFM scans taken across the partially relaxed sample surface shows significant variation of the dark contact potential across the film free surface. When compared with AFM morphology scans of the same area, one notices that the areas with high contact potential correlate well with the locations of edge dislocations on the sample surface. The localization of the 2.9 eV defect at edge dislocations in the partially relaxed BST film may lend some insight into the absence of the 2.9 eV transition in the SPS spectra from the strained BST film. If edge dislocations offer an avenue for migration of the 2.9 eV defect through the BST films then the absence of the dislocations in the strained BST film might prevent the significant diffusion of the defect to the surface.

![Figure 23](image.png)

Figure 23.(a) KPFM surface map from relaxed BST film (b) AFM topography map taken at the same site

Observations of trends in oxygen series help to develop a more thorough explanation for the nature of the 2.9 eV defect. In the oxygen series, XRD high theta-2theta scans demonstrate variation in the diffraction angle of the (200) diffraction peak.
The shifts in the diffract angles correspond well with changes in growth conditions. The diffraction angle is observed to decrease with increasing substrate temperature corresponding to an elongation of the film c-axis parameter as growth temperature is increased. The diffraction angle also demonstrates a shift to lower values for higher oxygen pressures during crystal growth here indicating that higher oxygen growth pressures producing tetragonally strained films.

Using the diffraction angles observed in the theta-2 theta and the bulk BST lattice constant reported in literature\textsuperscript{28}, calculations of the lattice parameters for the oxygen series were performed, the results of which are presented below in Tables 2 and 3. The impact of oxygen vacancy defects on the BST lattice has been thoroughly investigated in the literature. The introduction of an oxygen vacancy into the lattice is expected to affect the nearest neighbor distance through a reduction in the Coulomb attraction forces between anion and cation atoms. It is then expected that an elongation of perovskite lattice parameter is accompanied by the incorporation of an oxygen vacancy resulting in a tetragonally distortion of the lattice.\textsuperscript{31}

The oxygen series demonstrates a decrease in the c-axis parameter of BST epilayers with decreasing growth oxygen pressures. If the unit cell volume of the BST film is taken to remain constant under different strain conditions, the decrease in the c-axis parameter observed with decreasing oxygen can then be attributed to the incorporation of oxygen vacancies into the BST lattice and a subsequent expansion of the a-axis parameter as reported elsewhere.\textsuperscript{31}
Figure 24. High resolution Theta-2Theta scans for BST films grown under increasing oxygen pressure

<table>
<thead>
<tr>
<th>200W $\text{O}_2$ Plasma, $T_c = 800^\circ\text{C}$</th>
<th>C-Axis Parameter</th>
<th>Strain (Relative to Bulk BST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1E-7 Torr</td>
<td>4.028236</td>
<td>2.058%</td>
</tr>
<tr>
<td>4E-7 Torr</td>
<td>4.040336</td>
<td>2.364%</td>
</tr>
<tr>
<td>1.2E-6 Torr</td>
<td>4.053462</td>
<td>2.697%</td>
</tr>
</tbody>
</table>

Table 2. C-axis lattice parameters and strain values calculated for films grown under increasing oxygen pressures

Elevated growth temperatures have previously been demonstrated to increase the incorporation of oxygen vacancies into BST thin films.\textsuperscript{11} The oxygen series of film shows a clear increase in c-axis parameters as growth temperature of the films is increased. If more oxygen vacancies were being incorporated into the film at higher temperatures it
would be expected that the c-axis parameter should decrease in proportion to the growth temperature as is the case for increasing oxygen. Here the opposite trend is observed, indicating that further investigation is necessary to fully understand the impact of oxygen vacancies on the BST lattice. Additionally, the slight variations in oxygen pressure during growth of the oxygen series at different temperatures may complicate the temperature trends in the c-axis parameter.

![Graph showing Theta-2Theta scans for BST films grown under increasing substrate temperature.](image)

Figure 25. High resolution Theta-2Theta scans for BST films grown under increasing substrate temperature

<table>
<thead>
<tr>
<th>200W O₂ Plasma</th>
<th>C-Axis Parameter</th>
<th>Strain (Relative to Bulk STO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc = 700, P(O₂) = 1.3E-6 Torr</td>
<td>3.995322</td>
<td>1.224%</td>
</tr>
<tr>
<td>Tc = 800, P(O₂) = 1.2E-6 Torr</td>
<td>4.053462</td>
<td>2.697%</td>
</tr>
<tr>
<td>Tc = 900P(O₂) = 9.2E-7 Torr</td>
<td>4.072151</td>
<td>3.171%</td>
</tr>
</tbody>
</table>

Table 3. C-axis lattice parameters and strain values calculated for films grown with increasing substrate temperature
DRCLS spectra obtained from the oxygen series show the same well-resolved emissions at 1.6 eV, 1.89 eV, 2.22 eV, and 2.95 eV as well as shoulder at 3.1 eV. Again the 2.95 eV emission is observed to be the primary feature in all spectra. Here the 2.9 eV defect exhibits an interesting trend when plotted as a function of beam energy for the different samples. Films grown at higher oxygen pressures (\(\sim 1E-6\) Torr) exhibit relatively constant 2.95 eV emission intensity through the thickness of the BST films and into the STO substrate. Films grown at lower oxygen pressures (3E-7 Torr) exhibit uniform 2.95 eV emission through the epilayer but increase strongly into the substrate depending on oxygen growth pressure. The extent that the 2.95 eV emission increases into the substrate scales with decreasing oxygen pressure, suggesting an out diffusion of oxygen from the substrate to the growing epilayer film. The out diffusion of oxygen from the STO substrate is further reinforced by the variations observed in the c-axis parameters of the BST oxygen series films. Films grown under conditions expected to produce oxygen vacancies show a significant increase in 2.9 eV emission intensity into the STO substrate while those grown under conditions predicted to minimize the formation of oxygen vacancies show little or no increase in 2.9 eV emission intensity into the substrate. Indicating that oxygen is diffusing out of the substrate to compensate the oxygen vacancies within the BST films.
Figure 26.2.9 eV emission intensity vs. beam energy for oxygen film series

To further study the nature of the 2.9 eV emission, a film was grown under extremely reducing conditions. The film was brought to a growth temperature of 800°C under an oxygen pressure of 5E-7 Torr to retard the promotion of oxygen related defects at the substrate surface. After reaching growth temperature, the oxygen supply to the growth chamber was closed isolating the film from an external oxygen suppl. Film growth was monitored by observing RHEED intensity oscillations and the BST film was grown to a thickness of 20nm.

RHEED diffraction patterns (Figure 27) obtained at the conclusion of film growth exhibited the expected diffraction pattern and indicated epitaxial growth of the BST film
Figure 27. RHEED diffractions patterns for film grown with no external oxygen supply

In plane (a-axis) and out of plan (c-axis) XRD scans show diffraction peaks for the grown epilayer. The in plane (a) lattice constant of the epilayer, calculated from the XRD data, demonstrate that the epilayer is lattice matched to the STO substrate. The calculated out of plane lattice constant is significantly larger than that expected of bulk BST indicating that the epilayer is tetragonally strained.

Figure 28. High resolution theta-2theta XRD scan (left) and omega-2theta scan (right) for BST grown with no external oxygen
An XPS depth profile of the structure was carried out to determine the elemental composition through the thickness of the film. The sample, transferred under vacuum to the XPS analysis chamber, had no opportunity to react with oxygen in the atmosphere limiting any observation of oxygen in the spectra to an out diffusion process from the STO substrate. The depth profile of the heterostructure shows a 60% composition of oxygen, as expected of a stoichiometric BST sample, through the thickness of the epilayer and into the STO substrate.

![Graph showing XPS depth profile of BST film growth with no external oxygen](image)

Figure 29. XPS depth profile of BST film growth with no external oxygen

Here the full extent of oxygen migration from the STO substrate to the BST epilayer is demonstrated. In the absence of an external oxygen supply, ordered crystal growth
proceeds through an out diffusion of oxygen from the STO substrate resulting in an epitaxial BST film. With these results, the origin of the 2.9 eV defect emission is attributed to the formation of oxygen vacancies. Oxygen vacancies manifest in the STO substrate as a result of an out diffusion of O atoms into the film to compensate for vacancies produced in films grown under reducing conditions.

An emission at similar energies (~2.8 eV) has recently been observed in photoluminescence studies of Ar$^+$ irradiated and donor doped STO. In these studies, the 2.8 eV emission is attributed to recombination of excess carriers introduced by electron dopants (oxygen vacancies) at self trapped exaction sites localized around the vacancies.$^{32,33}$ These results are agreeable with the trends observed in this study which suggest an increase in 2.9 eV emissions with the introduction of oxygen vacancies. Additionally, the mobility of these 2.9 eV defects observed and their identification at dislocation at the BST film surface correlate well with the migration of oxygen vacancies observed in STO.$^{13}$
Chapter 5: Conclusions and Future Work

In this work an investigation into the nature of point defects in barium strontium titanate-strontium titanate heterojunctions has been undertaken. By varying growth parameters such as shutter duration, substrate temperature and oxygen pressure during the growth of BST thin films, variations in the quantity and distribution of defects formed at the film interfaces and through the bulk of the films were observed. Defect transitions were probed through the BST film and into the material interface using depth resolved cathodoluminescent and observed transitions that correlate well with defects reported in the current literature. Using surface photovoltage spectroscopy we have characterized the nature of these transitions and assigned positions of the defects within the BST band gap.

The results presented here shows some correlation with earlier cathodoluminescence studies of A side vacancies observed in BTO.

This work also serves to further the understanding of the 2.9 eV defect observed in BST. This work demonstrates that the nature of this defect state is clearly correlated with the incorporation of oxygen vacancies within the BST lattice. Furthermore, the results presented here suggest that oxygen atoms within the BST and STO lattices are mobile and that oxygen migration occurs to compensate for the formation of oxygen vacancies within the film.

Future work is directed towards the fabrication and characterization of varactors made from the MBE grown BST films. By correlating defect observations with the electrical characteristics of the BST varactors further correlations may be made between
the impact of these native point defects and their impact on the dielectric properties of BST.
References


