Atomistic Investigation into the Interface Engineering and Heteroepitaxy of Functional Oxides on Hexagonal Silicon Carbide through the Use of a Magnesium Oxide Template Layer for the Development of a Multifunctional Heterostructure

A Dissertation Presented
by
Trevor L. Goodrich
to
the Department of Chemical Engineering
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in
Chemical Engineering

Northeastern University
Boston, Massachusetts
June 20, 2008
NORTHEASTERN UNIVERSITY
Graduate School of Engineering

Dissertation Title: Atomistic Investigation into the Interface Engineering and Heteroepitaxy of Functional Oxides on Hexagonal Silicon Carbide through the use of a Magnesium Oxide Template Layer for the Development of a Multifunctional Heterostructure

Author: Trevor L. Goodrich
Department: Chemical Engineering

Approved for Dissertation Requirements of the Doctor of Philosophy Degree

[Signatures and dates]

Date

Date

Date

Date

Date
This dissertation is dedicated to my family and friends for all their support and encouragement, motivating me to become the engineer that I am. Thank you.
Acknowledgments

I am grateful for all the opportunities and experiences that I have been exposed to during my studies at Northeastern University and the Chemical Engineering Department. I would especially like to acknowledge my advisor, Dr. Katherine Ziemer for inspiring me and motivating me in the field of material science and interface engineering. Without her guidance, I would not be the engineer that I am today.

I would also like to acknowledge the support of my past and present co-workers in the Interface Engineering Laboratory. I thank Brian Doyle and Joseph Tsai for taking me under their wings when I first started and teaching me about ultra high vacuum and molecular beam epitaxy. I thank Joseph Parisi for his tireless efforts and devotion to the lab for the development and refinement of the hydrogen furnace. I thank Christopher McLaughlin, Joseph Lavoie, and Alex Avekians for their efforts in calibration and characterization of equipment. I thank Natalia Maximova and Bing Sun (孙冰) for their support around the laboratory and inquisitive questions. I would especially like to thank Zhuhua Cai (蔡祝华) for all her efforts and contributions over the last four years. Her lively spirit and calming demeanor created a wonderful work environment.

I would further like to thank the staff and students of the Center for Advanced Microgravity Materials Processing, under the direction of Dr. Albert Sacco, Jr., for their time and assistance with various characterization techniques. I thank the staff and students of the Center for Microwave Magnetic Materials and Integrated Circuits, under the direction of Dr. Vincent Harris for use of their equipment and expertise in functional materials. I thank Dr. Charles Ahn and his group at Yale University, Dr. Jon-Paul Maria and his group at North Carolina State University, Dr. David Muller and his group at Cornell University, and Dr. Alan Doolittle and his group at Georgia Institute of Technology, for their collaboration with this research.

I would like to thank the Department of Chemical Engineering at Northeastern University for partial funding during my studies. Further, I would like to acknowledge the Office of Naval Research contract numbers N0014-06-1-0761, N00014-04-1-0426, and N00014-06-1-1020 and Dr. Colin Wood, Program Manager, for funding as part of the Epitaxial Multifunctional Materials and Applications – Multiple University Research Initiative (EMMA-MURI).

I would like to acknowledge my Ph.D. committee members who have supported me throughout my research; Dr. Katherine Ziemer (Chemical Engineering, Northeastern University), Dr. Albert Sacco, Jr. (Chemical Engineering, Northeastern University), Dr. Daniel Burkey (Chemical Engineering, Northeastern University), Dr. Donald Heiman (Physics, Northeastern University), and Dr. Alan Doolittle (Electrical and Computer Engineering, Georgia Institute of Technology).

Finally, I would like to thank my family and friends who motivated and encouraged me both in and out of the laboratory. To my parents, Terry and Debra Goodrich, who supported me throughout my entire collegiate career; to my brother, Jarod Goodrich, with whom I have always shared a healthy academic competition with, and to my future wife Michelle Carberry, who was always there for me and motivated me to be the best engineer possible. I thank you all.
Advancements in integrated circuit technology are quickly approaching the threshold of silicon semiconductor electronics. In order to break away from the confinements of standard device architecture and silicon’s intrinsic material limitations, it is necessary to make an innovational change toward a new generation of novel materials with diverse functionality and superior mechanical, electrical, and magnetic properties that can perform under high-power, high-frequency, high-temperature application requirements. In order for the realization of a next-generation device, it will be necessary to diverge from traditional semiconductor processing into a wide bandgap semiconductor platform. Further, the realization of a next-generation device necessitates the development of novel functional materials that can accommodate the increased performance requirements of both the wide bandgap semiconductor platform and enable multifunctionality; one device interacting with the environment in multiple ways. The novel materials proposed are functional oxides, which can be tuned statically or dynamically to interact with their environment in different ways and can couple with each other to make multifunctional heterostructure devices.

Through molecular beam epitaxy, this research explores the use of a magnesium oxide (MgO) template layer and the interface formation mechanism of an oxygen bridge for effective heteroepitaxy of high-quality, ferroelectric barium titanate (BTO) on 6H-SiC. High quality, single crystalline MgO(111) is obtained with a smooth surface (RMS < 0.5 nm) and a stepped morphology conformal to the underlying 6H-SiC morphology, but is inherently twinned due to the ionic nature of a (111) oriented rocksalt structure. The smooth, conformal 2-D growth mechanism of MgO prefers to grow in tension with a 3.3% lattice mismatch, requires the presence of atomic oxygen, and transitions to a more 3-D growth mode when the thickness reaches ~10 nm. The engineered MgO surface is both effective and necessary to promote the pseudo-hexagonal, heteroepitaxy of BTO(111). Similar to MgO, BTO(111) prefers to grow in tension with a 5.3% lattice mismatch and is inherently twinned with a 6-fold symmetry, due to 60° in-plane rotations. The resulting epitaxy alignments for the BTO/MgO/6H-SiC results in a BTO{111}||MgO{111}||6H-SiC{0001} out-of-plane relationship and a BTO{110}||MgO{110}||6H-SiC{1120} in-plane relationship. A multilayered heterostructure was fabricated consisting of ferrimagnetic barium hexaferrite (BaM), ferroelectric BTO, the MgO template layer, and the wide bandgap semiconductor 6H-SiC (BaM/BTO/MgO/6H-SiC). The BTO layer of the heterostructure has ferroelectric properties with a saturated polarization around 4.7 µC/cm² and a striped domain structure. The BaM layer shows little uniaxial magnetic anisotropy due to mixed orientations. Although the individual functional properties were not optimized, the integration and demonstration of multiple functionality within a single heterostructure is an important contribution toward the realization of a next-generation, multifunctional device.
### Table of Contents

Acknowledgments................................................................................................................ i
Abstract ............................................................................................................................... ii
Table of Contents ............................................................................................................... iii
List of Figures .................................................................................................................... vi
List of Tables .................................................................................................................... xv
1.0 Introduction ................................................................................................................... 1
2.0 Background ................................................................................................................... 4
    2.1 Semiconductors ........................................................................................................ 5
        2.1.1 Direct and indirect bandgap semiconductors ................................................. 7
        2.1.2 Wide bandgap semiconductors ................................................................... 8
        2.1.3 Silicon carbide polytypes .......................................................................... 11
    2.2 Functional oxides ..................................................................................................... 13
    2.3 Multiferroics and multifunctional oxides ............................................................... 16
    2.4 Ferro- and ferri- electric and magnetic materials .................................................. 19
        2.4.1 Ferroelectric materials ............................................................................. 20
        2.4.2 Ferro- and ferri- magnetic materials ....................................................... 25
    2.5 Epitaxy and mismatch ............................................................................................. 27
        2.5.1 Lattice mismatch ....................................................................................... 28
        2.5.2 Thermal mismatch ................................................................................... 32
        2.5.3 Band offsets and band bending ................................................................. 33
    2.6 Growth mechanisms ............................................................................................... 36
    2.7 Growth methods ....................................................................................................... 39
    2.8 Integration of functional oxides on wide bandgap semiconductors by MBE ....... 44
3.0 Critical Literature Review ............................................................................................ 46
    3.1 Oxides on oxides: lattice matched epitaxy .......................................................... 48
        3.1.1 Interface engineering and strain-induced functionality .................................. 49
        3.1.2 PTO/STO heterostructure via MBE ............................................................ 50
    3.2 Oxide on semiconductor heteroepitaxy ............................................................... 53
5.1 6H-SiC surface preparation

5.1.1 As-received 6H-SiC preparation and characterization

5.1.2 Hydrogen cleaned 6H-SiC characterization

5.2 Heteroepitaxial integration of oxides on 6H-SiC

5.2.1 Oxygen bridge approach and challenges

5.2.2 MgO/6H-SiC heteroepitaxy: Initial studies

5.2.3 The role of oxygen on the nucleation of MgO

5.2.4 MgO growth mechanism and physical properties

5.2.5 Thermal stability and interface breakdown

5.2.6 Temperature impact on the surface structure of MgO(111)

5.2.7 MgO/6H-SiC band bending and offsets

5.3 Potential applications for MgO/6H-SiC heterostructure

5.3.1 MgO/6H-SiC MOSFET

5.3.2 MgO as a heteroepitaxial template layer

5.3.2.1 PLD grown BTO on MgO/6H-SiC template

5.3.2.2 PLD grown BST on MgO/6H-SiC template

5.4 Integration of BTO on 6H-SiC by MBE

5.4.1 Establishing operating conditions window

5.4.2 Interpretation of BTO RHEED pattern

5.4.3 BTO epitaxy alignments

5.4.4 Film thickness, temperature, and growth rate effects on BTO/MgO/6H-SiC

5.5 Electrical characterization of BTO/MgO/6H-SiC

5.5.1 Electric force microscopy

5.5.2 P-E hysteresis characterization

5.6 Multifunctional oxide heterostructure on 6H-SiC

6.0 Conclusions

7.0 Recommendations

8.0 Glossary

9.0 References

Appendix
List of Figures

**Figure 1.1**: Tie diagrams first developed by Heckmann in 1925 and later refined by Nye in 1957 used to represent the relationships between different functional properties of a material [1, 2]. Where \( E = \) electric field, \( T = \) temperature, \( H = \) magnetic field, \( D = \) displacement, \( M = \) magnetization, \( S = \) entropy, \( \varepsilon = \) strain, and \( \sigma = \) stress. ................................................................................................................2

**Figure 2.1**: Band diagrams for a) indirect Si [24], b) direct GaAs [25], c) indirect \( 4H\)-SiC [26], and d) direct GaN [27]. The Si and GaAs band structures are characteristic of traditional semiconductors, while \( 4H\)-SiC and GaN band structures are characteristics of next-generation, wide bandgap semiconductors.8

**Figure 2.2**: Different stacking sequences for SiC; (a) top view of the two subsequent stacking options, (b) side view of 3\text{C}-SiC, (c) side view of 4\text{H}-SiC, and (d) side view of 6\text{H}-SiC. .................................................................12

**Figure 2.3**: 3-D schematic representation of the stacking sequence for 3\text{C}-SiC and 6\text{H}-SiC polytypes [33]. ..................................................................................................................13

**Figure 2.4**: Schematic comparison between the ferro-, antiferro-, ferri-, and para-effects for functional electric and magnetic materials after removal of an applied field. The large black arrow designates the direction of the applied field. For electrically functional materials, the arrows represent the electric dipole moment. For magnetically functional materials, the arrows represent the magnetic dipole moment. ...........................................................................................15

**Figure 2.5**: Illustration of a) multifunctional oxide heterostructure schematic on a wide bandgap semiconductor [35], b) TEM of ferroelectric PTO and paraelectric STO heterostructure [36], c) high resolution TEM image showing the shared TiO\text{2} bridging mechanism between the PTO and STO multilayers [36], and d) demonstration by M. Liu, et al. of the coupling between nickel ferrite and PZT [21]. ..................................................................................................................18

**Figure 2.6**: Schematic illustration of BTO polarized in the (001) direction (top row) and (111) direction (bottom row). The polarization potential is greatest in the (001) direction due to the greater displacement of atoms within the crystal. ..........21

**Figure 2.7**: P-E hysteresis loop, which includes saturated polarization (\( P_s \)), remnant polarization (\( P_r \)), and coercive field (\( E_c \)). .....................................................................................................................23

**Figure 2.8**: P-E hysteresis loops for PZT (a) (001), and (b) (111) at different Zr:Ti ratios. The P-E hysteresis loops illustrate the static tenability of functional oxide materials [9]. .....................................................................................................................24

**Figure 2.9**: Schematic illustration of BaM crystal structure [7] with the ideal VSM hysteresis loop for single crystalline BaM in easy and hard direction. The characteristic S shape for magnetization along the easy axis and the diagonal line for magnetization along the hard axis are a result of the high inherent uniaxial magnetic anisotropy..................................................................................................26

**Figure 2.10**: Schematic illustration of 3:2 lattice matching. Three unit cells of the film match the lattice spacing of two unit cells of the substrate. ........................................29
Figure 2.11: Schematic illustration of lattice matching for MgO(111) growth on 6H-SiC(0001) to illustrate the similarities in atomic position of the pseudo-hexagonal (111) on the hexagonal (0001). Because of the similarities in atomic arrangement, cubic MgO prefers to grow in the (111) orientation on hexagonal substrates such as 6H-SiC and GaN.

Figure 2.12: Simplified band structure diagram for the MgO/GaN interface [59] derived from the precise XPS characterization of the VBM and core level emissions. a) XPS core level spectra and VBM of Ga3d, b) XPS core level spectra and VBM of Mg2p, and c) simplified band diagram of the MgO/GaN interface. The Fermi level is represented by the dotted horizontal line, the conduction band is represented by EC, and the valence band is represented by EV.

Figure 2.13: Schematic illustration of basic atomic nucleation of impinging atoms on a substrate through vapor deposition [46]. The circular nucleation site does not represent a liquid phase nucleation but rather is used to illustrate the contact angle between the nucleation island and the substrate surface.

Figure 2.14: Schematic illustrates of the three characteristic growth modes, including Van der Merwe (2-D), Stranski-Kranstanov (2-D → 3-D), and Volmer-Weber (3-D).

Figure 2.15: Illustration of a solid source effusion cell with the labeled variables that impact the atomic flux within the molecular beam [69].

Figure 3.1: Schematic illustration of source flux pulses for growth of alternating PTO and STO layer “superlattice” [36].

Figure 3.2: XRD scan showing the (00l) orientation diffractions for [(PbTiO3)10/((SrTiO3)10)]15 “superlattice” [36].

Figure 3.3: XRD scans of: (a) PZT/Al2O3/4H-SiC, (b) PZT/4H-SiC, and (c) PZT/SiO2/4H-SiC. The * denoted the reflections for the pyrochlore phase of Pb2Ti2O6. As expected, the hexagonal 4H-SiC and Al2O3/4H-SiC surfaces promoted the pseudo-hexagonal (111) orientation of the PZT films.

Figure 3.4: XRD scan of polycrystalline PTO film with no preferred orientation on 4H-SiC via pulsed laser ablation [117].

Figure 3.5: EDS scan showing (a) effectiveness of MgO as an interlayer to prevent diffusion of Pb into Si substrate resulting in more abrupt interfaces between the PZT/MgO and MgO/SiO2 and (b) diffusion of Pb into the Si substrate in the absence of an MgO interlayer [86].

Figure 3.6: Orientation saturation and strain ratio dependence on film thickness for epitaxial PTO grown on MgO [87].

Figure 3.7: Comparison of stresses between PZT and MgO, STO, and KTO; (a) effective lattice strain, (b) lattice/thermal strain ratio, and (c) net elastic strain.

Figure 4.1: Images of a) custom built hydrogen flow furnace, b) Ta foil strip used as the heating element (straight and folded into a boat) and c) furnace during operation with a 6H-SiC sample placed on the Ta-boat.

Figure 4.2: UHV system consisting of two interconnected chambers. The chambers are separated by a UHV compatible gate valve. The growth chamber consists of a remote oxygen atom source, solid source effusion cells (Mg, Ba, Fe), a Ti
sublimator, and RHEED system. The analysis chamber consists of a XPS hemispherical analyzer and an AES single pass CMA.  

Figure 4.3: Illustrations of how RHEED can be used for interpretation of crystal structure, growth rate, and surface features. a) characteristic crystal structure including single crystalline, polycrystalline, 3-D islands, and 2-D layer-by-layer growth (top to bottom, respectively) [143], b) growth rate determination by diffraction spot intensity oscillations for a layer-by-layer growth mode [144], c) diffraction spot shape due to transmission through different sized 3-D features [143], d) Kikuchi lines characteristic of a smooth surface, and d) chevron diffraction characteristic of surface faceting.  

Figure 4.4: Interpretation of RHEED pattern for hydrogen cleaned 6H-SiC(0001) surface. Careful interpretation of the RHEED pattern can reveal a great deal of valuable information regarding the crystal structure, orientation, and surface features.  

Figure 4.5: A schematic illustration of T-Phase EFM characterization. The initial trace (1) scans the surface morphology while the retrace (2) offsets the topology by $\Delta z$ and applies a set voltage bias. When the biased tip passes over a polarized domain, the tip is either attracted or repelled from the surface depending on the direction of the bias voltage.  

Figure 5.1: Representations of a typical as-received, research grade, epi-ready 6H-SiC(0001) two-inch wafer. a) photograph of polished 6H-SiC(0001) orientation, b) RHEED pattern of degreased 6H-SiC(0001)-(1×1) surface, and c) AFM of 6H-SiC(0001) illustrating nanometer deeps scratch due to mechanical polishing.  

Figure 5.2: AES characterization of the Si-terminated (red) and C-terminated (blue) orientations of as-received 6H-SiC. a) Differentiated survey scans illustrating the presence of Si, C, and O. b) Tight (elemental) scans of Si(LMM) Auger transition illustrating the differences in the local bonding environment. The Si orientation has relatively higher Si-O bonding compared to the C orientation, which has relatively higher Si-C bonding. c) Tight scans of C(KLL) Auger transition which show strong C-Si bonding for both orientations, which is inferred from the characteristic W shape.  

Figure 5.3: XPS characterization (Al Kα x-rays) of the Si-terminated (red) and C-terminated (blue) orientations of as-received 6H-SiC. a) Survey scans illustrating the presence of Si, C, and O. b) Tight (elemental) scans of C1s photoemission illustrating the differences in the local bonding environment. The Si orientation has relatively lower C-O bonding compared to the C orientation. c) Tight scans of Si2p photoemission illustrating primarily Si-C bonding. The slight asymmetry at the higher binding energy is due to Si-O bonding, but is not as evident as the C-O bonding due to the smaller chemical shift.  

Figure 5.4: AFM characterization and RMS roughness analysis of the effects of gas flow rate and flow ratio on the surface morphology of 6H-SiC. Blue represents a constant Ar:Hi flow ratio and red represents a constant total gas flow rate. The letters A through I correspond to the parameters listed in table 5.3. The AFM image with the green outline corresponds to the same cleaning procedure performed on the S-terminated orientation.
Figure 5.5: The surface roughness (RMS) of hydrogen cleaned 6H-SiC significantly increases with increased Ar:H₂ volumetric flow ratios. All other variables (temperature, time, heating, cooling) were held constant. .............................................131

Figure 5.6: Boltzmann's energy distribution for argon atoms flowing through the hydrogen furnace. The left image represents typical volumetric flow rates for argon through the furnace. The right image illustrates the entire energy distribution profile. The low kinetic energy of the argon atoms at the flow rates of interest indicates no physical contribution to the 6H-SiC etching mechanism. ..........................133

Figure 5.7: AES characterization and comparison of the Si-terminated and C-terminated orientation before and after hydrogen cleaning. a) Representative survey scans that indicate only Si, C, and O. Note the general change in peak intensities before and after hydrogen cleaning, due to the removal of contaminants and changes in bonding. b) Tight scans of Si(LMM) Auger transitions. The increase in Si-O (70 eV) is seen for the Si-terminated orientation and an increase in Si-C (80 eV) is seen for the C-terminated orientation. c) Tight scans of C(KLL) Auger transitions that indicate an increase in carbide (C-Si) carbon for both orientations. .......................................................136

Figure 5.8: XPS characterization and comparison of the Si-terminated and C-terminated orientation before and after hydrogen cleaning. a) Representative survey scans that indicate only Si, C, and O. Note the general change in peak intensities before and after hydrogen cleaning, due to the removal of contaminants and changes in bonding. b) Tight scans of C1s photoemission. The decrease in C-O bonding is seen for both orientations. The C-terminated orientation results in a C-H terminated surface after hydrogen cleaning (bright blue). c) Tight scans of Si2p photoemission indicating primarily Si-C bonding for both orientations. For the Si-terminated orientation, The slight asymmetry at the higher binding energy is due to Si-O surface adlayer bonding. ..........................138

Figure 5.9: Structural characterization by RHEED of Si-terminated 6H-SiC before (top) and after (bottom) hydrogen cleaning. The (1×1) pattern characteristic of as-received 6H-SiC is transitioned to a silicat e adlayer reconstruction with a √3×√3 R30° structure. The adlayer structure is characterized by the formation of fractional Laue rings at L1/3 and L2/3. The AFM image is used to define the corresponding directions of the incident electron beam .........................................................140

Figure 5.10: Structural characterization by RHEED of C-terminated 6H-SiC before (top) and after (bottom) hydrogen cleaning. The (1×1) pattern characteristic of as-received 6H-SiC is maintained even after hydrogen cleaning. The AFM image is used to define the corresponding directions of the incident electron beam. ..............................................................................................141

Figure 5.11: Schematic representation for the reconstruction of the √3×√3 R30° adlayer relative to bulk 6H-SiC. a) Top view of the simplest repeating unit of the 6H-SiC structure with appropriate atomic spacings. b) Top view of the hexagonal array for 6H-SiC. c) Designation of the silicon atoms (yellow) responsible for the √3×√3 R30° reconstruction. d) Top view of the silicon atoms of the √3×√3 R30° reconstructed hexagon. Note the 30° rotation between the reconstructed hexagon and the bulk hexagon. e) Top view of entire √3×√3 R30°
silicate adlayer reconstruction overlaid on 6H-SiC.

f) Side view of entire $\sqrt{3}\times\sqrt{3} R30^\circ$ silicate adlayer reconstruction on 6H-SiC along the [11 2 0] direction.

**Figure 5.12:** Strain contrast, cross-sectional TEM image of hydrogen cleaned 6H-SiC(0001). The characteristic ABCACBA stacking sequence that makes up the 6H-SiC polytype is clearly visible. The substrate is atomically flat, but could not resolve the silicate adlayer reconstruction.

**Figure 5.13:** The morphology and crystal structure of MgO is influenced by magnesium flux and substrate orientation. The left set corresponds to MgO grown on Si-terminated 6H-SiC, where increased Mg flux results in conformal, single crystalline MgO. The right set corresponds to MgO grown on C-terminated 6H-SiC, where an increase in Mg flux increases the crystallinity, but results in a poor morphology [149].

**Figure 5.14:** Under a constant oxygen (combination of O and O$_2$) environment and constant substrate temperature of 140 °C, an increase in magnesium flux linearly increases the MgO growth rate. This supports a magnesium absorption controlled growth mechanism. However, the non-zero intercept indicates a faster nucleation rate than growth rate. The magnesium absorption controlled growth mechanism was observed for both SiC orientations [88].

**Figure 5.15:** AFM characterization of MgO nucleated and grown under various oxygen environments [88]. For all samples, the magnesium fluence and substrate temperature was held constant. Figures (a) through (d) correspond to samples 1 through 4, respectively. a) O and O$_2$ at a photomultiplier reading of 35 mV, b) molecular oxygen, c) O and O$_2$ at a photomultiplier reading of 35 mV for 1 minute followed by 4 minutes of molecular oxygen, d) exposure to O and O$_2$ at a photomultiplier reading of 35 mV for 1 minute with no magnesium flux followed by 5 minutes of Mg and molecular oxygen.

**Figure 5.16:** Proposed mechanisms for the nucleation of MgO in the presence of atomic oxygen (a) and molecular oxygen (b). The presence of atomic oxygen results in a 2-D nucleation and growth mechanism.

**Figure 5.17:** The epitaxy alignment possibilities for single crystalline MgO(111) on 6H-SiC(0001) with a $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction. a) MgO(111) can be in tension (red) with a 3.3% mismatch or in compression (blue) with a 10.5% mismatch. b) XRD $\theta$-2$\theta$ scan illustrating only pseudo-hexagonal epitaxy of MgO.

**Figure 5.18:** RHEED characterization of the epitaxial alignment of MgO on 6H-SiC(0001) with a $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction. a) Schematic representation of 6H-SiC(0001) with a $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction in real space. b) Schematic representation of the reciprocal space translation of 6H-SiC(0001) with a $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction. c) Predicted RHEED pattern for 6H-SiC(0001) with a $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction and the actual observed RHEED pattern. d) RHEED pattern for MgO(111) deposited on the 6H-SiC(0001) surface illustrating the preferred tensile epitaxial alignment.

**Figure 5.19:** ARXPS comparison of the OH/MgO ratio determined from the O1s photoelectron spectra indicating the OH surface termination of MgO films.

**Figure 5.20:** Characterization of the twinned MgO(111) crystal structure. a) RHEED images illustrating the onset and pronounced twinned features as MgO film
thickness increases [49]. The red box highlights the diffraction characteristic associated with a twinned structure. b) Cross-sectional schematic illustrating the stacking sequence of ideal, un-twinned MgO(111). c) Cross-sectional schematic illustrating the stacking sequence of twinned MgO(111). d) Schematic representation of two possible stacking sequences that are responsible for twinned MgO. Each ball (red and blue) represents a different Mg-O stack and rotational symmetry.

**Figure 5.21:** RHEED characterization of MgO(111) with a simulated 30° in-plane rotation (a – c) and observed 30° in-plane rotation for 50 nm MgO (f and g). a) RHEED pattern of 10 nm MgO(111) along <110> incident angle, b) RHEED pattern of 10 nm MgO(111) along <112> incident angle, c) superimposed image of RHEED patterns along the <110> and <112> incident angles of 10 nm MgO(111), d) identification of diffraction locations for superimposed image, e) identification of diffraction locations for 50 nm MgO(111), f) RHEED pattern of 50 nm MgO(111) along <110> incident angle, and g) RHEED pattern of 50 nm MgO(111) along <112> incident angle.

**Figure 5.22:** Cross-sectional TEM characterization of 20 nm MgO/6H-SiC(0001) indicating the transition from a 2-D growth mode to a 3-D columnar growth mode occurring at a thickness ~ 5 nm. Typical RHEED patterns are inserted to illustrate the transition from the higher quality, thin MgO (< 5 nm, red box), to thicker 3-D MgO (20 nm, blue box). The 3-D features are ~ 3 nm in size and below the detection limit of AFM (tip radius of curvature of 10 nm). The observed horizontal lattice fringes of 6H-SiC and MgO correspond to the out-of-plane lattice spacings of 6H-SiC(0001) and MgO(111), respectively [49].

**Figure 5.23:** schematic representation of the Stranski-Krastanov growth mode of MgO(111) on 6H-SiC. The initial nucleation and growth follows a 2-D growth mode, which transitions to a 3-D growth mode at a MgO thickness of 5 nm.

**Figure 5.24:** XPS tight scans of Si2p spectra for the four MgO samples that were exposed to different temperature and oxygen conditions. The increase in SiOx indicates a breakdown at the MgO/6H-SiC interface [48].

**Figure 5.25:** Thickness comparison of the MgO loss and SiOx formation after exposure to various elevated temperature and oxygen conditions. The decrease in MgO and increase in SiOx supports and etching/formation mechanism that requires available atomic oxygen and high temperatures [48].

**Figure 5.26:** MgO/6H-SiC interface breakdown increases significantly with increased temperature, indicating a kinetically controlled formation mechanism. The SiOx formation is dependent on both available atomic oxygen and temperature [48].

**Figure 5.27:** RHEED pattern for; a) hydrogen cleaned 6H-SiC(001) with a $\sqrt{3} \times \sqrt{3}$ R30° surface reconstruction, b) as-deposited MgO(111) with slight indication of 3-D features, and c) 3-D to2-D transition as indicated by the smoother, streaky pattern after heating to 650 °C. All RHEED images were collected at room temperature. L0 represents the zeroth Laue zone [48].

**Figure 5.28:** XPS characterization of the O1s spectra and corresponding RHEED pattern for MgO films [48, 49]; a) as-deposited MgO, b) MgO deposited at 140 °C then heated to 650 °C in vacuum (1.0×10⁻⁹ Torr), and c) MgO deposited at
650 °C. The decrease in OH and streakier RHEED patterns indicate a smoother MgO surface when heated or deposited at 650 °C.

**Figure 5.29:** XPS characterization used to determine the band offsets at the MgO/6H-SiC interface. a) Survey scan used to determine scaling and charge reference, b) valence band spectra illustrating the difference in valence states of 6H-SiC (red), 5 nm MgO (blue), and 10 nm MgO (green), and c) demonstration of precise VBM determination for 6H-SiC based on the method developed by Kraut, et al. [60, 61] and refined by Chambers, et al. [62].

**Figure 5.30:** Simplified band structure of the MgO/6H-SiC interface. The majority of the offset is seen in the conduction band, with an offset of 3.27 eV. The large conduction band offset makes it ideal for high frequency switching applications due to reduced tunneling currents.

**Figure 5.31:** C-V curves for MgO/6H-SiC parallel plate capacitor [129]. a) Characteristic depletion (negative bias) and accumulation (positive bias) curve for an n-type capacitor, b) hysteresis behavior with a width of ~0.8 V. The combination of frequency dependence and hysteresis behavior indicate the presence of interface state.

**Figure 5.32:** Inverse capacitance curve used to determine the dielectric constant of the MgO. The slope of the line is directly related to the dielectric constant (equation 5.8). The non-zero intercept indicates a series capacitor and the equivalent of 1.3 nm of SiO2 [129].

**Figure 5.33:** Typical leakage current measurement for an MgO/6H-SiC parallel plate capacitor. Histogram analysis of the breakdown statistics for the twenty-seven capacitors found the median breakdown voltage at 12 MV/cm [129].

**Figure 5.34:** AFM and XRD characterization of BTO deposited on 2.5 nm MgO/6H-SiC. The resulting film was 3-D with an RMS of 2.6 nm over a 1 µm² area but only (111) oriented, demonstrating the effective heteroepitaxy of BTO on MgO/6H-SiC.

**Figure 5.35:** Characterization and demonstration of the effectiveness of MgO as a heteroepitaxial template for BST on 6H-SiC. Column (a) represent BST deposited on 6H-SiC, which resulted in an amorphous 3-D film. Column (b) represents BST deposited on 2.5 nm MgO/6H-SiC, which resulted in only (111) oriented BST with macroscopic conformal growth to the stepped 6H-SiC surface but small 3-D features. Column (c) represents BST deposited on 10 nm MgO/6H-SiC, which also resulted in only (111) oriented BST with macroscopic conformal growth to the stepped 6H-SiC surface but small 3-D features. The top row is the GADDS image, the middle row is the θ-2θ line profile along the dotted blue line, and the bottom row represents the corresponding surface morphology. The single RHEED image is characteristic of BST(111).

**Figure 5.36:** a) Determination of a rough operating window for obtaining stoichiometric BTO by varying the Ti flux, which is limited to 0.5 A intervals on the power supply. Stoichiometric BTO lies between operating currents of 40.5 A and 41 A. b) XPS characterization of the BTO films indicates a lower binding energy shoulder for titanium rich films, which corresponds to excess TiO.
Figure 5.37: RHEED characterization of the crystal structure of BTO films grown on MgO/6H-SiC with various Ba/Ti stoichiometric ratios, as determined by XPS. As the Ba/Ti ratio deviates from 1.0 the resulting crystal structure becomes polycrystalline (Ba/Ti = 1.2 or 0.8) or amorphous (Ba/Ti = 1.4 or 0.6)...

Figure 5.38: RHEED sequences used to characterize the effectiveness of MgO(111) as a template layer for the heteroepitaxy of BTO(111) [48]. a) RHEED sequence of amorphous BTO deposition on 6H-SiC without a MgO template layer. b) RHEED sequence of heteroepitaxy of BTO on 6H-SiC with a 2.5 nm MgO template layer. c) XRD θ-2θ scans illustrating only (111) oriented BTO...

Figure 5.39: schematic representation of; a) 6-fold symmetry of the pseudo-hexagonal structure of MgO(111), and b) pseudo 6-fold symmetry of BTO(111). The numbered lines represent the planes of symmetry...

Figure 5.40: Interpretation of RHEED pattern characteristic of BTO(111). a) Characteristic RHEED pattern taken along the <110> incident angle. b) Larger image of the zeroth Laue Zone illustrating transmission dominated pattern. c) Identification of diffraction maxima. d) Reciprocal space model of BTO(111) illustrating two possible 60° rotational options. e) Correlation between the characteristic RHEED pattern of BTO(111) and the corresponding reciprocal space model. The reciprocal space model in part (e) is a combination of the two models illustrated in part (d)...

Figure 5.41: Epitaxy alignments for BTO(111) on 6H-SiC (a) and MgO/6H-SiC (b). For all epitaxy alignments, the green atoms represent tensile mismatch and the yellow atoms represent compressive mismatch. The direction references are relative to the surface structure of either 6H-SiC (a) or MgO (b)...

Figure 5.42: AFM and RHEED characterization of BTO deposited on MgO/6H-SiC at 650 °C at a rate of 0.5 nm/min [49]. The images correspond to different BTO thicknesses of; a) 1 nm, b) 3 nm, c) 10 nm, and d) 60 nm...

Figure 5.43: AFM and RHEED characterization of 60 nm BTO(111) deposited on MgO/6H-SiC at 650 °C (a) and 750 °C (b). The increase in substrate temperature increased surface mobility resulting in larger and fewer nucleation sites [49]...

Figure 5.44: AFM and RHEED characterization of 60 nm BTO(111) deposited at; a) 0.5 nm/min and 35 mV oxygen plasma, and b) 1.0 nm/min and 125 mV oxygen plasma. The increase in growth rate is due to the increase in TiO₂ formation at the increased oxygen plasma, and appropriately increasing the Ba flux to reestablish stoichiometry...

Figure 5.45: EFM characterization of 60 nm BTO(111) deposited on MgO/6H-SiC. a) morphology of BTO consists of stepped surface conformal to the underlying 6H-SiC, b) EFM with -10 V bias, c) EFM with -5 V bias, d) EFM with 0 V bias, e) EFM with 5 V bias, f) EFM with 10 V bias. For all EFM images, the z-scale was fixed at 0 – 70 a.u. and a tip offset (∆z) of 25 nm...

Figure 5.46: Line profile scans of BTO(111) comparing the domain structure at bias voltages of +10 V (red) and -10 V (blue). Because the BTO domains are static, opposite bias voltages should result in inverse line profiles...
**Figure 5.47:** Schematic representation of the horizontal discontinuity (vertical mismatch) for oxide integration of 6H-SiC that results from the different out-of-plane lattice spacing between the 6H-SiC, MgO, and BTO. 

**Figure 5.48:** a) P-E hysteresis characterization of 300 nm BTO(111) on MgO/6H-SiC. At positive electric field, the polarization is characteristic of ferroelectric BTO, while the negative electric field is characteristic of the dielectric properties of 6H-SiC. b) Close-up of the onset of leakage. The black solid line exaggerates the effect. c) Schematic of BTO/MgO/6H-SiC heterostructure. 

**Figure 5.49:** Leakage measurement for BTO/MgO/6H-SiC. The breakdown voltage (red dashed line) corresponds to an applied field of ~700 kV/cm. 

**Figure 5.50:** P-E hysteresis illustrating only the ferroelectric contribution of the BTO/MgO/6H-SiC structure. The positive applied field corresponds to polarization measurements obtained on the top Cu electrode. The negative applied field remains characteristic of MgO/6H-SiC. 

**Figure 5.51:** Determination of saturated polarization of BTO(111) deposited on MgO/6H-SiC after the removal of all dielectric and leakage contributions. 

**Figure 5.52:** Surface morphology characterization by AFM of; a) ferroelectric BTO(111) template layer, b) subsequent BaM layer, and c) zoomed in image of BaM surface. 

**Figure 5.53:** VSM characterization of BaM/BTO/MgO/6H-SiC heterostructure. Magnetization in the parallel (red) and perpendicular (blue) directions are similar in shape, indicating a lack of uniaxial anisotropy. 

**Figure 7.1:** Schematic illustration of two possible induction coil configurations; a) vertical configuration for real time temperature measurement, but restricted H₂ flow, and b) horizontal configuration for unobstructed H₂ flow but restricted temperature measurement. The stand will be made of molybdenum, tantalum, tungsten, or pyrolytic carbon. 

**Figure 7.2:** TEM and EELS characterization can be used to help determine the interface bonding states of the multilayers and the formation of an oxygen bridge. a) TEM of MgO/6H-SiC. The red line represents the EELS analysis location. b) EELS spectra O-K in MgO. c) EELS spectra of Kg-K in MgO. d) EELS spectra of O-K in STO at different oxygen vacancies (δ) [156]. The distinction between O-K spectra may be a useful tool for determination and characterization of an oxygen bridge formation.
# List of Tables

**Table 2.1:** Comparison of the electrical properties of Si, 6H-SiC [30, 32], and GaN [31]. ........................................................................................................................................9

**Table 2.2:** Thermal expansion coefficients at room temperature for wide bandgap semiconductors 6H-SiC and GaN, dielectric MgO, ferroelectric BTO and BST, and ferrimagnetic BaM. The units for the thermal expansion coefficients are ppm/K. .........................................................................................................................32

**Table 3.1:** Lattice constant and thermal expansion coefficient comparison of PTO compared with bulk MgO, STO, and KTO at room temperature and c700 °C [126]. ........................................................................................................................................75

**Table 4.1:** A list of Auger electron emission energies and sampling depths for selected elements that are of interest for this dissertation. ...........................................................................................................98

**Table 4.2:** A list of photoelectron energies and sampling depths for selected elements that are of interest for this dissertation. ........................................................................................................100

**Table 5.1:** Compositional analysis of the Si-terminated and C-terminated orientation by AES and XPS. .................................................................................................................................122

**Table 5.2:** System limitations for each independent variable of the hydrogen flow furnace. Note that temperature, heating rate, and cooling rate are not independent variable, but rather dependent on the current a width of the Ta boat. ................................................................123

**Table 5.3:** A list of gas flow rates and volumetric flow ratios used for hydrogen cleaning of 6H-SiC. Blue represents a constant Ar:H₂ flow ratio and red represents a constant total gas flow rate. The letters A through I correspond to AMF characterization illustrated in figure 5.4. ..................................................................................128

**Table 5.4:** A list of temperature and oxygen exposure conditions for evaluating the stability of the MgO/6H-SiC interface. ..................................................................................................................175

**Table 5.5:** List of binding energies determined by core level emissions and VBM spectra collected by XPS. These values were used to determine the band offsets at the MgO/6H-SiC interface. ..................................................................................................195

**Table 5.6:** List of important ferroelectric properties that were extracted from P-E hysteresis characterization of BTO/MgO/6H-SiC at various voltage biases. ..........241

**Table 5.7:** Comparison of ferroelectric properties of the BTO/MgO/6H-SiC structure with ferroelectric properties of BTO(111) reported in literature. .................................242
1.0 Introduction

In recent years functional oxide materials, including barium titanate (BTO), barium strontium titanate (BST), bismuth ferrite (BFO), lead titanate (PTO), lead zirconate titanate (PZT), and hexagonal barium ferrite (BaM), have attracted much attention for a wide range of sensory and communication devices because of their unique electrical and magnetic properties. Both military and consumer needs demand increasingly smaller, more efficient, portable components that can be integrated into a single, multifunctional heterostructure for a new generation of materials and functionality. Current devices are often confined to a single functionality and are limited by the performance of both the silicon based substrate and the properties of the functional material. As a result, multiple components with a single functionality need to be independently integrated into a single, large, inefficient device. In order to meet the demands and requirements for a new generation of multifunctional heterostructure devices, new novel materials and substrates need to be incorporated. These requirements encourage the development and integration of multifunctional and multiferroic oxide heterostructures on wide bandgap semiconductors, such as silicon carbide (SiC) or gallium nitride (GaN).

By integrating functional oxides on a wide bandgap semiconductor, such as hexagonal silicon carbide (6H-SiC) or GaN, next-generation device architectures can be developed for high-temperature, high-power, high-frequency applications where existing silicon-based electronics breakdown. The concept of multifunctional heterostructures and multiferroics (discussed in further detail in section 2.3) is best illustrated through a tie
diagram, which is used to correlate the multifunctionality of a material by its inherent properties. A representation of a tie diagram is illustrated in figure 1.1.

![Tie Diagram](image)

**Figure 1.1**: Tie diagrams first developed by Heckmann in 1925 and later refined by Nye in 1957 used to represent the relationships between different functional properties of a material [1, 2]. Where E = electric field, T = temperature, H = magnetic field, D = displacement, M = magnetization, S = entropy, ε = strain, and σ = stress.

A true multiferroic (bismuth ferrite, BFO) is inherently multifunctional in the sense that it exhibits two or more functional ferro-properties. However, through materials engineering and careful material selection, multilayers of functional oxides can coupled together into a multifunctional heterostructure.

The goal of this dissertation is to demonstrate the successful integration and characterization of functional oxides and a functional oxide heterostructures on 6H-SiC. In order for success, specific objective must be completed. These objective included; effective cleaning and preparation of the starting 6H-SiC surface, heteroepitaxial integration of various functional oxides on the 6H-SiC, integration of a multilayered heterostructure, and the characterization of the functional properties of the oxide layers. Each oxide layer needs to be of high quality and have a smooth surface, which will
ultimately act as an abrupt interface when integrated with the subsequent deposition of an additional functional oxide. The successful demonstration of a multilayered heterostructure on SiC would contribute to the progress towards the development and optimization of a next-generation, multifunctional device.
2.0 Background

Within the past decade, the demand for a new generation of functional materials has progressed to include novel functional oxides, such as perovskite ferroelectrics (BTO, BST, BFO, PTO, PZT) and hexagonal ferrites (BaM). These functional oxides by themselves have many applications such as ultrasonic transducers, field-effect transducers (FET) [3], volatile and non-volatile random access memory (RAM) [4], microelectromechanical systems (MEMS) [5], circulators, and microwave monolithic integrated circuits (MMIC) [6, 7]. Although the functional properties of these materials have been optimized for the specific device application, their functionality and intrinsic properties have not been integrated into a multifunctional heterostructure with tunable electric and magnetic properties. The functional properties of the different oxide materials can be controlled by various means, including stoichiometry [8-11] and induced lattice strain [12-15]. Further, by coupling the properties of individual materials into a multilayered structure, it is possible to create a heterostructure where the properties of one layer can directly influence the properties of the second layer [8, 16-23] giving rise to a complex, tunable, multifunctional device.

In order to progress towards a new generation of functional devices, it is also necessary to consider replacement semiconductor substrates to succeed the silicon-based semiconductor substrates. Although silicon is considered the benchmark semiconductor for existing technologies, its intrinsic properties do not meet the requirements and demands for next-generation devices, which require high-power, high-frequency
applications. These issues can be met by replacing the silicon substrates with wide bandgap semiconductors, such as SiC and GaN.

Before next-generation multifunctional devices can be realized, there are many challenges that must be overcome. These challenges include substrate surface preparation, the heteroepitaxial growth of the functional oxides, and the coupling of the functional properties between the individual multilayers. In order to address these issues, it is necessary understand the functional properties of each material and how they are affected by different variables including crystal structure, stoichiometry, temperature, lattice strain, electric fields, and magnetic fields. Through this understanding, it will be possible to engineer a multifunctional heterostructure on a wide bandgap semiconductor that meets the objectives that are required for the end goal of a tunable next-generation device.

2.1 Semiconductors

Semiconductors are materials that exhibit properties similar to both conductors and insulators. However, semiconductors differ from conductors and insulators in their band structure. Band structures are comprised of a conduction band and a valence band. The energy difference between the valence band and conduction band is referred to as the bandgap energy ($E_g$).

For insulators, the electrons in the valence shells form strong bonds between atoms, which typically results in a large bandgap (5 – 10 eV) between the valence band and conduction band. As a result, external energy is required to excite an electron form the valence band to the conduction band. This external energy can be supplied from
different sources including an applied electric field, elevated temperature, or photon excitation. In addition, once the electrons have been excited from the valence band to the conduction band, the transport properties of an insulator result poor electron and hole mobility. Therefore, insulating substrates are not typically used for device applications.

Conductors however, have no bandgap because the valence band and conduction band overlap. Therefore, the conduction band naturally contains electrons and is free to conduct. However, an external source is still required for the transport and conduction of electron.

Semiconductors have properties analogous to both conductors and insulators. Similar to insulators, the valence band and conduction band do not overlap. Traditionally, the badgap of a semiconductor is less than 5 eV. However, more importantly is the intrinsic transport properties of the material once the electrons have been excited form the valence band to the conduction band. Unlike insulators, semiconductors have high electron and hole mobility once the electrons are free to conduct. This property is similar to the transport property of a conductor. Due to the presence of a bandgap, all semiconductors can be considered pseudo-insulators because they do not conduct at room temperature without external excitation.

Semiconductors can be further classified based on their physical and electrical properties. In general, a semiconductor is either a narrow bandgap semiconductor, such as Si ($E_g = 1.11$ eV) and GaAs ($E_g = 1.43$ eV) or a wide bandgap semiconductor, such as SiC ($E_g = 3.03$ eV) and GaN ($E_g = 3.39$ eV). Although there is no defining bandgap classification between narrow bandgap semiconductors and wide bandgap semiconductors, materials that have bandgap energies greater than ~ 2 eV are typically
considered to have a wide bandgap. Depending on the band structure, the semiconductor (narrow or wide) has either a direct or and indirect band structure.

2.1.1 Direct and indirect bandgap semiconductors

As the name imply, a direct bandgap has a direct transition from the valence band maximum to the conduction band minimum. The direct band structure enables the electrons in the conduction band minimum to combine with holes in the valence band maximum. For an indirect bandgap, the transition between the valence band maximum and conduction band minimum is offset. The offset band structure requires additional assistance, typically in the forma of a phonon or crystal defect, for electron-hole combination. Figure 2.1 illustrates the actual band diagrams for Si (indirect, narrow), GaAs (direct, narrow), 4H-SiC (indirect, wide), and GaN (direct, wide).
Figure 2.1: Band diagrams for a) indirect Si [24], b) direct GaAs [25], c) indirect 4H-SiC [26], and d) direct GaN [27]. The Si and GaAs band structures are characteristic of traditional semiconductors, while 4H-SiC and GaN band structures are characteristics of next-generation, wide bandgap semiconductors.

2.1.2 Wide bandgap semiconductors

Wide bandgap semiconductors are semiconductors that have a bandgap energy typically greater than 2 eV. Because wide bandgap semiconductors have larger bandgap energies, they are capable of operation under harsher ambient conditions. This makes them of particular interest for high-power, high-temperature, high-frequency applications.
The two wide bandgap semiconductors that are of interest for devices are SiC and GaN. SiC is an indirect wide bandgap semiconductor that has many different polytypes, which have different structural and semiconducting properties. The SiC polytype nomenclature is used to classify the differences in the crystal structure and stacking sequence of the covalently bonded SiC tetrahedrons. The three most common polytypes for SiC are 3C-SiC, 6H-SiC, and 4H-SiC. Further explanation of the different SiC polytypes will be discussed later in section 2.1.3.

GaN differs from SiC in that it is a direct bandgap semiconductor comprised of alternating layers of ionically bonded gallium and nitrogen. The ionicity of the alternating layers results in a polar surface, which requires thermodynamic stabilization. Although both SiC and GaN offer superior electrical and mechanical properties over silicon, for high-frequency device applications, GaN is superior to SiC due to its superior electron mobility, hole mobility, and electric breakdown field [30-32]. Table 2.1 compares some basic properties of Si, 6H-SiC, and GaN.

**Table 2.1**: Comparison of the electrical properties of Si, 6H-SiC [30, 32], and GaN [31].

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>6H-SiC</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>1.12</td>
<td>3.03</td>
<td>3.39</td>
</tr>
<tr>
<td>Electric Breakdown Field (kV/cm)</td>
<td>300</td>
<td>2500</td>
<td>5000</td>
</tr>
<tr>
<td>Electron Mobility (cm²/V s)</td>
<td>1500</td>
<td>500</td>
<td>1000</td>
</tr>
<tr>
<td>Hole Mobility (cm²/V s)</td>
<td>600</td>
<td>101</td>
<td>200</td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm K)</td>
<td>1.5</td>
<td>4.9</td>
<td>1.3</td>
</tr>
<tr>
<td>JFOM†</td>
<td>1</td>
<td>400</td>
<td>728</td>
</tr>
<tr>
<td>BFOM‡</td>
<td>1</td>
<td>29</td>
<td>133</td>
</tr>
</tbody>
</table>

† Johnson’s Figure of Merit: for high-power, high-frequency, discrete amplifiers [29]
‡‡ Baliga’s Figure of Merit: for high-power, high-frequency, unipolar switches [28]

The properties listed in table 2.1 characterize the semiconducting behavior of each material. The electric breakdown field is the maximum magnitude of applied electric
field before the conducting properties of a semiconductor begins to breakdown. Breakdown is defined by the exponential increase in the conducting properties of the material, which are often a result of permanent structural damage. Semiconductors with higher electric breakdown fields can operate under higher applied operating voltages. Electron mobility is used to describe how strongly the motion of an electron is influenced by an applied electric field. Although the dimensions of mobility appear to be related to area (cm²), it is actually defined as the drift velocity (cm/s) divided by the electric field (kV/cm). The motion of the electrons is in the opposite direction of the applied field. Hole mobility is analogous to the electron mobility. However, the motion of the holes is in the same direction as the applied electric field and they typically have much slower drift velocities than electrons under the same applied electric field. Thermal conductivity is used to determine how readily the semiconductor can dissipate heat through conduction. This is particularly important for high current density application where significant amounts of heat are generated.

Both the Johnson’s Figure of Merit (JFOM) [29] and Baliga’s Figure of Merit (BFOM) [28] are used as a basis for comparison of how various semiconductors compare to Si, which is considered to be the standard of the semiconductor industry. Both FOM’s are based on intrinsic electrical properties of the semiconductors. The JFOM takes into account the breakdown voltage and saturated electron drift velocity and relates to high-power, high-frequency, discrete amplifiers. The BFOM takes into account the relative permittivity, electron mobility, and electric breakdown field and relates to high-power, high-frequency, unipolar switches.
The physical and electrical properties of both SiC and GaN, when compared to Si, indicate the enhanced performance of wide bandgap semiconductors and how they can be implemented into a more robust device capable of handling more extreme conditions. The increased electric breakdown field, thermal conductivity, and saturated electron drift velocity contribute to SiC and GaN being more compatible with high-power, high-frequency applications. Incorporating wide bandgap semiconductors into communication, electronic, or sensory applications, results in higher power, higher frequency devices that are of particular interest for military, aerospace, and commercial applications.

2.1.3 Silicon carbide polytypes

Silicon carbide is an indirect, wide bandgap semiconductor that has over two hundred different polytypes. The most popular polytypes of SiC are 6H-SiC, 4H-SiC, and 3C-SiC. With this nomenclature, the number designates the number of atomic stacks per unit cell, and the letter designates the crystal structure. An atomic stack is defined as one SiC tetrahedron. For example, 6H-SiC has six stacked tetrahedrons per unit cell, which are arranged in a hexagonal (H) structure. Other crystal structures include cubic (3C-SiC) and rhombohedral (15R-SiC). The stacking sequence can be as high as twenty-one atomic layers per unit cell. Figure 2.2 below illustrates the difference in stacking sequence between 3C-, 4H-, and 6H-SiC. Using spheres to designate one SiC tetrahedron, there are three stacking options per row. For general characterization, the nomenclature A, B, and C are used. With a base layer, A, the two subsequent stacking options are B or C. Assuming the second layer consists of B, the two stacking options for the next layer will be A or C.
Figure 2.2: Different stacking sequences for SiC; (a) top view of the two subsequent stacking options, (b) side view of 3C-SiC, (c) side view of 4H-SiC, and (d) side view of 6H-SiC.

The repeating pattern of tetrahedrons is responsible for the numerous polytypes of SiC, enabling different electrical properties for different structures of SiC. The basic repeating pattern for 3C-, 4H-, and 6H-SiC are designated as ABCABC, ABCBABC, and ABCACBA, respectfully. The atomic arrangement and stacking sequence are also responsible for the crystal structure of the polytype. Figure 2.3 [33] below illustrates the different 3-D stacking sequence of 3C-SiC and 6H-SiC. The black dots represent the carbon atoms and the hollow dots represent the silicon atoms.
Figure 2.3: 3-D schematic representation of the stacking sequence for 3C-SiC and 6H-SiC polytypes [33].

Although there are many different SiC polytypes, only a few are being considered for next-generation, wide bandgap semiconductor substrates. This is in part due to their commercial availability and quality. Currently, only 6H- and 4H- polytypes are commercially and of suitable quality for device integration. Both of these polytypes are similar in crystal structure (hexagonal) and semiconducting properties. Therefore, 6H-SiC and 4H-SiC substrates are readily available and capable of meeting the demands of next-generation devices when integrated into a multifunctional heterostructure.

2.2 Functional oxides

The properties of functional oxides are sensitive to changes in their environment, which makes them ideal candidates for a new generation of sensors and dynamic devices. Such changes include temperature, mechanical stress, electric field, or magnetic field.
When integrated with a semiconductor, it is possible to utilize the properties and functionality of the oxide films for various communication and sensory devices. To further advance the performance and functionality of these oxides for next-generation devices, it will necessary to integrate multiple oxide layers onto a wide bandgap semiconductor and couple their functional properties for multifunctional purposes.

There are many different types of functional oxides with a wide range of electrical and magnetic properties. A few examples include ferro-, antiferro-, ferri-, and para-electrics and magnetics, piezoelectrics, and pyroelectrics. The prefix ferro- is used to describe a material that exhibits hysteresis properties (magnetization or polarization) and has the ability to maintain a permanent moment (magnetic or electric) in the absence of an applied field. The prefix antiferro- relates to a material that has no net moment, due to an equal number of moments in opposite directions. Ferri- refers to a material that consists of both ferro- and antiferro- components but is still able to maintain a permanent moment in the absence of an applied field. Para- refers to a material that contains a moment in the presence of an external field, but does not maintain a moment once the field is removed. A schematic of the ferro-, antiferro-, ferri, and para- effects after the removal of an applied field are illustrated in figure 2.4.
Figure 2.4: Schematic comparison between the ferro-, antiferro-, ferri-, and para- effects for functional electric and magnetic materials after removal of an applied field. The large black arrow designates the direction of the applied field. For electrically functional materials, the arrows represent the electric dipole moment. For magnetically functional materials, the arrows represent the magnetic dipole moment.

The prefixes piezo- and pyro- are terms used to describe materials that are sensitive to mechanical stress and temperature, respectively. All ferroelectrics are inherently piezoelectrics and pyroelectrics. However, not all piezoelectrics and pyroelectrics are necessarily ferroelectrics [34]. Further explanation of the ferroelectric effect is discussed in section 2.4.1. The functional properties of interest for the objective of this dissertation are ferroelectric BTO and BST, and ferrimagnetic BaM. Although BTO and BST have similar structures and properties, the presence of strontium introduces a paraelectric component at room temperature, in the form of STO, to the inherent ferroelectric nature of the BTO. Depending on the atomic arrangement and stoichiometry of a functional oxide film, it is possible to manipulate and tune the various functional properties to meet the application requirements of a specific application.
2.3 Multiferroics and multifunctional oxides

Interest in multiferroic and multifunctional oxide structures is motivated by the concept of engineering the functional properties of a single device architecture to perform in a variety of situations and applications, which would otherwise require the use of multiple devices. The relationships between various functional properties within a crystal were first illustrated by Heckmann in 1925 [1] and then later refined by Nye in 1957 [2]. Figure 1.1 in the introduction section illustrates the tie line relationships between the thermal, electrical, and mechanical properties of a typical ferroelectric material. As indicated in the figure, temperature, stress, and electric field are all related through different effects, which can be utilized to engineer and tune the functionality of a material in order to optimize the device capability. The relationship can be extended to include the relationship between electric and magnetic properties in such materials as BFO, which is both ferroelectric and ferromagnetic.

The concept of multiferroics and multifunctionalities is to optimize the inherent coupling between different functional properties within a material or multilayer. Continuing with the example of BFO, since BFO is ferroelectric, it is also inherently piezoelectric. Therefore, by applying an external electric field, the crystal will undergo mechanical stress (piezo response) within the lattice. This stress and deformation will then impact the ferromagnetic properties. The result is a multifunctional material whose magnetic properties can be tuned and optimized through the application of an electric film. Inversely, the electrical properties of BFO can be tuned by the application of an external magnetic field.
True multiferroic materials are defined as materials that have two or more of the ferro- properties. Due to the limited number of traditional multiferroic materials, exceptions have been made that now classify materials that are both ferro- and antiferro- to be considered multiferroic. By the modified convention, a whole class of perovskite materials (including PZT) and hexagonal BaM can be considered multiferroic. Multiferroic materials are of particular interest because of their intrinsic functionality, which are inherently coupled. However, with true multiferroic materials, the material and functionality is limited to the intrinsic couple effects. The narrow range of tunable parameters (stoichiometry) and lack of true multifunctionality, traditional multiferroic materials do not offer the level of tuning (dynamic or static) necessary next-generation, multifunctional applications.

An alternative to multiferroic materials is the idea of a multifunctional heterostructure, where multiple layers of functional materials are integrated into a single device. However, in order for a heterostructure to be multifunctional, it is necessary to engineer the coupling between the individual functional films. BTO is a ferroelectric/piezoelectric. By applying an electric field across the BTO, the crystal with undergo mechanical strain (piezo response). By integrating a magnetic material (BaM) on the BTO, the piezoelectric effect of the BTO can induce a magnetoelastic effect in the BaM. The combined effect will result in a multifunctional heterostructure where the functional properties of the two oxide layers are coupled. The magnetic properties of the BaM can be dynamically tuned through the application of an external electric field. An example of a novel multifunctional oxide stack is illustrated in the following figure [35] along with an actual PTO/STO heterostructure [36]. The electrical properties of the
PTO/STO heterostructure can be tuned by varying the thicknesses of the alternating ferroelectric (PTO) and paraelectric (STO) layers.

**Figure 2.5:** Illustration of a) multifunctional oxide heterostructure schematic on a wide bandgap semiconductor [35], b) TEM of ferroelectric PTO and paraelectric STO heterostructure [36], c) high resolution TEM image showing the shared TiO$_2$ bridging mechanism between the PTO and STO multilayers [36], and d) demonstration by M. Liu, *et al.* of the coupling between nickel ferrite and PZT [21].

For the schematic heterostructure in the previous figure and the actual functional heterostructure, the properties of the multilayers can be coupled together by an atomic bridge that bonds the multiple layers together and carries the induced stress and strain of the BTO across the interface to the BaM. The atomic bridge that is responsible for the
The physical bonding of the multilayers is also responsible for the coupling of the functional properties. The most likely bridging mechanism will be the formation of an oxygen bridge between the layered functional oxide materials. The high resolution TEM image of the PTO/STO multilayer illustrates the bridge being formed by the sharing of TiO₂. Figure 2.5 (d) demonstrates the effective coupling between the magnetic properties of nickel ferrite (NFO) and electrical properties of PZT. In the presence of an applied field, the piezoelectric properties of the PZT impact the magnetostriction properties of the NFO, which in turn impacts the magnetic properties.

Unlike BFO, whose multiferroic properties are inherently coupled, it is possible to couple the specific properties the individual layers. A BaM/BTO structure can have both ferroelectric properties (BTO) and ferrimagnetic properties (BaM). However, if these properties can be coupled, then new magnetoelastic and magnetostrictive functionality can arise. By integrating multilayers of functional materials into a composite structure, rather than integrating a single multiferroic, a superior device can be fabricated. Within the heterostructure, it is possible to choose specific materials (ferroelectric, ferrimagnetics, etc.) based on their individual properties in order to meet the overall property requirements of the application.

### 2.4 Ferro- and ferri- electric and magnetic materials

Ferro- and ferri- are prefixes used to define the orientation and alignment of the electric or magnetic moments within a crystal when an external field is applied. For ferro- and ferri- electric materials, the dipole moment is aligned parallel to the applied electric
field. Similarly, for ferro- and ferri- magnetic materials, the magnetic moment is aligned parallel to the applied magnetic field.

2.4.1 Ferroelectric materials

Ferroelectric materials are materials that possess a permanent dipole moment. This polarization is what gives rise the desired ferroelectric properties of the material. When coupled with a semiconductor, the inherent properties can be implemented into a variety of sensory and communication devices.

The most common type of ferroelectric is the perovskite ferroelectric. Perovskite structures are of the stoichiometry ABO₃ and typically have tetragonal crystal structures. At a certain temperature, all perovskite ferroelectric materials lose their ferroelectric properties because of the atomic rearrangement from the perovskite structure (ABO₃) to a cubic pyrochlore structure (A₂B₂O₆). The temperature, at which this transition occurs, is referred to as the Curie temperature. Once the ferroelectric properties are lost, the materials are no longer ferroelectrics, but rather paraelectrics. By cooling the sample below the Curie temperature, it is possible to regain the ferroelectric properties. The Curie temperature is an important property to consider when selecting a material for use in high-power applications where heat may be generated.

The dipole moment of the ferroelectric material is a result of atomic shifting within the unit cell. For BTO, the barium atoms occupy the eight corners of the unit cell (A), the titanium occupies the center atom (B), and the oxygen occupies the eight faces. The atomic arrangement within the ferroelectric crystals is such that any atomic displacement (< 1 Å) results in an equally stable state. This stable state of displacement is
what is responsible for the permanent dipole moment and is referred to as polarization (P). Figure 2.6 illustrates the dipole moment and atomic displacement for polarization in the (001) and (111) directions of tetragonal BTO. The black atoms represent the corner Ba atoms, the yellow atom represents the center Ti atom, and the red atoms represent the face centered O atoms.

![Schematic illustration of BTO polarized in the (001) direction (top row) and (111) direction (bottom row). The polarization potential is greatest in the (001) direction due to the greater displacement of atoms within the crystal.](image)

**Figure 2.6:** Schematic illustration of BTO polarized in the (001) direction (top row) and (111) direction (bottom row). The polarization potential is greatest in the (001) direction due to the greater displacement of atoms within the crystal.

In order to obtain strong ferroelectric properties, it is necessary to have a sufficient volume of ordered dipole moments that result in a usable net dipole moment. Therefore, for real, non-ideal films, there is a minimum grain size and film thickness for which sufficient ferroelectric properties can be obtained. Currently, BTO ferroelectric properties have been demonstrated on films as thin as 4 nm and grains ~20 nm in size [37].
Single crystal ferroelectrics grown in the absence of an electric field are inherently electrically twinned, whereby the net polarization of the structure is zero due to the equal number of oppositely oriented domains. This is because any domain volume with an oriented polarization must be electrically twinned by an equivalent domain volume with opposite orientation in order to maintain a net charge of zero. When an electric field is applied to a ferroelectric film the material begins to polarize, which orients the electrically twinned domain walls. Eventually the film reaches a state of saturated polarization ($P_s$). At this point, any increase in the electric field will have no affect on the net polarization of the dipoles. When the field is removed, the material undergoes partial reorientation, resulting in remnant polarization ($P_r$) if the crystal is below the Curie temperature. Reversal of the electric field results in reverse polarization. The point at which the applied electric field returns to a net polarization of zero is referred to as the coercive field ($E_c$) and is a measure of power consumption. Small coercive fields, less than 100 kV/cm [9], are important for memory applications where polarization switching is important. The less power required to switch polarization, the more efficient the device.

The polarization properties of a film are characterized by a P-E (polarization – electric field) hysteresis loop. The remnant and saturated polarization as well as the coercive field are all used to characterize the properties, functionality, and ferroelectric nature of the film. A schematic representation of a P-E hysteresis loop is illustrated in figure 2.7. The polarization of the film is measured as an electric field is swept from zero to a positive saturation in the forward direction, and then swept back through zero to a negative saturation in the reverse direction.
One common approach to tuning the ferroelectric properties of a perovskite material is through the addition of a fourth element. Two examples of this are BST (Ba$_{1-x}$Sr$_x$TiO$_3$) and PZT (PbZr$_{1-x}$Ti$_x$O$_3$). For BST, the corner (A) atoms of the perovskite structure are a mix of Ba and Sr, resulting in a combination of BTO and STO. At room temperature, BTO is inherently ferroelectric, while STO is inherently paraelectric. By varying the ratio of Ba:Sr, it is possible to incorporate both the ferro- and para-electric nature of the BST to obtain the desired properties [38-40].

For PZT, the center atom (B) of the perovskite structure is a mix of both Zr and Ti. At room temperature, PTO is ferroelectric, while lead zirconate (PZO) is antiferroelectric. By combing the two and varying the ratio of Zr:Ti, it is possible to tune the ferroelectric properties of the PZT material. The primary difference between these two examples is the location of the substituted atom. Substitution in the A site for BST combines ferro- and para-electric properties, while substitution at the B site combines ferro- and antiferro-electric properties. Further, it is possible to substitute both A and B
sites allowing for a combination of ferro-, antiferro-, and para- electric properties for the tuning of a material [8-10, 38-42].

Kanno, et al. [9] reported the effect of the Zr:Ti ratio and crystal structure orientation on the polarization PZT thin films. The ratios of interest were 40:60, 53:47, and 70:30. The orientations of interest were (001) and (111) because of their strong polarization directions. Figure 2.8 [9] shows the effects of stoichiometry and orientation on the polarization of PZT films.

![Figure 2.8](image)

**Figure 2.8**: P-E hysteresis loops for PZT (a) (001), and (b) (111) at different Zr:Ti ratios.

The P-E hysteresis loops illustrate the static tenability of functional oxide materials [9].

From the previous figure, it was reported that the orientation of the crystal structure was much more influential on the polarization of the PZT films than stoichiometry. This is due to the preferred (001) polarization orientation for tetragonal perovskites [9, 39, 43-45]. However, when highly oriented (001) films were obtained, the stoichiometry was more significant than with highly (111) oriented films. This is due to the inherent ferroelectric nature of PTO and antiferroelectric nature of PZO. By decreasing the Zr:Ti ratio, the polarization should be expected to increase, due to the
increased ferroelectric contribution. This effect is most evident when polarized in the (001) direction. By varying the Zr:Ti ratio, it is possible to manipulate the ferroelectric properties of the film in order to obtain the desired properties for a specific device application. Although tuning the electrical properties of a ferrimagnetic material (PZT) by controlling the stoichiometry offers a range of functionality, it is a static variable. However, by coupling this functionality with a magnetoelastically susceptible material, it is possible dynamically tune the electric and magnetic functionality.

2.4.2 Ferro- and ferri- magnetic materials

Ferro- and ferri- magnetic materials are very similar to their electrical counterparts. Similar to the alignment of the electric dipole moment responsible for ferro- and ferri- electricity, ferro- and ferri- magnetism is a result of an alignment of magnetic dipoles. Ferromagnetic materials are materials whose magnetic dipoles uniformly align in the presence of a magnetic field and remain in a magnetized state when the field is removed. Ferrimagnetic materials, such as BaM, consist of ferromagnetic and antiferromagnetic dipoles, where some of the magnetic moments remain aligned after the magnetic field is removed.

One promising characteristic of BaM is its high inherent magnetic anisotropy, which is defined as the non-uniform alignment of the magnetic dipoles in every direction. For symmetric structures like iron, there is no anisotropy, meaning that the magnetization is equal in all directions. However, due to its hexagonal crystal structure, BaM has a high uniaxial magnetic anisotropy in the (0001) direction, which is considered the easy-axis.
Figure 2.9 illustrates the crystal structure of BaM, with magnetization directions in the easy and hard axis. The VSM hysteresis loop is characteristic of single crystalline BaM.

Similar to P-E hysteresis for ferroelectric materials, the magnetic properties of ferro- and ferri- magnetic materials can be characterized by vibrating sample microscopy (VSM). VSM hysteresis scans closely resemble the hysteresis of P-E hysteresis scans and are schematically illustrated in figure 2.9. However, instead of measuring polarization based on an applied electric field, magnetization is measured as an applied magnetic field is swept.

Before the functional properties of functional oxides can be coupled and tuned in a multifunctional heterostructure, it is necessary to integrate the functional films onto a semiconducting substrate. For the development of a next-generation, multifunctional
device, the wide bandgap semiconductor 6H-SiC was chosen. Success first requires the epitaxial integration of high quality, crystalline films on the 6H-SiC.

2.5 Epitaxy and mismatch

Epitaxy is defined as the extension of single crystal growth on top of a crystalline substrate [46]. There are two types of epitaxy; homoepitaxy and heteroepitaxy. Homoepitaxy refers to epitaxial growth where the film and substrate are the same material with the same crystal structure and orientation. Heteroepitaxy refers to film growth where the film is a different material than the substrate. Heteroepitaxy is more complex because the growth must accommodate compatibility issues between the film and substrate. These issues include, but are not limited to, lattice mismatch, chemical interactions, and thermal mismatch. By the strict definition of epitaxy, heteroepitaxy is not technically possible due to the fact that the two dissimilar materials will have different physical properties, resulting in a mismatch between the film and substrate. However, convention defines heteroepitaxy as the integration of a single crystalline film on a single crystalline substrate. Heteroepitaxy is the most commonly studied type of epitaxy, as it is necessary for the integration of oxides and metals in the standard silicon-based microchip manufacturing.

Many of the difficulties and defects that arise during heteroepitaxial film growth of oxide materials on semiconductors are a result of lattice mismatch or thermal mismatch. Although these mismatches are important for studying the heteroepitaxy of dissimilar materials, it is also important to consider electronic mismatch between the
functional films and semiconductors, which is a result of band bending at the interface of the oxide film and semiconductor.

### 2.5.1 Lattice mismatch

Lattice mismatch is a difference in the lattice parameter of the bulk film material from the lattice parameter of the bulk substrate material. Lattice mismatch can be defined by the following equation.

\[
mismatch = \frac{a_{i+1} - a_i}{a_{i+1}}
\]

Eqn. 2.1

Where \(a_i\) is the bulk lattice parameter of the substrate and \(a_{i+1}\) is the bulk lattice parameter of the subsequent film. Thus when the lattice mismatch is a negative value, the film is under tensile strain. When the lattice mismatch is positive, the film is under compressive strain. A second form of this equation can also be used, where the \(a_{i+1}\) in the denominator is substituted by \(a_i\). However, the form listed in equation 2.1 is often used because it represents the strain of the film with respect to the bulk relaxed state of the film.

During film growth, the lattice and thermal mismatch between the film and substrate need to be absorbed within the growing film. Therefore, it is not uncommon for the lattices to be strained and deviate from bulk values without defect formation. As a result, the lattice parameter of the thin film often differs from the lattice of parameter of the bulk material. The critical thickness of a film, where the crystal properties of the thin film reach that of a bulk crystal, is usually on the order of a few monolayers. In some
instances, the strain can be maintained through extended thickness, which can act to induce properties that would otherwise be absent [12].

Lattice strain can also be compensated for by unit cell arrangement or lattice matching. This can occur when the atom-to-atom lattice spacing of the film is significantly different than that of the substrate, but the net lattice spacing between a series of atoms is similar. This is illustrated in the following figure where three unit cells of cubic film can align with two unit cells of a cubic substrate.

![Figure 2.10: Schematic illustration of 3:2 lattice matching. Three unit cells of the film match the lattice spacing of two unit cells of the substrate.](image)

The previous schematic illustrates a simplified example of how lattice matching can compensate for a large lattice mismatch. The mismatch between atom pairs in the film and substrate results in a lattice mismatch around 33%. However, the net lattice spacing between four atoms in the cubic film is similar to the net lattice spacing between three atoms in the cubic substrate. Although the net lattice strain across the schematic structure is small, not every atom of the film is matched to an atom in the substrate at the interface, which can lead to dangling bonds or different bonding structure at the interface including adsorption of a small atom (hydrogen). Such effects could be detrimental for the integration of piezoelectric materials because they exhibit mechanical strain and
deformation under an applied electric field. If the piezoelectric film is not strongly bound at the interface to the substrate, then the film could delaminate.

Atomic alignment is also an issue when trying to grow a film with a cubic structure on a hexagonal substrate. An example of this is cubic MgO on hexagonal 6H-SiC. The hexagonal structure of the 6H-SiC is not well matched to the cubic structure of the MgO. However, by growing the cubic MgO in the (111) direction, it is possible to create a pseudo-hexagonal structure. This is illustrated in figure 2.11 where cubic MgO(111) with a lattice spacing of \(a = b = c = 4.213 \text{ Å}\) is overlaid on hexagonal 6H-SiC(0001) with a lattice spacing of 3.08 Å. The equivalent lattice spacing of one unit cell in the MgO pseudo-hexagonal structure is 5.958 Å. However, for MgO(111), there are two atoms within the lattice spacing. Comparing the atom to atom lattice spacing, the lattice mismatch between 6H-SiC(0001) and MgO(111) is approximately -3.4%. The grey atoms of the 6H-SiC are representative of the Si atoms, while the black atoms of the MgO are representative of O.
Figure 2.11: Schematic illustration of lattice matching for MgO(111) growth on 6H-SiC(0001) to illustrate the similarities in atomic position of the pseudo-hexagonal (111) on the hexagonal (0001). Because of the similarities in atomic arrangement, cubic MgO prefers to grow in the (111) orientation on hexagonal substrates such as 6H-SiC and GaN.

If the lattice mismatch between the film and substrate are too large, then the resulting film is often polycrystalline. This issue can be addressed through the addition of an interlayer or template layer between the substrate and the film. By selecting a material with a lattice spacing in between that of the mismatched substrate and film, it is possible to promote the preferred crystalline orientation and heteroepitaxy [45, 47-50]. The crystalline quality of the interlayer can be single crystalline, polycrystalline, or amorphous. Depending on the application, the interlayer can be used as template layer [15, 45, 47-51], an insulating layer [52], or a diffusion barrier [43, 53].
2.5.2 Thermal mismatch

Thermal mismatch is dependent on the thermal expansion coefficient of the films relative to the substrate. The equation for calculating thermal mismatch between the film and substrate is same as the equation for calculating lattice mismatch, with the exception of replacing the lattice spacing with the appropriate thermal expansion coefficients. Table 2.2 lists the thermal expansion coefficients at room temperature for $6H$-SiC, GaN, MgO, BTO, BST, and BaM, which are the materials of interest for this dissertation.

Table 2.2: Thermal expansion coefficients at room temperature for wide bandgap semiconductors $6H$-SiC and GaN, dielectric MgO, ferroelectric BTO and BST, and ferrimagnetic BaM. The units for the thermal expansion coefficients are ppm/K.

<table>
<thead>
<tr>
<th>$6H$-SiC</th>
<th>GaN</th>
<th>MgO</th>
<th>BTO</th>
<th>BST</th>
<th>BaM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c: 14.0 [58]</td>
</tr>
</tbody>
</table>
and island formation. In extreme cases, the thermal mismatch between the film and substrate may be severe enough to cause film delamination.

It is important to consider the lattice and thermal mismatch between the films and substrates during heteroepitaxy. In addition to the inherent mismatch between dissimilar materials, it is also necessary to understand the mechanisms behind the nucleation and growth of the films.

### 2.5.3 Band offsets and band bending

Band bending occurs at the interface between two materials have different bandgaps and band energies. As mentioned previously, the bandgap is defined as the energy difference between the valence band maximum (VBM) and the conduction band minimum (CBM). Located between the VBM and CBM is the Fermi level. This is the maximum allowable energy state. For n-type materials (extra electrons) the Fermi level is shifted towards the conduction band. For p-type materials (extra holes) the Fermi level is shifted towards the valence band. When two dissimilar materials are integrated their interface band structure requires that their Fermi levels align. The alignment results in an offset between the conduction bands and valence bands. This is illustrated in figure 2.12 for the integration of MgO on the wide bandgap semiconductor GaN [59].
Figure 2.12: Simplified band structure diagram for the MgO/GaN interface [59] derived from the precise XPS characterization of the VBM and core level emissions. a) XPS core level spectra and VBM of Ga3d, b) XPS core level spectra and VBM of Mg2p, and c) simplified band diagram of the MgO/GaN interface. The Fermi level is represented by the dotted horizontal line, the conduction band is represented by $E_C$, and the valence band is represented by $E_V$.

The simplified band structure for the MgO/GaN interface shows band offsets for the conduction band ($\Delta E_C$) and valence band ($\Delta E_V$) at 3.2 eV and 1.2 eV respectively. The offsets are due to the dissimilar bandgaps and the alignment of the Fermi levels, which is represented by the dotted line. The Fermi level is shifted towards the conduction band of the GaN because it is n-type. However, the MgO is not doped, resulting in the Fermi level lying midway between the valence band and conduction band.

One proposed method for determining interface band offsets is by precise measurement of the valence band edge through XPS [60, 61]. For metals, the valence
band edge should be expected to be 0 eV due to the overlap of the valence band and conduction band. For other materials, including oxides, the valence band edge will shift towards a higher binding energy on the XPS spectra. Linear extrapolation of the valence band edge can be used to determine the valence band maxima (VBM), which is defined as the zero-intercept of the valence band edge with the linear background of the XPS spectra. This method for determining the VBM has been used in conjunction with density of state (DOS) modeling to reliably determine the band offsets for different material interfaces [59-63]. Chamber, et al. [62]. Demonstrated that the VBM method proposed by Kraut, et al. [60, 61] is effective at precisely determined and evaluating the band offsets for various oxides, including perovskite structures, on Si and LaAlO$_3$ substrates. Therefore, this method was used for determining the band offsets for the MgO/6H-SiC interface.

Determining the band bending and offsets is important for characterizing the electronic compatibility of a heterostructure. If the band offsets are insufficient, it can result in unacceptable tunneling current between the semiconductor and oxide film, which would be detrimental to the maximizing the polarization switching of a ferroelectric – wide bandgap semiconductor heterostructure [59, 64, 65]. In order to successfully integrate electrically and physically effective interface and heterostructure, it will be necessary to consider all the mismatch conditions (e.g. lattice, thermal, bandgap) in order to engineer a next-generation multifunctional heterostructure.
2.6 Growth mechanisms

Through molecular beam epitaxy, it is possible to understand thin film nucleation and growth mechanisms, which are essential to the successful integration of thin film functional oxides on wide bandgap semiconductors.

Nucleation and growth mechanisms for vapor deposition of films on a solid substrate are influenced by a variety of parameters including substrate surface chemistry and structure, substrate temperature, vapor chemical species, and species flux to the surface. In general, the growth mechanisms can be controlled kinetically or thermodynamically. Determining how the impinging atoms in the vapor phase interact with the substrate surface is a key component to understanding the nucleation and growth mechanisms for epitaxial film integration.

Film nucleation and growth mechanisms are controlled by the chemical and physical interaction between the impinging vapor phase atoms, substrate surface atoms, and the atoms that have already nucleated on the substrate. These interactions are highly dependent on surface free energy and surface chemistry. This is illustrated in figure 2.13 [46].
Figure 2.13: Schematic illustration of basic atomic nucleation of impinging atoms on a substrate through vapor deposition [46]. The circular nucleation site does not represent a liquid phase nucleation but rather is used to illustrate the contact angle between the nucleation island and the substrate surface.

The chemical interactions are illustrated in figure 2.13 by $\gamma$, where the subscripts $f$, $v$, and $s$ represent the film, vapor, and substrate, respectively. When an atom impinges on the surface, depending on the chemical interactions it can become incorporated in an existing nuclei, desorb, or migrate along the surface depending on the atom-surface interactions. However, individual atomic mobility is not limited to these three actions. They are purely simplified actions that are used to describe the theoretical action of the mean atomic flux to the surface. Atomic migration and continued nucleation are dependent on the horizontal components of the interfacial tensions that surround the film nucleus, which is described by Young’s equation [46].

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta$$

Eqn. 2.2

Where $\theta$ is the contact angle of the nucleus and is solely dependent on the surface interactions of the substrate and film. Based on Young’s equation, there are three generalized theories based on the chemical interaction that are used to describe different
growth modes; Volmer-Weber (3-D island growth, $\theta > 0$), Frank-Van der Merwe (2-D layer-by-layer growth, $\theta \approx 0$), and Stranski-Krastanov (S-K, layer-by-layer growth followed by island growth). Schematic illustrations of the three growth modes are illustrated in figure 2.14.

![Schematic Illustrations of Growth Modes](image)

**Figure 2.14:** Schematic illustrates of the three characteristic growth modes, including Van der Merwe (2-D), Stranski-Krastanov (2-D $\rightarrow$ 3-D), and Volmer-Weber (3-D).

The chemical interactions for each growth mode are described below in equations 2.3, 2.4, and 2.5, respectively.

\[
\gamma_{sv} < \gamma_{fs} + \gamma_{fv} \quad \text{Eqn. 2.3}
\]

\[
\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv} \quad \text{Eqn. 2.4}
\]

\[
\gamma_{sv} > \gamma_{fs} + \gamma_{fv} \quad \text{Eqn. 2.5}
\]

After the initial stages of nucleation the interaction between the film and substrate can be neglected ($\gamma_{fs} = 0$) with regards to the resulting growth mode. By removing the film substrate from the equations, equation 3 then illustrates that the chemical interaction between the vapor and film outweighs the interaction between the vapor and substrate, resulting in 3-D island growth. Inversely, equation 2.4 illustrates that the impinging atoms have a greater affinity to the substrate rather than the film, resulting in layer-by-
layer growth. In the case of S-K growth, nucleation and the initial stages of growth are indicative of layer-by-layer growth.

Experimentally, it is commonly seen that after a critical thickness of several monolayers the growth mode transitions to island growth. The reason for this is not fully understood, and the lack of a complete and accurate growth theory limits the development of atomic growth modeling. It is theorized that any disturbance in the binding energy and surface chemistry associated with layer growth may be responsible [46]. Through the use of MBE, it is possible to precisely evaluate the influence of various processing parameters (growth rate, substrate temperature, flux species, etc.) on the growth mode of the functional oxides. If decreased surface mobility is responsible for the 3-D growth mode transition, MBE and UHV call allow the level of control necessary to decrease the impingement rate of the vapor species as well as increase the substrate temperature. By precisely tuning these variables, it is possible to increase the surface mobility and minimize 3-D nucleation sites.

2.7 Growth methods

There are many different deposition techniques used for thin film growth. The most popular techniques include chemical vapor deposition (CVD), pulsed laser deposition (PLD), sol-gel, rf sputtering, and molecular beam epitaxy (MBE).

CVD is a popular deposition technique for semiconductor device fabrication. It involves a chemical reaction of gaseous precursors, from which the products consist of solid material growth and gas phase decomposition products. Films are deposited at pressures ranging from millitorr up to atmospheric resulting in complex gas phase
reactions and films that are typically amorphous or polycrystalline. Therefore a post deposition anneal is often necessary to improve crystallinity. In addition, CVD does not often allow for the level of tunable control over the processing parameters necessary for single crystalline film growth.

PLD is a deposition technique that requires a vacuum chamber and lower background pressures. A laser beam is focused on a target with a stoichiometric ratio similar to the desired stoichiometry of the film. When the laser impacts the target, a resulting plume of atoms and molecules leaves the target surface and impinges on a substrate. Since this method is a physical deposition technique that does not offer atomic level control over the growth species, the material is sputtered onto the substrate and often results in polycrystalline films, which require a post deposition anneal for improved crystallinity. As a result, the ultimate crystal structure and orientation of films grown via PLD are highly dependent on thermodynamic stability of the film and film/substrate interface.

Radio frequency (rf) sputtering is similar to PLD in that a plume of atoms or molecules of the film material from a solid source is responsible for film growth. A radio frequency generates a plasma plume from a target source. The atoms in the plasma are then sputtered onto the substrate. Similar to PLD, the resulting films are often polycrystalline. Post deposition annealing can improve the orientation and crystallinity of the films. However, the methodology limits control over the species flux and crystal formation.

Sol-gel is a solution based technique that incorporates chemical reactions and is often used to grow bulk ceramics and other polycrystalline films. The precursors start as
a chemical solution (sol), which then undergoes hydrolysis or condensation into an integrated network (gel). The gel solution is then coated onto the substrate either through submersion or spin coating. To initiate crystallization, the substrate can be heated or seeded with a compound that will ultimately be incorporated into the film. The resulting film is often amorphous or polycrystalline. After the “gel” film is crystallized, it is necessary to dry the film by placing the substrate and film in a furnace where it is annealed rapidly up to temperatures just under the melting point of the film. The process is repeated until the desired film thickness is obtained. The sol-gel technique offers little control over the crystal structure of growth mechanisms of the films and is typically used for thin powder ceramic fabrication [66-68].

The aforementioned growth techniques operate under ambient pressures or in the millitorr range, which can lead to substrate contamination prior to deposition or film contamination during growth from residual gasses or compounds. In order to improve the crystallinity, they often require a post deposition anneal at temperatures beyond the deposition temperature. In addition, the processing parameters and methodology do not allow for understanding the nucleation and growth mechanisms on the atomic level, which is needed for engineering a process capable of growing single crystalline, stoichiometric films with desired orientation.

MBE is a growth technique that does allow for atomic level control. This is because it utilizes the benefits of ultra high vacuum (UHV). Under UHV conditions, there is a low background chamber pressure typically less than $10^{-9}$ Torr, which results in a large mean free path ($\sim 10^4$ km at $10^{-9}$ Torr) and low contamination rates of approximately one monolayer every 50 minutes. Thus MBE offers precise control over
processing parameters such as the atomic flux impinging the surface and the atomic species within flux, which is necessary for understanding the nucleation and growth mechanisms of thin films. Different types of MBE include solid source MBE, gas source MBE, plasma assisted MBE, and metal organic MBE. Regardless of the type of MBE, each method is based on the same principle, which involves a vapor phase source flux between $10^{12} - 10^{16}$ [46] atoms/cm$^2$ sec. At this flux, the resulting growth rate can range from a few angstroms per minute up to hundreds of nanometers per hour depending on the incorporation efficiency of the impinging atoms. This is in contrast to CVD, PLD, and rf-sputtering operating at increased fluxes where the growth rate can be as high as microns per hour. In addition, at the higher operating pressures (millitorr) there is the issue of surface contamination. When considering the importance of the interface between the functional oxide and the substrate, it is essential to minimize the contamination rate prior to film deposition. This can be accomplished through the use of UHV and MBE.

The most common type of MBE is solid source MBE, where a solid material, generally a pure element, is heated in an effusion cell to generate a local vapor pressure on the order of $10^{-5}$ Torr. The source is introduced into the chamber as a point source beam, which is oriented toward the substrate. As the molecular beam exits the source towards the substrate, the flux decreases as function of the distance squared. The further the substrate is from the source, the lower the impinging flux. The atomic flux is calculated by the following equation. Figure 2.15 illustrates the atomic flux dispersion from a solid source effusion cell used for MBE growth.
\[
\phi = \frac{3.51 \times 10^{12} PA}{\pi L^2 \sqrt{MT}} \tag{Eqn. 2.6}
\]

Where:
- \( \phi \) = atomic flux (#/cm\(^2\)sec)
- \( P \) = vapor pressure (Torr)
- \( A \) = aperture area (cm\(^2\))
- \( L \) = distance from source to substrate (cm)
- \( M \) = molecular weight (g/mol)
- \( T \) = temperature (°C)

Figure 2.15: Illustration of a solid source effusion cell with the labeled variables that impact the atomic flux within the molecular beam [69].

In addition to the atomic level control offered by MBE, the UHV environment that is associated with MBE, allows for the preservation of metastable species including charged ions. The ability to use reactive atomic oxygen, oxygen radicals, or ozone as the oxygen source for functional oxide epitaxy offers a new level of control towards understanding the nucleation and growth mechanisms that is not possible by CVD, PLD, or rf-sputtering.

At these low vapor pressures, it is possible to have precise control over the individual species on an atomic level, which is essential for the understanding the effects of different processing parameters on the nucleation and growth mechanisms of thin films. This dissertation focuses on the deposition and integration of oxide films on 6H-SiC by MBE in order to successfully engineer a process capable of fabricating high
quality, single crystalline films for the eventual integration of a multifunctional heterostructure.

**2.8 Integration of functional oxides on wide bandgap semiconductors by MBE**

The integration of oxides on semiconductors by MBE is a concept that was first published in 1979 [52, 70]. However, the field did mature to functional oxides and wide bandgap semiconductors until much more recently in 2004 [70, 71]. Although some growth techniques including CVD, PLD, sol-gel, and rf-sputtering have successfully grown polycrystalline functional oxides on semiconductor substrates [66, 68, 72-75], they are limited by their methodology and cannot produce the quality films necessary for next-generation multifunctional device fabrication. This is because the existing growth techniques do not offer the needed atomic level control that is associated with MBE. However, current research can be used to qualitatively analyze the effects of certain variables, such as growth temperature, starting surface of the substrate, film stoichiometry, crystallinity, and orientation.

Currently, little research has focused on the integration of functional oxide growth (BTO, BST, BFO, BaM) by MBE on wide bandgap semiconductors [48, 49, 70]. Although MBE has been used to deposit high quality, single crystalline functional oxides on lattice matched substrates (BST/STO), little has addressed the issue of integrating the functional film onto a mismatched semiconductor (Si, GaAs) or wide bandgap semiconductor (SiC, GaN). Through the use of MBE and UHV, it is possible to study and understand the nucleation and growth mechanisms of various functional oxides and further engineer a process to effectively integrate these oxides with desired functional
properties on wide bandgap semiconductors. To accomplish this, it is important to understand the relationships between processing parameters and growth mechanisms, growth mechanisms and films characteristics, and film characteristics and film properties. This is essential to the successful development of a process for integrating stoichiometric, single crystalline functional oxides and multifunctional heterostructures on wide bandgap semiconductors. Thin film growth via MBE offer atomic level control of growth parameters that can potentially be tuned to produce functional films that exceed the electrical and physical demands required for further advancement in semiconductor device fabrication and novel multifunctional device heterostructures.
3.0 Critical Literature Review

As semiconductor and integrated circuit devices continue to decrease in size, there is a growing need for the development of next-generation materials for new devices and heterostructures with multifunctional capabilities [76]. One possible solution to the increasing demands is the development of a new generation of functional materials known as functional oxides [70]. These oxides can be integrated into a multilayer, multifunctional heterostructure on wide bandgap semiconductors for a next-generation multifunctional device with dynamic tunability and diverse functionality.

Current semiconductor device technology is on the cusp of the limitations of silicon and other traditional semiconductors. In order to move towards the realization of next-generation devices, which require high-power, high-temperature, high-frequency, applications that can operate in harsh environments, it is necessary to develop a new material system that is integrated on wide bandgap semiconductors, like SiC and GaN. However, the caveat of integrating a new semiconductor technology is the demand for developing a new generation of functional materials whose functionality can meet or exceed the operating requirements of the wide bandgap semiconductor.

Silicon semiconductor device technology is the benchmark material integrated circuit technology because its native oxide (SiO$_2$) is easily formed and acts as an excellent dielectric insulating layer. Although the wide bandgap semiconductor SiC can be oxidized to form a SiO$_2$ dielectric layer, the dielectric properties of the SiO$_2$ are grossly inadequate for the accommodating the high-power, high-frequency potential of
the SiC substrate. Therefore, new high quality dielectric materials and functional oxides need to be developed.

In order address the requirements for next-generation multifunctional devices, it is necessary to successfully integrate high-quality functional oxides (BTO, BST, BFO, PZT, BaM) on wide bandgap semiconductors (SiC, GaN). “Success” will require that the functional oxides be high quality single crystalline with tunable (dynamic and/or static) functionality, while maintaining an abrupt and effective interface, where “effective” has different requirements as defined by the desired coupling between adjacent layers. A thorough and critical review into the history and current progress of functional oxide tuning and heteroepitaxy can help unfold and focus the technical issues to be overcome in order for next-generation applications to become a reality.

Current research into functional oxide integration and complex multifunctional heterostructures can be divided into two schools of thought. One focuses on the integration of functional oxides on lattice matched substrates, which are typically non-semiconducting, while the other focuses on the integration of functional oxides on semiconductors. Although the integration of functional oxides on lattice-matched, non-functional substrates is not practical for device applications, the resulting films are often of very high quality, which helps to understand the intrinsic functionality of the materials. These films are also often grown by MBE, which allows fundamental research into the mechanism and capability of tuning the functional properties of the materials. On the other hand, integration on semiconductors allows for the fabrication of working devices and testing the capabilities of functional oxide heterostructures in real-world applications. However, since the functional oxides and semiconductors have dissimilar properties, the
complex heteroepitaxy often results in films that are of lower quality than their lattice matched counterparts, which can greatly affect the overall functionality. A critically analysis of the progress for both pathways can incorporate the findings and understandings necessary for the successful integration of high-quality functional oxides on wide bandgap semiconductors for next-generation device applications.

3.1 Oxides on oxides: lattice matched epitaxy

Based on the crystallographic similarities in most tetragonal perovskite ferroelectrics, it is possible to extract commonalities in the processing conditions and mechanisms responsible for high-quality, crystalline growth. Since most perovskite ferroelectric materials of interest are tetragonal ferroelectrics, the desired orientation of the film is (001), which results in the highest polarization potential. In the (001) direction, the base of the crystal structure has a square, in-plane geometry. Therefore, a cubic material or tetragonal material with a similar in-plane lattice spacing can be used as a substrate. Depending on the material of interest, the substrate selection can range from simple rocksalt structures like MgO [47, 48, 51, 77-89], to cubic perovskites like strontium titanate (STO) [12, 14, 15, 51], to more complex multi-component oxides like La$_{1-x}$Sr$_x$CoO$_3$ (LSCO) [3, 90-92]. By using more complex oxide substrates like LSCO, it is possible to vary the stoichiometry of the crystal and therefore the lattice parameter in order to engineer a substrate that closely matches the lattice properties of the functional film.
3.1.1 Interface engineering and strain-induced functionality

Since most lattice-matched substrates are typically not functional semiconductors, their feasibility for device integration is not considered. Rather, one focus of lattice-matched epitaxy is to study the intrinsic mechanical and electrical properties of the functional ferroelectric including: stress and strain effects on polarization, dielectric constant of the film as a function of thickness relative to bulk values, capacitance of the film as a function of thickness relative to bulk values, and polarization of the film as a function of thickness relative to bulk values. Through careful engineering of interfaces and interfacial strain, it is possible to enhance or even induce ferroelectric properties in an otherwise non-functional material [12, 13, 56, 93]. For example Haeni, et al. [12] demonstrated strain-induced room-temperature ferroelectricity in thin film STO by selective substrate engineering and controlling the biaxial strain of the STO lattice. STO is inherently paraelectric down to 0 K, due to the cryogenic Curie temperature of the material. However, it has been predicted [94, 95] and observed [40, 96, 97] that the Curie temperature for ferroelectric and paraelectric materials could be increased by several hundreds of degrees by atomic substitution or induced biaxial strain [40, 94, 96-98]. Having the ability to tune the ferroelectric properties and ferro-/para- electric transition is of great interest for microwave devices because the dielectric constant of the material can be tuned by applying a static electric field at GHz frequencies [99, 100].

Further, the properties of bulk or thin film ferroelectric materials can be manipulated by controlling the crystal quality [83], crystal orientation [44, 45], and grain size [37]. It is well understood that the quality of the ferroelectric material (single crystalline, poly crystalline, amorphous, etc.) greatly impact the functional properties of
the oxide material. This is due how easily the ferroelectric domains alignment when an electric field is applied. The lack of any ordered crystal structure (amorphous) cannot be polarized because there is no ordered atomic displacement during polarization. Polycrystalline films have the potential to exhibit strong polarization, provided the polycrystallinity is due to in-plane rotation of the crystallites, but uniform out-of-plane orientation [37, 101]. This is due to the physical formation of domain walls within the polycrystalline material, and is typically characteristic of bulk ceramic materials. However, if the polycrystallinity is due to random order, the mixed orientations inhibit strong remnant polarization of the domains. This is due to the difference in polarization potential between the various orientations [66, 102].

The heteroepitaxy of lattice matched oxides can be used as a basis for understanding the intrinsic properties of bulk ferroelectric materials, as well as enhanced and induced (strain, stress, atomic substitution) properties of thin films can be optimized by interface engineering to tune the functional properties of the oxide. MBE offers the atomic level control that is necessary for studying the mechanisms contributing to the engineering functionality of various thin film functional oxides.

3.1.2 PTO/STO heterostructure via MBE

Lead titanate (PTO) is a perovskite ferroelectric that is very similar to barium titanate (BTO) in crystal structure and ferroelectric properties. It consists of a combination of stoichiometric PbO (BaO for BTO) and TiO₂ in a tetragonal structure. For both PTO and BTO, the Pb and Ba are significantly more volatile than Ti. Therefore, it is
possible to extract some similarities in the growth mechanisms between the two materials systems.

Jiang, et al. [36] reported epitaxial growth of alternating STO/PTO (SrTiO\textsubscript{3}/PbTiO\textsubscript{3}) layers on a lattice matched La-doped STO(001) substrate via reactive MBE. The STO(001) and PTO(001) consist of alternating layers of SrO (or PbO) and TiO\textsubscript{2}. By alternating the atomic fluxes of Sr and Ti in an ozone environment, it was possible to obtain epitaxial, stoichiometric STO. This was expected due to the layered nature of the (001) orientated STO. However, due to the volatility of Pb for PTO, the Pb flux was maintained while the Ti flux was alternated on and off. A schematic representation of the flux sequence is illustrated in figure 3.1 [36]. This sequence was repeated to produce a \([(\text{PbTiO}_3)_{10}/(\text{SrTiO}_3)_{10}]_{15}\) “superlattice”.

![Figure 3.1](image)

**Figure 3.1:** Schematic illustration of source flux pulses for growth of alternating PTO and STO layer “superlattice” [36].

It was reported that the growth rate of PTO was fully dependent on the flux of Ti, while the Pb overpressure was designed to compensate for excess Pb volatization at the growth temperature of 580 °C. The oxygen source for both STO and PTO was supplied by reactive ozone at a background pressure of 2.0×10\textsuperscript{-5} Torr. The thickness of each STO and PTO layer was controlled to a thickness of ten unit cells, 41 Å and 39 Å respectively. This level of control is a major advantage of MBE and UHV. Similarities between the
PTO and BTO materials systems can be correlated due to the relatively high volatility of Ba (and BaO) compared to Ti. As a result, in order to obtain stoichiometric BTO, it may be necessary to run the Ba flux in excess to account for increased volatility. The expected orientation of tetragonal BTO on a hexagonal substrate ($6H$-SiC) is (111). In this crystallographic orientation, the layered BaO/TiO$_2$ structure that is present in the (001) orientation, is lost. Therefore, it will not be possible to emulate the same alternating flux technique that was used.

XRD characterization of the $[(\text{PbTiO}_3)_{10}/((\text{SrTiO}_3)_{10})]_{15}$ “superlattice”. Jiang, et al. reported that the XRD scans indicated a highly (00l) oriented “superlattice”, which would be expected for the epitaxial growth of PTO on STO(001). Figure 3.2 [36] shows the XRD scan of the STO/PTO multilayer heterostructure. The authors reported that the representative diffraction peaks for each interlayer are clearly visible and are indications of excellent regularity of the periodic structure, with the formation of abrupt interfaces.

![Figure 3.2: XRD scan showing the (00l) orientation diffractions for $[(\text{PbTiO}_3)_{10}/((\text{SrTiO}_3)_{10})]_{15}$ “superlattice” [36].](image)
The formation of abrupt interfaces is most likely a result of good lattice matching and epitaxy as well as atomic level control characteristic of MBE and UHV. Nothing was reported by the authors about the lattice matching, but by comparing bulk properties, the lattice parameters for STO and PTO are 3.929 Å and 3.967 Å, respectively. This results in a lattice mismatch of 1%, where PTO is under compressive strain and STO is under tensile strain. Jiang, et al. demonstrated tunable control over processing parameters by MBE, which will be essential to understanding the nucleation and growth mechanisms of single crystalline perovskite ferroelectrics on a variety of substrates, including 6H-SiC.

From the results discussed, there are several key components that may be useful for the successful heteroepitaxy of BTO by MBE. First, the barium flux may need to be run in excess in order to account for the relatively high volatility of barium compared to titanium. Second, the deposition temperature of 580 °C was sufficient for depositing crystalline STO and PTO. This temperature may translate well to the heteroepitaxy of BTO due to the similarities in crystal structure. Finally, the overpressure (2.0×10⁻⁵ Torr) of reactive ozone most likely prevents the deposition of metallic species. Although the MBE system discussed in this dissertation is not equipped with ozone, it does have the capability of supplying reactive atomic oxygen or oxygen ions. Therefore, by running the oxygen in excess, it should be possible to fully oxidize the barium and titanium in the BTO crystal.

3.2 Oxide on semiconductor heteroepitaxy

The heteroepitaxy of lattice matched oxides on oxides is important for understanding the intrinsic functionality of the oxides as well as the mechanisms for the
engineering and optimizing the functional properties. However, in order for the functional oxides to be integrated into a next-generation device, they need to be integrated onto a functioning semiconductor. Silicon surface preparation is a well established process [103], as it is the benchmark semiconductor for today’s integrated circuit technology. For next-generation devices, it is necessary to transition from silicon-based technology toward wide bandgap semiconductors. Although some work has focused on the chemical preparation of GaN [104], it is beyond the scope of this dissertation. Rather, the surface preparation of SiC is of importance.

3.2.1 6H-SiC substrate surface preparation

Successful integration of functional oxides into an electrically effective device requires the formation of an abrupt interface between the functional oxide film and the semiconductor. Therefore as an initial step, it is necessary to establish smooth, reproducible starting surfaces on the 6H-SiC substrates. It is important to understand how interfaces between the wide bandgap semiconductors and oxide films form in order to understand and characterize the effectiveness of the interface and starting surface. The “effectiveness” of the surface preparation will be dependent on the formation of a smooth, reproducible surface that can be used for the heteroepitaxy of high-quality oxide films.

Although it is possible to purchase SiC substrates that are epi-ready or already have an epi-layer, these options are considerably more expensive than wafers that have been mechanically polished. As a result, the surfaces of the as-received wafers are often covered in oxygen and carbon contamination, as well as scratches that are tens of
nanometers deep. Research grade, mechanically polished 6H-SiC substrates were used for all the substrates discussed in this dissertation. In order to remove the contamination and scratches, *ex-situ* hydrogen cleaning has been described in the literature through a number of different apparatus, including CVD chambers, quartz-tube furnaces, hydrogen plasmas, and hydrogen flow furnaces [105-112]. Although each of these methods are unique in their set-up and operation, they are all based on the same etching mechanism where molecular hydrogen (or hydrogen plasma) is used to etch the SiC by forming volatile CHₓ compounds that are easily removed at the high processing temperatures, typically greater than 1100 °C. Through careful control over the processing variables, including temperature, hydrogen flow rate (pressure), exposure time, and heating/cooling rate, each method has demonstrated the effective removal of scratches and residual contamination. Due to the dissimilarities between the various methods, it is difficult to draw any mechanistic conclusions that are independent of the processing method. As an example, SiC cleaned in a hydrogen flow furnace or quartz-tube reactor are often run at ambient pressures with hydrogen flow rates as high as tens of liters per minute. These conditions are significantly different than the conditions used in CVD chambers or hydrogen plasmas, which require pressures in the millitorr range and much lower exposure rates (~1 slpm) to hydrogen. As a result, the final state of the SiC surface may be significantly different on an atomic level. Although the various cleaning procedures may result in the same macroscopically stepped surface, the conditions run at ambient pressures often result in the formation of a silicate adlayer [107, 109] while those performed in vacuum (millitorr) contain no oxygen.
Judging by the lack of results reported in the literature [107-109], little characterization has been performed on the chemical analysis of hydrogen-cleaned SiC by the various methods. However, there is an abundance of structural and morphological characterization. Structural characterization of hydrogen cleaned SiC has been reported on a wide range of different adatom surface reconstructions. Depending on the cleaning method and processing conditions used, the most commonly reported reconstructions are 3×3 and $\sqrt{3}\times\sqrt{3} R30^\circ$ [107, 109]. However, surface reconstructions can also include a simple 1×1 structure, a 6×6 superstructure or a carbon rich 6$\sqrt{3}\times6\sqrt{3} R30^\circ$ structure [110]. Although the 3×3 and $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstructions are the most energetically favorable [107, 109, 110] the chemical composition of the adlayer may be different whether it was obtained under ambient pressures or millitorr pressures. For example, when the SiC is processed ex-situ, in a hydrogen flow furnace or quartz-tube furnace, the resulting surface reconstruction will be composed of a silicate adlayer due to the presence of residual oxygen and outgassing within the furnace [107, 109]. However, when processed in a vacuum environment, the same reconstruction can be obtained, but due to the absence of residual oxygen in the vacuum environment, the reconstruction results in a silicon-rich adlayer [107, 109]. In either case, the 3×3 surface reconstruction requires higher temperatures to form than the $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction. As a result, the surface coverage of the 3×3 reconstruction is often incomplete.

Morphological characterizations of the various hydrogen cleaned surfaces all indicate the successful removal of the scratches that were a result of the mechanical polishing [108]. The resulting surface consisted of atomic steps that were one unit cell high (~1.5 nm for 6H-SiC) and hundreds of nanometers wide. The actual step width is
dependent on the off-axis cut of the SiC wafer. Higher step densities are obtained with larger off-axis cut angles.

A common trend that was reported among the various cleaning methods was the formation of silicon-rich droplets. The size and density of the droplets was found to increase with increased cooling rate. This is due to the formation of a silicon-rich surface as the hydrogen reacts with the carbon to form volatile CHₓ during hydrogen exposure at elevated temperatures. During high temperature exposure, the Si atoms on the surface can also volatize, considering the temperatures used are typically around (or higher than) the melting point of silicon (1414 °C). If the sample is cooled too quickly, there is insufficient time for the Si-rich surface to coalesce into a uniform adlayer, resulting in Si-droplet formation. Therefore, it is necessary to cool at a sufficiently slow rate in order to minimize droplet formation. However, given the significantly different processing conditions between the various methods, no common cooling rate emerged. As an initial step for establishing a processing procedure for the custom built hydrogen flow furnace discussed in this dissertation, it will be necessary to consider the cooling rate.

Besides Si-droplet formation, another effect that was observed was overetching. This occurred due to an imbalance between the cleaning temperature, hydrogen exposure, and cleaning time [107, 109, 113, 114]. After successful hydrogen cleaning, the resulting morphology of the SiC consisted of a stepped surface with straight step edges. Overetching was defined in literature [107, 109, 113, 114] as the formation of a wavy step edge. This is most likely due to the etch rate being faster than the atomic mobility on the surface and within the lattice. As a result, the mobile atoms within the SiC are not able to form the energetically stable stepped surface, before they are removed by the
hydrogen etch. Therefore, in order to optimize the effectiveness (smooth, stepped surface) of the hydrogen cleaning procedure, the etch rate will need to be tuned to allow the surface to form the desired smooth, stepped surface. One option for controlling the etch rate is through the addition of an inert diluent gas (Ar). The diluent can be used to regulate the available hydrogen at the substrate surface while maintaining a high atom mobility at elevated temperatures.

By optimizing the processing parameters of each individual cleaning method, the resulting SiC structure and morphology indicates that hydrogen cleaning is a promising technique for establishing a reproducible, effective starting surface for subsequent film growth. Although few absolute similarities can be extracted from the literature, it was possible to extract similarities that impact the effectiveness of the hydrogen cleaning. These variable include cooling rate, cleaning temperature, gas flow rate (gas composition), and cleaning time. Consideration of these variables will be used to optimize the processing procedure of the custom built hydrogen flow furnace for establishing a reproducible, smooth, stepped, 6H-SiC starting surface for use in the this dissertation. Once an effective cleaning procedure has been established, it will be possible to investigate the heteroepitaxial integration of functional oxides on the wide bandgap semiconductor.

3.2.2 Heteroepitaxial growth of PZT on hexagonal SiC

PZT is another perovskite ferroelectric with similar crystal and ferroelectric properties to BTO. Little research has focused on the integration of perovskite ferroelectrics directly on hexagonal SiC. Koo, et al. [115] conducted a study of the
heteroepitaxial integration of PZT grown on different 4H-SiC substrates. Although 4H-SiC is a different polytype of SiC than 6H-SiC, they do have many similar crystalline properties (both hexagonal structures with similar in-plane lattice spacings; 3.07 Å for 4H- and 3.08 for 6H-). Therefore, it is possible to extract similarities in the mechanisms contributing to the heteroepitaxy of tetragonal PZT on hexagonal SiC.

The three substrates of interest to Koo, et al. were Al₂O₃/4H-SiC, SiO₂/4H-SiC, and 4H-SiC directly. Characterization of the films’ epitaxy was performed with XRD, shown in figure 3.3 [115]. Based on the observed XRD spectra, the PZT films were all polycrystalline, but consisted of strong (111) diffraction peaks. This was a result of the influence of the hexagonal substrates and the preferred pseudo-hexagonal epitaxy of the (111) orientation of tetragonal ferroelectrics.

![Figure 3.3: XRD scans of: (a) PZT/Al₂O₃/4H-SiC, (b) PZT/4H-SiC, and (c) PZT/SiO₂/4H-SiC. The * denoted the reflections for the pyrochlore phase of Pb₂Ti₂O₆. As expected, the hexagonal 4H-SiC and Al₂O₃/4H-SiC surfaces promoted the pseudo-hexagonal (111) orientation of the PZT films [115].](image-url)
The PZT/Al$_2$O$_3$/SiC heterostructure was designed to study the influence of an oxide interlayer, PZT/SiC was designed to study the integration of PZT on a wide bandgap semiconductor with a direct interface, and PZT/SiO$_2$/SiC was designed to compare PZT growth on SiC to previously studied growth of PZT on Si, which typically involved a SiO$_2$ interlayer. In addition, the Al$_2$O$_3$ interlayer reduced the minimized tensile mismatch from 30% (PZT/4H-SiC) to 17% (PZT/Al$_2$O$_3$/4H-SiC). Considering the large mismatch between the PZT and starting surfaces, it is not too surprising that the resulting films were polycrystalline. If this epitaxy corresponds to the BTO/6H-SiC epitaxy that is of interest for this dissertation, then it will be necessary to consider an alternative interlayer (MgO) that is better lattice matched to the substrate and functional oxide that will promote high-quality, single crystalline integration.

The third substrate (SiO$_2$/4H-SiC) was designed to correlate PZT growth on a wide bandgap semiconductor 4H-SiC with existing methods of PZT growth on Si semiconductors, in order to fit with standard device fabrication techniques. However, in the event that the SiO$_2$ layer did promote high-quality, single crystalline PZT, the ultimate performance of the device would be limited by the breakdown properties of the SiO$_2$ dielectric layer, which cannot meet the performance capabilities of the wide bandgap semiconductor (4H-SiC) or the novel functional oxide (PZT).

Mou, et al. [116, 117], reported growing crystalline PTO on 4H-SiC, with conflicting results compared to figure 3.3 (b). The authors reported through XRD characterization that the resulting PTO film was polycrystalline with no preferred orientation. Rather than have an intense (111) diffraction peak, the resulting PTO had a
minimal (111) diffraction peak compared to other random orientations. The XRD scan is illustrated in the figure 3.4 [117].

Figure 3.4: XRD scan of polycrystalline PTO film with no preferred orientation on 4H-SiC via pulsed laser ablation [117].

The discrepancy between the heteroepitaxy of PTO/4H-SiC and PZT/4H-SiC may be attributed to the difference in lattice parameters or the addition of fourth element in the PZT. Although PZT is a combination of PTO and PZO (lead zirconate, an antiferroelectric), it lattice parameters and crystal properties can be adjusted based on the relative amount of Zr:Ti. PTO has lattice parameters of $a = b = 3.867 \, \text{Å}$ and $c = 4.033 \, \text{Å}$. By replacing Ti with Zr, it is possible to increase the $a$ and $b$ lattice parameters to 4.14 Å (PZO is a pseudo-cubic structure, $a = b = c$). However, by substituting Ti for Zr, the ferroelectric properties will also be affected due to the antiferroelectric nature of the PZO. It is possible the reduced epitaxy of PTO/4H-SiC is a result of increased tensile mismatch due to the smaller lattice parameter of PTO compared to PZT. If lattice mismatch is responsible for the lack of epitaxy, then the successful heteroepitaxial integration for this dissertation of BTO on 6H-SiC will require the use of a lattice matched template layer.
One possible option is cubic MgO, which is closely matched to both 6H-SiC (3.4%) and BTO (4.4%). However, before BTO can be integrated on the 6H-SiC or MgO/6H-SiC, it is important to understand why BTO is of particular interest as a functional oxide.

3.2.3 Barium titanate epitaxy

Barium titanate is a perovskite ferroelectric that is of particular interest because of its ferroelectric properties, optical properties, and high dielectric constant [66, 118]. BTO has been studied extensively for a variety of different applications ranging from bulk ceramic powders [37, 57, 66, 102], to solid state memory devices [40, 119], to optical waveguides [120]. One general consensus indicates that the minimum temperature for crystallization of BTO is between 400 °C and 500 °C [44, 45, 67, 73]. This is similar to the deposition temperatures and annealing temperatures that are used for the crystallization of various other tetragonal perovskite ferroelectrics [121]. However, in most cases this is the temperature that is required to crystallize as-deposited BTO that was initially amorphous or polycrystalline [44, 45]. When BTO is deposited by more sophisticated deposition techniques including MOCVD, MBE, or PLD, the crystal structure and quality can be engineered and maintained at lower temperatures with better control over the processing conditions.

Crystalline BTO was also deposited using a multi-step temperature profile by MBE on LAO [44]. Initially, 2 monolayers (ML) of amorphous BTO was nucleated and grown at 320 °C and then crystallized at 600 °C. An additional 8 ML was deposited as the temperature was decreased from 600 °C to 300 °C. Finally, 30 ML of crystalline BTO was deposited at 280 °C. Although the multi-step temperature profile may not be of
particular interest or this dissertation, there is evidence that the homoepitaxy of BTO does not require the same high deposition temperature as the nucleation and heteroepitaxy of BTO. If this growth mechanism hold true for different deposition techniques and film orientations, it could be of great importance for device integration where high deposition temperature are undesirable due to increased interface breakdown and interdiffusion. One popular candidate to minimize interface issues and promote the epitaxy of perovskite ferroelectrics is MgO because of its optical and electrical properties as well as its rocksalt structure, which is a close lattice match to many tetragonal, perovskite ferroelectrics.

Crystalline BTO has been reported by metal organic chemical vapor deposition (MOCVD) on MgO substrates [73, 74] and MgO buffered Si [51]. This heteroepitaxy is of particular interest for this dissertation because of the use of MgO as a template layer for high-quality BTO integration. The BTO was reported to be single crystalline (001) oriented with a cube-on-cube epitaxy. However, due to the lack of atomic level control over the nucleation and growth of the BTO, the resulting films were rough (RMS > 10 nm). This roughness would be unacceptable for use in a multilayered heterostructure, which would require the subsequent integration of a magnetic material. Although (001) is the preferred orientation for BTO and other tetragonal ferroelectrics, it is not the expected orientation for the heteroepitaxy of BTO on a hexagonal substrate (6H-SiC). Rather, the pseudo-hexagonal structure of BTO(111) is the most likely epitaxial orientation. However, it is the pseudo-hexagonal structure of the BTO(111) that will enable and promote the subsequent heteroepitaxy of hexagonal ferrites (BaM) into a multilayered, multifunctional heterostructure. Before BTO can be successfully integrated onto the 6H-
SiC wide bandgap semiconductor, it is necessary to consider the heteroepitaxy of a high-quality MgO template layer.

3.3 MgO heteroepitaxy and heteroepitaxial template

One of the key components to this dissertation, is the use of high-quality, single crystalline MgO as a heteroepitaxial template for the integration of functional oxides on 6H-SiC. Before that can be accomplished, it is necessary to understand the growth mechanisms of MgO and its effectiveness at promoting the heteroepitaxy of tetragonal perovskites.

3.3.1 Growth of MgO via MBE

Yadavalli, et al. [122] reported on homoepitaxial growth of MgO via MBE on MgO(001) substrates. This study was designed to determine the effects of temperature on the homoepitaxial growth mechanisms of a MgO. Understanding the growth mechanisms from this study can be used to design the type of MBE environment needed for heteroepitaxial growth of single crystalline MgO films on 6H-SiC. Yadavalli, et al. evaporated Mg from an effusion cell and provided molecular oxygen as a molecular beam through a nozzle, with a working pressure below 10^{-6} Torr. The substrate temperature was varied from room temperature to 1000 °C. The MBE system used for the research discussed in this dissertation can use molecular oxygen or combination of atomic and molecular oxygen, which is generated from the remote oxygen atom source.
MgO growth was started with the substrate temperature at 1000 °C and slowly lowered. RHEED was used real-time to monitor the surface coverage and crystallinity of the growing film. As the temperature of the substrate was lowered, it was reported that there was a critical temperature around 43 °C where the RHEED pattern transitioned from the typical MgO(001) pattern to a pattern that corresponds to crystalline metallic Mg(0001). This is important for understanding the minimum growth temperature that MgO could effectively be grown. Although or the interest of this dissertation, MgO will be grown on 6H-SiC, the heteroepitaxy and influence of the substrate will not necessarily remain as the film continues to grow. Therefore, it is important to consider the homoepitaxial growth mechanisms as well as the heteroepitaxial nucleation and growth mechanisms. It was also reported that under higher O₂ fluxes, MgO nucleation occurred at lower growth temperatures. This was hypothesized by Yadavalli, et al. to be a result of more Mg being captured by the O₂ resulting in less Mg desorption from the substrate surface. It was proposed by the authors from these results that oxygen flux is responsible for determining the growth rate of MgO. However, this would only be true at elevated growth temperatures because at lower temperatures, excess Mg could condense on the substrate surface, resulting in the observed metallic magnesium RHEED pattern.

Using step thickness measurements the growth rate of the MgO film at 200 °C, Yadavalli, et al. estimated to be 0.24 Å/sec. From calculations of involving the appropriate O₂ background flux of 10²⁰ atoms/cm² sec (10⁻⁶ Torr) and an assumed sticking efficiency of one, the expected growth rate would be 160 Å/sec. Comparing this to the observed growth rate of 0.24 Å/sec, the authors estimated the O₂ sticking efficiency of 0.15%. Doing the same for Mg, the incorporation efficiency at 200 °C was estimated to
be 20%. In addition to the poor sticking efficiency of oxygen, it is also important to note that oxygen was introduced to the system as molecular oxygen. Therefore, more energy was required to break the O-O bond to form MgO rather than oxygen being introduced as a reactive species like atomic oxygen or ozone. This could account for the poor sticking coefficient of oxygen and further support the hypothesis of Yadavalli, et al. that oxygen flux determines the growth rate of epitaxial MgO assuming oxygen is supplied as molecular oxygen. Although the molecular oxygen was supplied in excess compared to magnesium, the availability of oxygen may have been limited by the dissociation of O$_2$ into O. Therefore, the incorporation efficiency of 0.15% is not representative of the amount of incorporated oxygen relative to the amount of available dissociated oxygen.

Using a combination of atomic oxygen and molecular oxygen, as supplied by the remote oxygen atom source, it will be possible to investigate the role of atomic oxygen versus molecular oxygen in the MgO growth mechanism. This information could help understand the role of each species (Mg, O, O$_2$) in the heteroepitaxy of MgO on 6H-SiC.

Similar results were reported by Hoerman, et al. [123], which may support the hypothesis regarding oxygen being responsible for the growth rate of MgO. In their study, MgO was grown via MOMBE on a Si(001) substrate that had been carbonized with a 3C-SiC interlayer. The purpose of the 3C-SiC interlayer was to prevent the formation of an amorphous SiO$_2$ interlayer, which the authors reported to result from MgO growth of Si directly through the same process. It was also reported that the 3C-SiC interlayer acted to relieve the lattice strain between MgO and Si. The estimated lattice mismatches are; MgO/Si -22%, MgO/3C-SiC -3%, 3C-SiC/Si 20%. The objective of the study was to determine the growth characteristics of MgO/3C-SiC/Si using a single
metalorganic precursor for both the carbonization of Si(001) and growth of MgO. Although the MOCVD growth technique is not similar to MBE, it may be possible to extract some similarities between the heteroepitaxy of MgO on 3C-SiC and MgO on 6H-SiC and the role of oxygen plasma on the growth mechanism of MgO.

It was observed by the authors that in the absence of oxygen, the magnesium acetylacetonate precursor (Mg(acac)$_2$) could be used to carbonize both carbonize the Si to form an interlayer of 3C-SiC and form MgO when oxygen was introduced. After the deposition and characterization of the 3C-SiC interlayer, oxygen plasma (10$^{-5}$ Torr) was introduced into the chamber, which was reported by the authors to initiate the nucleation of MgO. Although the principles behind MOMBE are different that solid source MBE, the results reported by Hoerman, et al. indicate the importance of oxygen on the growth mechanism of MgO on SiC. Considering the same organic precursor was used for both the carbonization of Si and the deposition of MgO, there is evidence that MgO will readily form when both magnesium and oxygen are available. This can be extended to the growth of MgO by MBE on 6H-SiC. However, due to the nature of MOMBE, it was not possible to study the effect of increased Mg on the growth mechanism of MgO. This is due to the complex metal organic precursor that was used for magnesium. Rather, only the impact of oxygen could be investigated.

Hoerman, et al. reported that by maintaining a constant oxygen plasma background pressure of 10$^{-5}$ Torr and constant precursor flux of 10$^{-7}$ Torr, the growth rate of the MgO could be varied by adjusting the plasma power. By increasing the plasma power, the relative amount of atomic oxygen in the plasma is increased. Therefore, the authors concluded that the MgO growth mechanism was limited by available oxygen.
Although this is a safe conclusion for the MOMBE system, it may not necessarily hold true for solid source MBE where the magnesium and oxygen (atomic/molecular) can be controlled independently. By having atomic level control over all species, it will be possible to study the impact of each element individually on the nucleation and growth mechanism of MgO on 6H-SiC.

Craft, et al. [59, 84] also reported on an oxygen controlled MgO growth mechanism on GaN(0002). At a deposition temperature of 650 °C and in the absence of any oxygen species, no magnesium metal was deposited on the GaN surface. This indicates that the deposition temperature was sufficiently high enough to prevent magnesium metal incorporation where the desorption rate was greater than the absorption rate. However, once molecular oxygen was introduced, the nucleation and growth of MgO was initiated. Although an oxygen absorption growth mechanism was reported, the effect of increasing oxygen pressure on the MgO growth rate was not reported. Therefore, it is not sufficient to conclude or hypothesize an oxygen limiting growth mechanism. Because MgO is a binary oxide, it is obvious that the presence of oxygen (and magnesium) is necessary for the formation of MgO. Once the oxygen was introduced into the system, the oxygen flux was in excess. However, similar to the results reported and discussed previously by Yadavalli, et al. the excess oxygen does not necessarily mean that every O₂ molecule can contribute to the growth of MgO. This is due to the required step of O₂ dissociation. Since no flux was varied, it is not possible to determine the actual limiting factor.

The MBE system used for MgO film growths discussed in this dissertation has the capability of varying each component independently. It will therefore be possible to
investigate the contribution of magnesium, atomic oxygen, molecular oxygen, and substrate temperature on the nucleation and growth mechanism of MgO on 6H-SiC. The Mg flux can be varied by simply increasing the effusion cell temperature. The relative amount of O:O$_2$ can be increased by increasing the power to the remote oxygen atom source. Once the growth mechanism of MgO has been thoroughly investigated, it will be possible to integrate high-quality, single crystal MgO on 6H-SiC for use as a template layer for subsequent functional oxide integration.

3.3.2 MgO as a template for tetragonal ferroelectrics

For years magnesium oxide (MgO) has been widely used as a diffusion barrier for various device applications [86]. It has been integrated into a wide range of lead based ferroelectric devices including ferroelectric field effect transistors (FEFET) [79] and non-volatile random access memory (NVRAM) [86, 124]. MgO is a highly crystalline oxide with a rocksalt structure, which when used as an interlayer for Pb-based film on Si substrates, has been proven to prevent lead diffusion into silicon substrates [89].

Basit, et al. [86] showed that highly oriented PZT films could be grown using a thin interlayer of MgO on Si. This MgO interlayer was used to minimize the interdiffusion of Pb from PZT into a SiO$_2$/Si substrate. This is of particular interest for preventing interface breakdown and creating an abrupt interface between the substrate and functional film. The PZT film was sputtered on the MgO at a temperature of 100 °C and annealed at 600 – 650 °C. It was reported that both the MgO film and the PZT film were highly (100) oriented, which was the same orientation as the original Si substrate, indicating a cube on cube epitaxy and minimized lattice mismatch between the PZT,
MgO, and Si. Although the PZT was initially amorphous, it is not uncommon to include an annealing step to crystallize the function film. However, depending on the deposition technique used, this step may not be necessary but may require higher deposition temperature. Regardless of the technique, the elevated annealing temperature or growth temperature may result in an interface breakdown if the materials are not thermodynamically stable, as is the case with most Pb-based materials with silicon. Such a breakdown would result in a non-abrupt interface between the functional film and semiconductor, which would be detrimental to the ultimate functionality of the device.

The effectiveness of the MgO interlayer as a diffusion barrier was characterized through energy dispersive x-ray spectroscopy (EDS), and the results are illustrated in figure 3.5 [86].
Cross sections of the PZT/MgO/SiO$_2$/Si and PZT/SiO$_2$/Si heterostructures were analyzed via EDS in order to characterize the interfaces between different layers. Based on figure 3.5 (a), the authors reported that the MgO interlayer was contained between the PZT layer and the SiO$_2$/Si substrate with an abrupt drop-off of Pb and Zr, indicative of the absence of interdiffusion between the PZT film and the MgO interlayer. However, in figure 3.5 (b), the Pb profile is shifted, indicating greater interdiffusion of Pb into the SiO$_2$/Si substrate without an MgO interlayer. Although EDS is a standard analysis technique used to quantify elemental composition, it spatial resolution is about 1 µm. Therefore, for the nanometer scale resolution reported by Basit, *et al.* in figure 3.5, each
data point is most likely a representation of an average composition across a much large area. For use in characterizing the degree of interdiffusion at the interface, where the interlayer thickness may be relatively thin compared to the lateral resolution, EDS may be insufficient for accurate concentration profiles across the interfaces. Therefore, from the results reported in figure 3.5, the actual abruptness of the PZT/MgO/SiO₂/Si interfaces cannot be accurately determined. However, the EDS results do indicate that the MgO does reduce the degree of Pb interdiffusion into Si. For more accurate characterization of the interfaces, it would be necessary to analyze the samples using high resolution TEM and EELS.

Although the results and effectiveness of the MgO interlayer cannot be accurately quantified, there are two key takeaways. First, the use of MgO as an interlayer enabled the heteroepitaxy of PZT on the Si substrate, even though an annealing step was required for crystallization. Second, regardless of the spatial resolution limitations of EDS, chemical characterization of the PZT/MgO/SiO₂/Si structure did reveal that the MgO was effective at minimizing (if not preventing) Pb diffusion into the substrate. These are two important properties to consider for the selection of MgO as a template layer for the integration of functional oxides on 6H-SiC.

In addition to acting as a diffusion barrier for Pb-based oxides on Si, it can be used as a template to alleviate various thermal and mechanical stresses. Lee, et al. [87, 125, 126] used different single crystalline, cubic oxide substrates, including MgO, STO, and KTaO₃ (KTO) to grow PTO films with various thickness ranging from 15 – 250 nm. It was reported that the thickness of the film played a very important role in both the final crystal structure and orientation, which were characterized using XRD and TEM. From
the PTO films characterization, the authors reported that lattice strain was much more influential on crystal structure and orientation than thermal strain. This is of particular interest due to the large thermal expansion coefficients of MgO and BTO relative to 6H-SiC (refer to table 2.2). This is especially true for thinner films (< 10 nm), which do not necessarily share the same lattice and thermal properties as their bulk counterparts.

It was reported that the formation of preferential c-axis orientation of PTO is as a result of compressive stress during film growth. Since the c-axis lattice parameter of a tetragonal perovskite (PTO and BTO) is larger than the a-axis orientation, better lattice matching at the film substrate interface would result from c-axis growth, where the smaller a/b lattice was in-plane. However, all PTO films were slightly polycrystalline, where as the thickness of the PTO film increased, there reached a critical point at which the preferential c-axis (001) orientation reached a maximum of approximately 75%. The relationship between PTO(001) orientation and PTO film thickness is illustrated in figure 3.6 [87], where the right axis (α) represents the percent c-axis orientation. The PTO film illustrated in the figure is for PTO grown on MgO(001). The left axis (K) represents the ratio of effective strain within the PTO film and is characteristic of the lattice mismatch at the growth temperature relative to the thermal mismatch. This is an important property to consider when investigating effect strain-enhanced ferroelectricity.
Figure 3.6: Orientation saturation and strain ratio dependence on film thickness for epitaxial PTO grown on MgO [87].

Little has been published about the effects of thermal strain. The authors hypothesized that at elevated growth temperatures the atomic arrangement of the film can be thermodynamically stable in a particular crystal structure and orientation. However, as the film is cooled, the difference in thermal expansion creates a buildup of stress. The film compensates for this by crystal structure transformation. This physical transition is a means of alleviating stress and is different than the transition that occurs at the Curie temperature. Unlike lattice strain, thermal strain cannot be absorbed within the crystal lattice during film growth. During the early stages of film growth, lattice strain can be absorbed by crystal lattice of the film. This is the principle concept behind strain-enhanced ferroelectricity and interface engineering, discussed previously in section 3.1.1. For example, when PTO was deposited on MgO, it was reported that the PTO was under compressive strain. Lee, et al. hypothesized that as the PTO film thickness increased, the accumulated lattice strain also increased. Once a critical thickness (not reported) was reached, the crystal structure of the PTO film transitioned from a strained single crystal to polycrystalline in order to alleviate the strain. As a result, the lattice parameter of the
growing PTO film is dependent on both film thickness and temperature. The temperature affects the lattice spacing based on the thermal expansion coefficient. The film thickness affects the lattice spacing as the film transitions from a strained thin film to bulk properties.

Lee, et al. continued to investigate the effects of thermal and lattice strain on the crystal structure and orientation by growing PTO on various substrates including MgO(001), KTO(001), and STO(001). These three substrates were chosen based on their lattice mismatch and thermal mismatch with PTO. Table 3.1 [126] below shows a comparison between PTO film properties and oxide substrate properties at both room temperature and the deposition temperature of 700 °C.

**Table 3.1**: Lattice constant and thermal expansion coefficient comparison of PTO compared with bulk MgO, STO, and KTO at room temperature and 700 °C [126].

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal Structure</th>
<th>Lattice Constant (Å)</th>
<th>Thermal Expansion Coefficient (×10⁻⁶/K)</th>
<th>Lattice Constant (Å)</th>
<th>Lattice Mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO₃</td>
<td>Tetragonal</td>
<td>a = 3.899</td>
<td>12.6</td>
<td>a = 3.9775</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 4.153</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>Cubic</td>
<td>a = 4.213</td>
<td>14.8</td>
<td>a = 4.2551</td>
<td>-6.524%</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>Cubic</td>
<td>a = 3.905</td>
<td>11.7</td>
<td>a = 3.9358</td>
<td>1.05%</td>
</tr>
<tr>
<td>KTaO₃</td>
<td>Cubic</td>
<td>a = 3.989</td>
<td>6.67</td>
<td>a = 4.0069</td>
<td>-0.735%</td>
</tr>
</tbody>
</table>

The three cubic oxide substrates were chosen by the authors because each substrate offered a different lattice and thermal strain. Growth of PTO on MgO should result in tensile strain and negative thermal strain (i.e. the thermal expansion coefficient of PTO is lower than that of MgO), PTO/STO should result in minimal lattice strain and minimal thermal strain, and PTO/KTO should result in relatively little lattice strain but positive thermal strain. Note that the lattice mismatch calculation used by Lee, et al. uses
the lattice parameters at 700 °C. The goal of the research performed by Lee *et al.* was designed to study the effects of lattice and thermal strain on PTO epitaxy with varying film thickness. The results of their research are summarized in figure 3.7 [126], where various strains are dependent of PTO film thickness. The strains of interest are: a) misfit strain, b) relative lattice to thermal strain, and c) net elastic strain.

![Figure 3.7](image)

**Figure 3.7**: Comparison of stresses between PZT and MgO, STO, and KTO; (a) effective lattice strain, (b) lattice/thermal strain ratio, and (c) net elastic strain [126].

In general, the previous figure illustrates that all strain within the PTO film decreases sharply during the initial stages of growth. This is due to the alleviation of strain through the formation of dislocation and other relaxation mechanisms. In addition, it should be expected that as the film thickness increases, the properties of the film will
become more characteristic of the bulk properties. Most interestingly, it the effect illustrated in figure 3.7 (c), which relates the net elastic strain to film thickness. Comparing the net elastic strain of PTO deposited on the three different oxide substrates, it is observed that PTO/MgO has the lowest net elastic strain. Interestingly, it does not have the lowest misfit strain or lattice/thermal strain ratio. This is of particular interest for this dissertation because it supports the use of crystalline MgO as an effective template layer for the heteroepitaxy of tetragonal perovskite ferroelectric. When combining the thermal and lattice mismatch of the function oxide and the MgO/6H-SiC template, it may be possible to minimize the net elastic strain at the interface and thus integrate high-quality BTO into a next-generation heterostructure.

MgO has been proven an effective diffusion barrier and template for the improved epitaxy of functional, perovskite ferroelectrics on various substrates. MgO has been used as both a template [51, 73, 79, 86, 89] and as a substrate [81-83, 85, 120] for the heteroepitaxy of various tetragonal perovskite ferroelectrics by different deposition techniques, including sol-gel, PLD, CVD, and MBE. Regardless of the deposition technique or processing procedure, when BTO was deposited on crystalline MgO(100), the resulting BTO exhibited a type of cube on cube epitaxy. However, because MgO is a cubic structure with lattice constants of \( a = b = c = 4.213 \) Å and BTO is a tetragonal structure with \( a = b = 3.994 \) Å and \( c = 4.038 \) Å, the resulting BTO films often exhibited a biaxial orientation. This is due to the fact that the in-plane lattice spacing of MgO (4.213 Å) is larger than the both the a and c lattice spacings of BTO. The tensile strain during BTO growth often promoted c-axis in plane, resulting in (100) oriented films with 90° rotation of domain walls. Similarly, as mentioned previously, when tetragonal
ferroelectric were deposited under compressive strain, the resulting films was highly c-axis oriented.

Since BTO is a tetragonal ferroelectric, the majority of research has focused on (001) oriented BTO in order to maximize the ferroelectric properties. However, the two most promising wide bandgap semiconductors (SiC and GaN) both have hexagonal crystal structures. As a result, when cubic (MgO, STO) or tetragonal (BTO, PZT, etc.) materials are integrated on the hexagonal substrates, the resulting orientation of the films is often (111). This is because the (111) orientation of a cubic structure corresponds to a pseudo-hexagonal structure. Although (111) oriented ferroelectrics have poor electrical properties relative to (001) oriented films, the pseudo-hexagonal structure can be used to further integrate hexagonal ferrites (BaM) into a multifunctional, next-generation device heterostructure with magnetoelastic and magnetoelectric coupling [17, 21-23, 127].

3.3.3 MgO integration on wide bandgap semiconductors

MgO is an ideal candidate for use as a heteroepitaxial template for many tetragonal, perovskite ferroelectrics because of its well matched lattice spacing. It has been demonstrated to be an effective template for heteroepitaxial growth of (100) and (001) oriented perovskites (BTO, BST, PZT, etc.) and can also be used as a template for (111) oriented growth. Much research has focused on the deposition of MgO on various substrates and orientation for a range of applications. Regardless of the application, trends can be extracted from the reported growth mechanisms in order to engineer a process suitable for the desired application. For use as a template layer, the initial nucleation and growth mechanisms of MgO are of particular interest since the ultimate
thickness of the MgO will be on the order of a few nanometers. Few researchers have studied the growth mechanisms of MgO on wide bandgap semiconductors (SiC, GaN). In addition to being used as an effective template layer and diffusion barrier, MgO is a promising candidate for next generation electron devices that require high switching frequencies and high power due to its high dielectric constant (\(\kappa = 10\)) and high threshold voltage [128, 129]. For Si based technology, SiO\(_2\) is considered the standard for use as a dielectric oxide. However, with the transition to wide bandgap semiconductors, SiO\(_2\) is insufficient for next generation microelectronics due to its low dielectric constant (~3.9). As a result, the maximum voltage and frequency of the device is limited by the properties of the dielectric rather than the semiconductor. MgO offers superior electrical properties of SiO\(_2\) for use as a dielectric layer on wide bandgap semiconductors because it has a dielectric constant that is very close to the dielectric constant of hexagonal SiC (\(\kappa \sim 10\)). In addition, it has a large bandgap of 7.8 eV and high thermal conductivity. However, one concern regarding the integration of MgO on SiC or GaN is the bandgap offset and bending. Researchers have demonstrated through the use of XPS that the majority of the band offsets are absorbed by bending in the valence band rather than the conduction band [59, 63]. This is in part because the wide bandgap semiconductors were all n-type, which shifted the Fermi level towards the conduction band.

MgO integration on SiC and GaN is relatively limited compared to the integration on Si or non-functional substrates. However, several groups [59, 63] have studied the integration of MgO on GaN and SiC for the potential use as a dielectric layer in a MOSFET (metal-oxide semiconductor field-effect transistor). MBE grown MgO on GaN or hexagonal SiC have all been reported to oriented in the (111) direction, due to the
pseudo-hexagonal structure with an in-plane lattice spacing is $\sqrt{2} \times a$, where $a$ is the lattice spacing of the cube. For the case of MgO, the in-plane, atom-to-atom spacing is 2.98 Å. Considering the hexagonal structure of GaN (in-plane lattice spacing of 3.19 Å) there are two potential epitaxy registries. One results in a tensile strain where the hexagon on the MgO overlays the hexagon of the GaN. The second results in a compressive strain where the hexagon of the MgO is rotated 30° from the hexagon of GaN. Both mismatches are approximately 7%, which helps aid in the understanding of the preferred strain and its impact on the nucleation and growth mechanisms of MgO. Through the use of RHEED and XRD, MgO was reported to prefer to grow with tensile strain [59, 63, 84, 128, 130]. This is not too surprising considering the tensile epitaxy allows for atom-to-atom alignment whereas the compressive epitaxy allows only 50% of the atoms to align. In addition to lattice mismatch, the thermal expansion coefficient of MgO ($14.8 \times 10^{-6}$ K$^{-1}$) is more than 2.5 times that of GaN ($5.6 \times 10^{-6}$ K$^{-1}$ for in-plane). Therefore at elevated growth temperatures, the tensile mismatch between the MgO and GaN will be reduced while the compressive mismatch would be increased. This coincides with effect of net elastic strain discussed previously for PTO grown on MgO. The aforementioned mismatches can be used as a basis for understanding the impact of individual stresses as well as net elastic stress on the heteroepitaxy of MgO on wide bandgap semiconductors.

Craft, et al. [84] reported that the MgO(111) deposited on GaN(0002) was highly twinned due to the 6-fold symmetry of the MgO(111) atomic structure. This observation is true for all cubic rocksalt structures (CaO) that are grown in the (111) orientation [84]. This same philosophy can be applied to the tetragonal perovskites, which are very similar to cubic structures. Chen, et al. [63] also reported twinned MgO(111) on GaN(0001) and
further observed through cross-sectional TEM that the twinned structure was due to an in-plane rotation of the MgO, which occurred when the film thickness reached 4 nm. Although both groups reported epitaxial growth of MgO on GaN, they also reported coalesced 3-D island growth mechanisms rather than a layer-by-layer growth mechanism. Since the (111) orientation of MgO consists of alternating layers of Mg and O, the overall MgO(111) film results in an alternating positive/negative ionic structure with a net polarity. As a result, the (111) orientation of MgO is not the most energetically favorable configuration. It was reported that this may be responsible for the 3-D growth mechanism. The alternating layers of oppositely charged magnesium and oxygen result in a dipole moment perpendicular to the surface. In order to minimize this instability, the surface cannot truly be terminated by a layer of oxygen or magnesium. Much research has been conducted to understand the true surface termination of MgO (111). Early work suggested the surface became faceted into neutral \{100\} planes [131, 132]. However, more recent research has discovered that faceting is not a favorable means of stabilization, but rather MgO(111) surface terminations of $\sqrt{3}\times\sqrt{3}$ $R30^\circ$, $2\sqrt{3}\times2\sqrt{3}$ $R30^\circ$, or $2\times2$ reconstructions are more favorable for minimizing electric dipoles [133-137]. Although these surface reconstructions are electrically stable, they often require high temperatures (> 800 °C) to form. Further research combining experimental and theoretical studies has supported the hypothesis that an -OH stabilized MgO(111)-(1×1) surface is most favorable and actually results in a surface termination that is more stable than the non-polar MgO(100) surface [137-139]. Understanding the mechanisms responsible for 3-D island formation as well as surface energy minimization is important for engineering a growth process capable of depositing smooth, single crystalline MgO on 6H-SiC.
MgO has also been integrated on 6H-SiC for characterization as a potential replacement for SiO₂ on 6H-SiC [128]. Similar to the MgO/GaN material system, the hexagonal structure of the 6H-SiC(0001) promoted (111) oriented MgO. No mention was made regarding the surface reconstruction of the 6H-SiC, but assuming a (1×1) reconstruction, the in plane lattice spacing of 3.08 Å has a lower tensile mismatch (~3.3%) with MgO(111) than GaN. As the deposition temperature of the MBE grown MgO [63] was increased from 100 °C to 400 °C, the authors reported an increase in crystallinity but also an increase in roughness (RMS = 4.64 nm to 11.7 nm), as indicated by XRD and AFM respectively. The roughness and 3-D features were again reported to be a result of the metastable nature of the MgO. Although the 6H-SiC starting surface consisted of atomic steps (several hundred nm wide and approximately one unit cell high). The final morphology of the MgO showed no indication of the underlying steps. This gives evidence to a growth mechanism that is independent of surface morphology and more dependent on the atomic interaction within the developing MgO microstructure rather than a step-flow or layer-by-layer growth mechanism. Understanding the preferred growth mode of MgO on 6H-SiC is of great importance for depositing a smooth and uniform, thin (few nanometers) MgO film of high-quality.

Since tetragonal structure (perovskite ferroelectrics) are very similar to cubic structures, due to the slight elongation of the c-axis lattice spacing, it is relatively safe to assume that the mechanisms responsible for the epitaxy of (111) oriented MgO may also promote (111) oriented ferroelectrics on 6H-SiC and GaN. Although the pseudo-hexagonal structure of (111) oriented perovskite ferroelectrics in not the ideal orientation for polarization and ferroelectric properties, it can be utilized to subsequently integrate
hexagonal ferrites (BaM) into a multifunctional heterostructure. Although lattice matching may be responsible for the epitaxial alignment of each subsequent oxide film, the growth mechanisms of tetragonal BTO and cubic MgO could be completely different. Understanding the specific growth mechanisms of both MgO and BTO are important for establishing a high quality heterostructure for the eventual integration of ferrimagnetic BaM into a multifunctional heterostructure.

### 3.4 Multifunctional device heterostructures

Although multiferroic materials have been the focus of much attention, there are actually very few materials with intrinsic multiferroic properties. A multiferroic material is a material that exhibits multiple ferroic properties (ferroelectric, ferromagnetic, etc.). As a result, the definition of multiferroic has been broadened to incorporate any heterostructure that exhibits multiferroic properties. Therefore, by integrating a ferrimagnetic (BaM) with a ferroelectric (BTO or BST) on a functional semiconductor, the resulting heterostructure can be termed a multiferroic heterostructure. Composite multiferroic structures offer higher potential for ultimate device performance over intrinsic multiferroics like BFO because the functional properties of the individual layers can be optimized, resulting a wide range of multifunctionality that can be tuned statically and dynamically.
3.4.1 Horizontal multifunctional arrays

Little research has focused on the integration of a multilayered functional oxide heterostructure. Several studies [17-19] have reported on the integration of ferrimagnetic BaM with ferroelectric BST on different substrates. The heterostructures of interest included BST/BaM/sapphire and BaM/BST/MgO. The sapphire substrate has a hexagonal crystal structure and was selected to optimize the ferromagnetic properties of the hexagonal BaM, while the cubic MgO(100) substrate was chosen to optimize the tetragonal properties of the BST.

For the BaM/BST/MgO heterostructure, the authors reported epitaxial BST(100) and only (00I) oriented BaM. This heteroepitaxy would result in the preferred orientations of both the BST and BaM layers, with the optimized ferroelectric and ferromagnetic properties out-of-plane. However, VSM characterization of the (00I) oriented BaM indicated a lack of anisotropy and no preferred orientation. Further AMF characterization indicated an acicular surface morphology, typically associated with the c-axis in-plane. The cubic epitaxy of the BST layer is expected based on the lattice matching between the cubic MgO and tetragonal BST. However, the lattice matching between the hexagonal BaM and tetragonal BST would be expected to promote a polycrystalline BaM layer with c-axis in-plane and minimal anisotropy. This is what was observed by VSM and AFM characterization, but not XRD.

For the BST/BaM/sapphire heterostructure, authors reported (00I) oriented BaM but (111) oriented BST. Due to the hexagonal crystal structure of the sapphire, the observed epitaxy between the BaM and sapphire resulted in a minimized lattice mismatch and was therefore expected. Similarly, the hexagonal structure of BaM(001) would be
expected to promote the pseudo-hexagonal orientation of BST(111). This is what was observed by XRD. In addition, VSM and AFM characterization of the BST/BaM/sapphire heterostructure both indicated the (00\ell) oriented BaM and (111) oriented BST. The combined characterization of the heterostructure on sapphire indicates that it is possible to integrate various materials with different functional properties into a multifunctional (multiferroic) device with tunable electric and magnetic properties. However, it should be noted that BST/BaM structure was integrated on a lattice matched substrate with poor semiconducting properties. In order to optimize the multifunctional properties into a potential device, it is necessary to integrate the multilayers onto a functioning semiconductor, such as SiC. The coupling of a ferroelectric and ferrimagnetic material is of particular interest for this dissertation because it illustrates the potential for a multifunctional heterostructure. However, both BaM/BST heterostructures discussed were integrated on non-functional substrates. In order for the true potential of a multifunctional heterostructure to be realized, it needs to be integrated onto a wide bandgap semiconductor for high-power, high-frequency applications.

3.4.2 Vertical multifunctional arrays

An alternative approach to the traditional multilayered was reported by Zheng, et al. [23] and Li, et al. [22] who demonstrated multiferroic behavior and magnetoelastic coupling between vertically structured BTO-CoFe_2O_4 [23] and PTO-CoFe_2O_4 [22] composite arrays. For both composite structures, the authors reported a dispersion of self-assembled ferrimagnetic CoFe_2O_4 rods (20 – 30 nm in diameter) embedded in the ferroelectric (BTO or PTO) matrix. The composite structures were deposited by PLD on
various crystalline substrates. The orientation and dispersion of the ferrimagnetic rods were reported to be dependent on the orientation and lattice of the substrate and the resulting strain/mismatch between the ferroelectric/substrate and ferrimagnetic/substrate. The authors further reported on strong magnetoelastic coupling between the two phases. This is due to the large contact area and ferroelectric/ferrimagnetic interface that results from the self-assembled vertically aligned structures. Unlike traditional horizontally aligned heterostructures, which have a limited two-dimensional, in-plane interface, the vertically aligned composite structures have significantly more interface area. As a result, the potential for increasing and optimizing the magnetoelastic and magnetoelastic coupling is enhanced. However, the vertically aligned composite structures do require thermodynamic phase separation. Further, the self-assembly of the ferroelectric/ferrimagnetic composite structure required selective strain engineering and substrate selection. As a result, the composite structures were deposited on STO(110) and (001), which is not a functional semiconducting substrate and thus has limited device potential.

Liu, et al. [20] reported on similar vertically aligned multiferroic composite structure consisting of matrix of core-shell nanowires. Ferroelectric PZT nanotubes were synthesized in an alumina template by electrodeposition and then NiFe$_2$O$_4$ was deposited by the same process to fill the PZT nanotubes, resulting in a NiFe$_2$O$_4$ core and a PZT shell. The authors reported that the composite nanowires exhibited both ferroelectric properties and magnetic properties, but did not demonstrate the effective coupling between the functional properties. Regardless, the authors did successfully demonstrate the potential of vertically aligned core-shell nanowires with ferroelectric and
ferrimagnetic functionality. Similar to the vertically aligned, self-assembled structures [22, 23], the NiFe₂O₄-PZT core-shell nanowires were not fabricated on a functional substrate, thus limiting the practical functionality of the structures.

3.5 Summary and critical approach

Integrated circuit and semiconductor technology is a field that is always evolving and requiring new, novel materials that can meet the increasing demands of smaller, more powerful, multifunctional devices. As with all engineering challenges, the ultimate goal can be broken down into more manageable objectives. By critically and thoroughly reviewing the current progress of literature regarding the individual aspects of the big picture, it is possible effectively and efficiently meet the requirements for success.

For the ultimate goal a fabricating a next-generation, multifunctional heterostructure, the individual aspects that must be addressed are; 1) reproducible and effective 6H-SiC surface preparation, 2) integration of high-quality, thin (few nanometers) MgO(111) for use as a heteroepitaxial template for tetragonal ferroelectrics, 3) integration of high-quality BTO(111) with functional ferroelectric properties, and 4) integration of high-quality ferrimagnetic BaM with magnetic properties. In addition to the integration of multiple layers of functional materials, a true multifunctional heterostructure will require magnetoelectric or magnetoelastic coupling of the BTO and BaM functional properties.

In order to meet the objective set forth for success, it is necessary to understand how the individual processing parameters affect the properties of the end product. For 6H-SiC surface preparation, it will be necessary to find a balance between the
heating/cooling rates, cleaning temperature, cleaning time, gas flow rate, and gas composition. Success will be defined by the formation of a reproducible starting surface with no unwanted residual contamination or scratches. This requires the complete removal of all scratches, the formation of atomic steps, the uniform stability of an adlayer reconstruction, and the absence of any excess carbon or silicon droplets. Once a reliable cleaning procedure has been established, the next step will be to integrate high-quality MgO.

A critical review of the literature regarding the hetero- and homo- epitaxy of MgO can help understand the mechanisms responsible for the high-quality growth of single crystalline MgO. The general trend suggest a growth mechanism that limited by the availability of oxygen. However, a complete study regarding the impact of individual species was not performed. In addition, the primary oxidation source for most MgO growth studies was molecular oxygen. Therefore, the incorporation of oxygen into the MgO lattice would require addition energy for the dissociation of O\textsubscript{2} to O. As a result, the direct impact of available oxygen (atomic oxygen) on the growth mechanism of MgO was not studied. Through the use of a remote oxygen atoms source and a solid source effusion cell, it will be possible to determine the impact of individual species (Mg, O, O\textsubscript{2}) on the nucleation and growth mechanism of MgO in order to engineer a growth process capable of depositing high-quality, single crystalline MgO for use as a heteroepitaxial template. The success of step will be defined by the effectiveness at promoting the heteroepitaxy of BTO and the formation of an abrupt interface between the BTO/MgO and MgO/6\textit{H}-SiC.
The heteroepitaxy of BTO on MgO can be correlated with the heteroepitaxy of other tetragonal perovskite ferroelectrics, due to the similarities in crystal structure. Therefore, by understanding the influence of processing conditions on the growth mechanisms of other tetragonal functional oxides, it may be possible to extract some similarities that can be implemented in the MBE growth of BTO on MgO/6H-SiC. The BTO must be single crystalline and smooth, since it will ultimately be used as a template for the subsequent integration of ferrimagnetic BaM. In addition to the deposition of smooth, high-quality BTO, the BTO must also be ferroelectric. Although the pseudo-hexagonal (111) orientation does not have superior ferroelectric properties, it should promote the heteroepitaxy of hexagonal ferrites (BaM) for magnetoelectric and magnetoelastic coupling between the ferroelectric BTO and ferrimagnetic BaM.

The final objective within the scope of this dissertation is to integrate a subsequent ferrimagnetic BaM layer onto the BTO/MgO/6H-SiC structure. Currently there is little research regarding the integration of hexagonal ferrites on tetragonal ferroelectrics, and even less regarding the integration on a functioning semiconductor. In order for the realization of next-generation multifunctional heterostructures, it will be necessary to demonstrate the successful integration of a BaM/BTO/MgO/6H-SiC heterostructure with magnetic and ferroelectric properties. As a next step, it will be important to demonstrate the successful coupling of the functional properties of the adjacent functional oxide layers.
4.0 Experimental Approach

In order to successfully engineer a process capable of growing single crystalline, epitaxial BTO and MgO on 6H-SiC with a controlled orientation and stoichiometry, it will be necessary to determine the roles and interactions of each individual species flux and processing parameters on the nucleation and growth of the oxide films. The growth and characterization capabilities available in the Interface Engineering Laboratory at Northeastern University consist of various in-situ, ex-situ, and real-time techniques. All thin oxide films were deposited by molecular beam epitaxy (MBE) in an ultra high vacuum (UHV) chamber with a base pressure of 2.0x10^{-9} Torr. The metals were supplied by solid source effusion cells (for Mg, Ba, and Fe) or a modified sublimator (for Ti), and the oxygen was supplied by a remote oxygen plasma source. In-situ reflection high energy electron diffraction (RHEED) was used real-time to monitor the crystal orientation and estimated growth rate. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were used to characterize the stoichiometry and bonding of the films. Atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) performed at Cornell University, and x-ray diffraction (XRD) performed at Yale University, North Carolina State University, and Northeastern University were used to characterize the surface morphology (roughness), surface features, atomic alignment, and crystallographic orientation. Electrical characterization on the MgO and BTO were performed by capacitance-voltage (C-V) and polarization-electric field (P-E) measurements at Yale University and Northeastern University.
4.1 Equipment specifications

The Interface Engineering Laboratory at Northeastern University has direct access to a wide range of powerful techniques whose specifications will be discussed in the following section. The equipment that will be discussed includes a custom built hydrogen flow furnace, two interconnected UHV chambers (one for analysis and one for oxide growth), XPS, AES, RHEED, effusion cells, AFM, and XRD.

4.1.1 Hydrogen flow furnace

One basic requirement for the successful integration of functional oxides on semiconductors is the formation of an abrupt and effective interface. In order to address this issue, it was necessary to develop a reliable, reproducible, and effective cleaning method in order to obtain a suitable starting surface on the 6H-SiC substrates. The solution was to design a custom built hydrogen flow furnace based on the extensive research and design of Ramachandran, et al. [108]. The custom furnace consists of a welded aluminum cube with an outer dimensional side length of 7.5 inches and a wall thickness of 0.75 inches and is illustrated in figure 4.1. The top of the furnace has a removable viewing port, which allows for direct temperature measurement through the use of a two color optical pyrometer (Omega, Omegascope OS3750 with a 2 mm analysis area). The sides of the furnace were fitted with internal water cooling to reduce the risk of burn injury to the user and help minimize outgassing of contaminants on the inside walls. Each face of the furnace was machined with threaded through holes, which were fitted with insulated power feedthroughs (front and back) and gas inlet/outlet (left and right). The gases (ultra-high purity hydrogen and/or ultra-high argon) were supplied
Independently by manual flow meters at flow rates ranging from 1 slpm up to 40 slpm. DC power for substrate heating was supplied by a Sorenson DCR 20-115B. The current was controlled manually and had a maximum current output of 150 A, but other equipment limitations (feedthroughs and wiring) limited the operating current to less than 100 A. On the inside of the furnace, the feedthroughs were equipped with copper clamps, which were used to secure a tantalum (ESPI Metals, 99.98% pure) strip 1 inch long × 0.5 inch wide 0.001 inch thick. A detailed description of the hydrogen cleaning procedure will be discussed later in section 4.2.1.

![Image of furnace](image1.png)  
![Image of Ta foil strip](image2.png)  
![Image of furnace during operation](image3.png)

**Figure 4.1**: Images of a) custom built hydrogen flow furnace, b) Ta foil strip used as the heating element (straight and folded into a boat) and c) furnace during operation with a 6H-SiC sample placed on the Ta-boat.

### 4.1.2 Ultra high vacuum chambers

Film growth and characterization was performed in two custom-designed UHV chambers. Prior to any growth experiments, all samples are loaded through a small load lock chamber that is attached directly to the analysis chamber but separated by a UHV-compatible manual gate valve. The load lock chamber is independently pumped by a mini turbo pump (Leybold, Turbovac 50). Once a sufficiently low pressure is obtained (approximately 2×10⁻⁸ Torr, as measured by an Ionivac hot cathode pressure gauge) the samples are transferred into the analysis chamber by use of a magnetic linear transfer
arm on to a manipulation stage with x, y, z, and θ movement. The analysis chamber is equipped with a Varian 500181B ion pump, which maintains a background pressure of approximately $2 \times 10^{-9}$ Torr (as measured by an ion gauge set with a nitrogen gas emission factor). The ion pump is an entrapment pump that consists of no moving parts in order to minimize vibration noise during XPS and AES characterization. The analysis chamber is equipped with AES, XPS, SED, Ar ion gun, and an electron flood gun (also referred to as a neutralizer). Further, the analysis chamber is lined with a μ-metal shield that is designed to absorb stray magnetic fields that could deflect electrons during the chemical electron spectroscopy characterization (XPS and AES).

The analysis chamber is connected to an adjoining UHV growth chamber, separated by a UHV-compatible manual gate valve, which allows for sample transfer between the two chambers with breaking vacuum and thus minimizing contamination. Transfer between the two chambers is again performed using a magnetic linear transfer drive. From the transfer arm, the sample is further transferred onto a custom built substrate heater, which can be moved in and out (z movement) as well as rotate (θ rotation). The custom built heater is capable of temperatures ranging from room temperature up to 900 °C, as measured by a type C thermocouple in direct contact to the molybdenum puck that the substrates are attached to. However, precise and accurate temperature measurements were performed using a two-color optical pyrometer, which typically read 50 – 75 °C below the thermocouple reading. A detailed explanation and discussion of the heater is documented in Brian Doyle’s thesis [140].

The growth chamber is equipped with a Leybold Turbovac 600C turbo pump with a pumping speed of 560 L/sec and has a Leybold Trivac D25B rotary vane forepump.
The background pressure in the growth chamber is \( \sim 2 \times 10^{-9} \) Torr, as measured by an ion gauge. The growth chamber is also fitted with a dual source, low temperature effusion cell (for Ba and Mg), a high temperature effusion cell (Fe), a modified Varian Ti-Ball (Ti), an Ar ion gun, a remote oxygen plasma source, and a RHEED system. Figure 4.2 shows the UHV system that was used for thin film functional oxide growth and characterization.

**Figure 4.2**: UHV system consisting of two interconnected chambers. The chambers are separated by a UHV compatible gate valve. The growth chamber consists of a remote oxygen atom source, solid source effusion cells (Mg, Ba, Fe), a Ti sublimator, and RHEED system. The analysis chamber consists of a XPS hemispherical analyzer and an AES single pass CMA.

### 4.1.3 Primary growth equipment

Both the growth and analysis UHV chambers are fitted with a variety of different equipment. The majority of the equipment used on a day-to-day basis for thin film growth will be discussed in further detail.
4.1.3.1 Solid source effusion equipment

For film growth, magnesium metal (99.98% shavings purchased from Alpha Aesar) and barium metal (99.9% rod purchased from Electronic Space Products International) were inserted into a SPECS Scientific Instruments dual source, low-temperature effusion cell cluster. The effusion cell cluster consists of two independently controlled and operated cells. Each cell consists of a 10 cc pyrolytic boron nitride (PBN) ceramic crucible, individual heating elements, individual type C thermocouple, integrated water cooling, and a manual shutter. For BaM film growth, the Fe was supplied by a Veeco Instruments EPI-16-M-L-7165 effusion cell with a 16 cc tungsten crucible charged with iron metal (99.999% granules purchased from Sigma-Aldrich. The Mg, Ba, and Fe fluxes were calculated based on the thermocouple temperature reading and vapor pressure calculations based on equation 2.6 discussed previously in section 2.7. By increasing the temperature of the appropriate cell (thermocouple resolution of 1 °C), the flux of that metal would increase. Similarly, by decreasing the temperature, the flux would decrease. By having the ability to maintain a stable cell temperature to within 1 °C, it was possible to fine tune the individual fluxes to obtain desired film chemistry. Typical fluxes ranged from $10^{12} - 10^{16}$ atoms/cm$^2$ sec with the maximum achievable flux being dependent on the melting point and vapor pressure of the respective material. Typically, the effusion cell temperatures were maintained at temperatures several hundred degrees Celsius below the melting point. If the material were to melt, when the material was cooled again, the ceramic crucible would crack.

The titanium metal was supplied using a Varian mini Ti-ball, which was originally designed for use as a titanium sublimation source for an ion pump and is based
on the design by Theis, et al. [141]. The Ti-ball is heated continuously at a current of 30 A in order to minimize crystalline domain reconstruction within the solid metal ball. At 30 amps, the mass loss of titanium is negligible and did not result in any unintended Ti contamination during other oxide film growths. Due to the fact that the Ti-ball was not originally designed as a tunable and precise metal source, the heating is limited by current interval of 0.5 A ranging from 30 A up to 50 A. As a result, in order to control the stoichiometry of Ti-containing oxide films, it was necessary to fix the Ti at a set current and adjust the other (Ba and O) to obtain the desired stoichiometry. Although the Ti-ball has severe limitations with respect to fine tuning of the flux, the stability of the flux remained fairly uniform throughout extended growth times (up to 10 hours).

4.1.3.2 Remote oxygen atom source

The oxygen was supplied through the use of an Oxford Applied Research remote oxygen rf-atom source model HD25. The plasma was generated within an Al$_2$O$_3$ discharge tube and exited through an Al$_2$O$_3$ aperture plate with 276 holes that were 0.2 mm in diameter. The size, quantity, and dispersion of the through holes minimized the line-of-site effect associated with UHV and created an oxygen environment at a pressure of 5.0×10^{-6} Torr, which corresponds to an O flux of 3.5×10^{15} atoms/cm$^2$ sec. Although the oxygen environment is a combination of oxygen species, the flux is represented on the basis of individual atoms. However, the chamber pressure reading is characteristic of molecular oxygen. Therefore, the flux calculation was performed on the basis of O$_2$ molecules and then multiplied by two. The oxygen flux was calculated from the following equation.
\[
\phi_O = 2\phi_{O_2} = 2\left(\frac{3.513 \times 10^{22} P}{\sqrt{MT}}\right)
\]

Eqn. 4.1

Where:

\(\phi\) = flux (#atoms/cm\(^2\) sec)

\(P\) = chamber pressure (Torr)

\(M\) = molecular weight (g/mol)

\(T\) = gas temperature (K)

The source was fitted with ion filter bias plates and an optical emission detector (OED). The ion filter bias plates were located at the end of the discharge tube and consisted of two parallel plates aligned parallel to the flow of oxygen. One plate was connected to ground, while the second was connected to a voltage source. When the plates were energized, by supplying a voltage bias between the two plates, any charged species (O\(^+\), O\(_2\)\(^+\), etc) would be deflected and removed from the neutral species. As a result, it was possible to use a variety of oxygen compositions during film growth. By varying the rf power to the source itself, it was possible to vary the relative amount of O\(_2\) that was cracked into different atomic oxygen and oxygen radical species. By turning the deflection plate bias on and off allowed for the use of neutral or neutral/charged oxygen. Direct measurement of the amount of atomic oxygen was made possible through the use of the OED, which was oriented line-of-site to the discharge tube where the plasma was being generated. By equipping the OED with an in-line optical filter, allowing only \(\lambda = 844\) nm (844 nm \(\rightarrow\) O generation), it was possible to qualify the amount of neutral atomic oxygen generated within the plasma. A higher emission reading corresponds to higher oxygen generation. The source could be operated in one of two modes; low plasma or high plasma. Low plasma was established at relatively low operating power and consisted of low atomic oxygen content, with an OED reading between 0.11 and 0.30 mV. High
plasma was established by operating at higher rf power and consisted of higher atomic oxygen content, with an OED reading between 30 and 450 mV.

4.1.4 Primary analysis equipment

Film characterization was performed both in-situ (RHEED, XPS, AES) and ex-situ (AFM, SEM, XRD, etc.). The typical characterization techniques that were used will now be discussed.

4.1.4.1. Auger electron spectroscopy

AES is a surface sensitive chemical analysis technique that is based on the emission of Auger electrons, which are a result of a relaxation mechanism once an atom has been excited by an incident electron (or photon). A detailed description of the Auger electron emission process and AES analysis can be found in appendix A. Because the Auger emission process is not a primary electron emission, the kinetic energy of the Auger electron must be less than the incident electron beam. Therefore, the sampling depth is often small. Table 4.1 lists the sampling depths of several Auger electrons that are of interest for this dissertation.

Table 4.1: A list of Auger electron emission energies and sampling depths for selected elements that are of interest for this dissertation.

<table>
<thead>
<tr>
<th>Element (transition)</th>
<th>KE (eV)</th>
<th>Depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (KLL)</td>
<td>92</td>
<td>1.9</td>
</tr>
<tr>
<td>C (KLL)</td>
<td>272</td>
<td>3.0</td>
</tr>
<tr>
<td>O (KLL)</td>
<td>503</td>
<td>4.5</td>
</tr>
<tr>
<td>Mg (LMM/KLL)</td>
<td>32/1174</td>
<td>1.6/8.5</td>
</tr>
<tr>
<td>Ba (MNN)</td>
<td>584</td>
<td>5.0</td>
</tr>
<tr>
<td>Ti (LMM)</td>
<td>418</td>
<td>4.0</td>
</tr>
<tr>
<td>Fe (LMM)</td>
<td>703</td>
<td>5.7</td>
</tr>
</tbody>
</table>
The AES spectra were used to identify and quantify the chemical composition of the substrates and films before and after film growth. Although quantification of the number of atoms from which an Auger electron was generated is difficult due to electron scattering and losses, the relative compositions of each element is very accurate, with an error typically less than one atomic percent. In addition, it is possible to extract bonding information from the AES spectra in order to characterize the local bonding environment of each element. Examples of AES spectra and bonding effects are illustrated in section 5.1.2 for 6H-SiC characterization.

The AES system used is a refurbished Perkin Elmer, Phi model 15-110B. It is a single pass cylindrical mirror analyzer. The incident electron beam can be operated up to 5 keV; however, typical operation was run at 2 keV. Depending on the settings and focusing of the optics, the minimum beam diameter was ~5 \( \mu \)m. Under these settings, AES characterization of the substrates and films had high spatial resolution and surface sensitivity, which is useful for characterizing the stoichiometry of thin films and uniformity across the sample surface.

4.1.4.2 X-ray photoelectron spectroscopy

XPS is another surface sensitive chemical analysis technique that was used to identify and quantify the chemical composition of the substrates and thin films. Unlike AES, XPS is based on the primary excitation of electrons that are generated from a photon (photoelectron). A detailed description of the photoelectron emission process and XPS analysis can be found in appendix A. Because the photoelectron emission process is a primary electron emission, the kinetic energy of the photoelectrons is dependent on the
kinetic energy of the incident photon. Therefore, the sampling depth is often deeper than that of Auger electrons. Table 4.2 lists the sampling depths of several photoelectrons that are of interest for this dissertation.

**Table 4.2:** A list of photoelectron energies and sampling depths for selected elements that are of interest for this dissertation.

<table>
<thead>
<tr>
<th>Element (emission)</th>
<th>Si (2p)</th>
<th>C (1s)</th>
<th>O (1s)</th>
<th>Mg (2p/1s)</th>
<th>Ba (3d5)</th>
<th>Ti (2p3)</th>
<th>Fe (2p3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KE (eV): Al Kα</td>
<td>1387.5</td>
<td>1202.0</td>
<td>955.0</td>
<td>1436.9/282.6</td>
<td>706.9</td>
<td>1032.8</td>
<td>779.9</td>
</tr>
<tr>
<td>Mg Kα</td>
<td>1154.5</td>
<td>969.0</td>
<td>722.0</td>
<td>1203.9/---</td>
<td>473.9</td>
<td>799.8</td>
<td>546.9</td>
</tr>
<tr>
<td>Depth (nm): Al Kα</td>
<td>9.7</td>
<td>8.6</td>
<td>7.2</td>
<td>9.9/3.1</td>
<td>5.8</td>
<td>7.7</td>
<td>6.2</td>
</tr>
<tr>
<td>Mg Kα</td>
<td>8.4</td>
<td>7.3</td>
<td>5.9</td>
<td>8.7/---</td>
<td>4.3</td>
<td>6.3</td>
<td>4.8</td>
</tr>
</tbody>
</table>

The multiple kinetic energies that are listed in the previous table are due to the incident energy of the photon, which can either be Al Kα (1486.6 eV) or Mg Kα (1253.6 eV). As a result, XPS spectra are often plotted as binding energy rather than kinetic energy, where the binding energy is ideally the incident photon energy minus the kinetic energy. The detector cannot directly measure binding energy, but rather it detects the kinetic energy of the generated electrons and the software converts the kinetic energy to binding energy based on the user defined incident energy. Because photoelectron emission is a primary excitation process, the core level electrons are highly sensitive to their local bonding environment. As a result, the position and shape of the photoelectron spectra can be used to extract the bonding states of specific elements. Examples of XPS spectra and chemical bonding shifts are illustrated in section 5.1.2 for 6H-SiC characterization.

The XPS system consists of a dual source, non-monochromated x-ray source (Phi model 04-548) and a hemispherical analyzer (Phi model 10-360). The two x-ray options
are Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) operated at 300 W. Careful calibration and fitting of gold and the Au4f7 photoelectron peak set the system’s minimum full width at half maximum (FWHM) of 1.2 eV with an 80% Gaussian/Lorentzian distribution, when run at a pass energy of 35.75 eV. Background subtraction was performed using the integrated Shirley method, which is the preferred method for inorganic crystalline solids [142]. The analysis spot size for XPS is controlled by a manually set aperture and was typically set at a diameter of 1.1 mm. Under these conditions, the XPS has a relatively poor spatial resolution than AES and typically has a deeper sampling volume. However, the combination of AES and XPS characterization can be used to accurately characterize the stoichiometry and bonding states of the substrates and thin films.

Both AES and XPS data collection and processing was performed using RBD Instruments (formerly RBD Enterprises) AugerScan software version 3.22.

4.1.4.3 Reflection high energy electron diffraction

RHEED is an in-situ characterization technique that is used for determining crystal structure, crystal orientation, and growth rate. In addition, careful interpretation RHEED pattern can be used to extract some very useful information about surface features. A detailed description of RHEED and interpretation of RHEED patterns can be found in appendix B.

RHEED is a surface diffraction analysis technique due to the glancing incident angle of the high energy electron beam. As a result, the resulting diffraction pattern is characteristic of only the top few monolayers of the crystal. Diffraction patterns are a result of the constructive interference of the diffracted electrons that obey Bragg’s law
and do not undergo any scattering losses. Figure 4.3 schematically illustrates the potential of RHEED.

**Figure 4.3:** Illustrations of how RHEED can be used for interpretation of crystal structure, growth rate, and surface features. a) characteristic crystal structure including single crystalline, polycrystalline, 3-D islands, and 2-D layer-by-layer growth (top to bottom, respectively) [143], b) growth rate determination by diffraction spot intensity oscillations for a layer-by-layer growth mode [144], c) diffraction spot shape due to transmission through different sized 3-D features [143], d) Kikuchi lines characteristic of a smooth surface, and d) chevron diffraction characteristic of surface faceting.
The previous figure illustrates how RHEED can be used for interpreting and extracting various features of the crystal. For a perfect single crystalline material, the diffraction pattern should consist of sharp, non-diffuse spots that form a ring, which is known as a Laue zone. The more diffuse the pattern, the less crystalline order. Amorphous RHEED patterns have a completely diffuse pattern with no observed diffraction spots. This is due to the fact that diffraction maxima require long range order for the constructive interference of the diffracted electrons. Polycrystalline films consist of the same Laue zones, but rather than sharp spots, the zones form well defined rings with no intensity variation. Interpretation of 3-D features and islands is significantly more involved. Once the surface becomes three dimensional, transmission effects begin to influence the RHEED pattern. Figure 4.3 (c) illustrates how the shape of the 3-D features can impact the shape of the transmission pattern. Further, if the 3-D features are faceted, the transmission pattern will exhibit chevron tails, which are a result of transmission through to the symmetric planes of the faceted feature.

RHEED can also be used to determine the growth rate of films. However, this is only possible if the growth mode of the film follows a 2-D layer-by-layer growth mode. As a new layer begins to deposit, the spot intensities within the RHEED pattern begin to diminish. This is due to electron attenuation through the new layer due to the disruption of long range order. As the layer becomes more complete, the crystalline order returns and the intensity increases. For a layer-by-layer growth mode, the oscillation of the spot intensity corresponds to growth rate of the crystalline film. This is illustrated in figure 4.3 (b).
In addition to determining the crystal structure and growth rate, other information can be extracted from the RHEED patterns. Figure 4.3 (d) illustrates the presence of Kikuchi lines. These lines are characteristic of atomically smooth surfaces of a single crystal. Therefore, from the presence of Kikuchi lines in a RHEED pattern it is possible to infer that the material is single crystalline with an atomically flat surface. Figure 4.4 shows the RHEED pattern and AFM image of hydrogen cleaned 6H-SiC(0001) and correlates the observed RHEED characteristics with the physical surface morphology.

![RHEED pattern and AFM image](image)

**Figure 4.4:** Interpretation of RHEED pattern for hydrogen cleaned 6H-SiC(0001) surface. Careful interpretation of the RHEED pattern can reveal a great deal of valuable information regarding the crystal structure, orientation, and surface features.

RHEED interpretation can also be helpful for determining surface reconstructions and relaxation mechanisms. For polar surfaces, like MgO(111), one possible surface reconstruction that can form in order to minimize surface energy is faceting. Faceting is a
physical reconstruction that can occur due to the formation of a partial crystal without the formation of new vertices in order to minimize the free energy of the surface. Although the crystal can still be single crystalline, the faceted features are three dimensional and can be observed in RHEED patterns by the presence of chevrons. This is illustrated in figure 4.3 (e). It is important to note that chevron tails can often be misinterpreted as part of a Kikuchi line. However, Kikuchi lines are characteristic of atomically smooth surfaces while chevrons are characteristic of transmission through 3-D faceted features. Therefore, distinction between the two is possible if care is taken when interpreting the RHEED patterns.

The RHEED system is a Staib Instruments RH-15 RHEED system with a maximum accelerating voltage of 15 keV. Typical RHEED images were obtained using an incident beam energy of 12.5 keV and a glancing angle of 2°. The RHEED images were digitally captured and processed using a k-Space Associates KSA 400 digital CCD camera and OEM software version 4.75.

4.1.4.4 Atomic force microscopy

AFM characterization of the substrates and films is very important for characterizing the surface morphology and roughness. AFM was used in order to evaluate the effectiveness of the ex-situ hydrogen cleaning procedure, by the removal of the scratches on the as-received 6H-SiC substrates. In addition to confirming the removal of scratches, AFM confirmed the formation of a smooth, uniform, surface that is necessary for the formation of an abrupt interface between the substrate and film. If the substrate surface were non-uniform or rough after ex-situ preparation, the film/substrate interface
would be less effective. The same AFM characterization was performed for all films that were deposited on the effectively prepared starting surfaces. The morphology of the thin films is equally as important as the morphology of the starting surface. This is because of the ultimate goal of integrating multiple layers of functional oxides into a multifunctional heterostructure. The surface morphology of each functional oxide film will ultimately be the starting surface for the subsequent functional oxide. As discussed previously in the background section, the formation of an abrupt interface is essential for the success of coupling the functional properties of the multilayers. Large features or grains could have a detrimental impact of the heteroepitaxy and effective integration of each subsequent layer.

AFM characterization was performed using an Ambios Technology 2SAAVO USPM. Typically, AFM characterization was performed in wave mode (non-contact/tapping) with the cantilever frequency around ~186 kHz and a tip radius of curvature less than 10 nm. The scan resolution was set at 1024×1024 and collected at a scan frequency of 1 Hz. In addition to tradition morphology characterization, the USPM could also be used for electric field microscopy (EFM) and magnetic force microscopy (MFM). EFM and MFM are characterization techniques similar to AFM, but rather than characterize the surface morphology and roughness, they are used to characterize the presence of electric and magnetic domains. EFM characterization is performed by applying a voltage bias between an electrically conducting tip and the sample. The presence of any electric domains would result in a deflection in the cantilever. MFM characterization is performed by scanning the sample with a magnetized tip. The presence of any magnetic domains would result in a deflection in the cantilever. Due to
the similarities in EFM and MFM operation and theory, only EFM will be discussed further.

EFM could be run in one of four modes, T-Phase, C-Phase, T-Amp, and C-Amp. The T- and C- correspond to Topology and Constant, respectively, while Phase and Amp correspond to the phase shift and vibration amplitude, respectively. For all four modes, the initial trace maps the surface topology. For the T- modes, the retrace automatically offsets the tip at a height $\Delta z$ (set by the user in nanometers) from the surface and follows the topology from the initial trace. For the C- modes, the retrace $\Delta z$ is not fixed, but rather the piezotube voltage is fixed. For –Phase modes, any deflection in the retrace is a result of a phase shift in the frequency of the oscillating tip. For –Amp modes, any defect in the retrace is a result of an amplitude variation in the oscillating tip. In order for there to be any deflection in the retrace, a potential is applied between the tip and the sample. This bias can be set between -10 V to 10 V. If a positive bias is applied between the tip and the sample, and the tip passes over a negatively charged domain, the tip with deflect downward. All EFM characterization discussed was performed in T-Phase mode with a $\Delta z$ of 25 nm and a scan rate of 0.25 Hz. Figure 4.5 schematically illustrates EFM operated in T-Phase mode.
Figure 4.5: A schematic illustration of T-Phase EFM characterization. The initial trace (1) scans the surface morphology while the retrace (2) offsets the topology by $\Delta z$ and applies a set voltage bias. When the biased tip passes over a polarized domain, the tip is either attracted or repelled from the surface depending on the direction of the bias voltage.

Note that EFM is not a read-write type characterization since the conducting tip never contacts the surface when a bias is applied. Rather, it is a qualitative characterization of the remnant polarized domains within the film. Any deflection in the cantilever is due to the biased tip passing over a polarized domain and being either attracted or repelled from the domain. If a positive bias is applied, when the tip passes over a negatively polarized domain, the tip will be attracted. In order to reliably determine the presence of polarized domains, the bias voltage should be performed at both a positive bias voltage to a negative bias voltage. The resulting EFM images should be inverse of each another. In addition, EFM scans collected at a zero bias voltage should result in no cantilever deflection and thus a blank image due to the subtraction of the topology after the initial trace.
4.1.4.5 Scanning electron microscopy

SEM characterization was performed in order to image the general features of the surface for the substrates and films. Although SEM is a qualitative characterization technique, it is a useful tool for imaging the surface on a relatively large scale (up to hundreds of micrometers). AFM characterization of the surfaces was limited to the 40 µm lateral movement of the piezotube. Therefore, it is possible that the images obtained by AFM would not accurately represent the surface characteristics. Multiple AFM scans could be collected across the sample surface in order to ensure an accurate representation. SEM was used in conjunction with AFM to accurately represent the surface features of the starting substrate and subsequent film. By having the ability to image the surface on the order of hundreds of micrometers, it was possible to characterize the defect density (micropipes, facets, droplet formation) of the 6H-SiC substrates as well as the density of large clusters (several tens of micrometers) that are not typical representations of the film surface. Although the defect of the 6H-SiC substrates is unavoidable, due to current manufacturing capabilities, the density of film defects can be addressed and minimized by adjusting the processing variables during film growth. Therefore, it is important to have both small scale characterization (AFM) and large scale characterization (SEM) in order to establish a uniform, high quality film.

SEM characterization was performed using a Hitachi S-4700 scanning electron microscope with an accelerating voltage of 2 keV and an emission current of 10 µA. The working distance was adjusted based on the desired spatial resolution, but was typically performed at 12 mm or 6 mm.
4.1.4.6 X-ray diffraction

XRD is an important characterization technique for determining the orientation and epitaxy of the crystalline materials. However, XRD is limited to films that are typically greater than 10 nm in thickness. This is due to the requirement of many diffraction planes for the constructive interference of Bragg’s law, which is necessary for the detection of diffracted x-rays. Although characterization of thin (less than 10 nm) was not possible, XRD was used to characterize thicker films in order to determine the orientation and epitaxy of the films. XRD data was collected using a Cu Kα (40 kV, 20 mA) on a Bruker D5005 θ:2θ Bragg-Brentano diffractometer equipped with a curved graphite crystal diffracted beam monochromator and a NaI scintillation detector. The system was equipped with a divergence and receiving slit set to 1.0 mm and a detector slit of 0.6 mm. Due to system limitations, only θ-2θ scans could be collected. Therefore, it was not possible to characterize in-plane stress or rotation. However, in conjunction with RHEED, a complete epitaxy picture could be determined. RHEED could be used to determine the orientation of the growing film as well as any in-plane rotation of the crystal lattice. XRD could be used to confirm the out-of-plane orientation and epitaxy. Although RHEED can be used to determine the in-plane lattice spacing (i.e. lattice strain) precise calibration using known standards was not performed, thus limiting the quantitative lattice spacing to relative differences. Knowing the orientation and epitaxial relationship between the film and substrate is important for understanding the alignment and growth of functional oxides on the wide bandgap semiconductors.
4.2 General experimental procedure

In order to meet the goals set forth in this dissertation for the ultimate integration of a multifunctional heterostructure on the wide bandgap semiconductor 6H-SiC, it is important to develop an experimental approach that addresses that is capable of meeting all the requirements for success. The complexity of overall objective was broken down into smaller, more specific objectives that could be addressed individually. These objectives could be simplified to; 1) 6H-SiC substrate surface preparation, 2) heteroepitaxial integration of a high-quality, single crystalline MgO template layer, 3) heteroepitaxial integration of high-quality, ferroelectric BTO, and 4) demonstration of the of a BaM/BTO/MgO/6H-SiC heterostructure. A detailed description of the daily operation can be found in appendix C.

4.2.1 6H-SiC substrate surface preparation

The surface of the as-received 6H-SiC surfaces consisted of residual oxygen and carbon contamination and deep (tens to hundreds of nanometers) scratches. Successful surface preparation would require the removal of unwanted surface contaminants, removal of scratches, and the production of a smooth, uniform, reproducible surface.

Surface preparation was performed using a custom built hydrogen flow furnace. In order to obtain the desired quality and reproducibility of the starting surface, various processing variables were adjusted. These variables included heating and cooling rate, ultimate temperature, cleaning time, gas flow rate, and gas composition. The heating and cooling rates were limited based on the operation of the power supply, which was manually controlled but limited to the precision of the analog needle gauge. As a result,
the precision of the current output was limited to 2.5 A (halfway in between the 5 A tick marks). The heating rate was further limited by the deformation of the Ta boat, which was used as the heating element during cleaning. When the heating rate was too fast, the Ta boat would deform resulting in poor contact with the backside of the substrate. The cooling rate was also limited by the formation of Si droplets on the surface of the 6H-SiC. When cooled too fast, Si droplets would form across the substrate surface, resulting in an unsuccessful cleaning. Therefore, it was necessary to establish appropriate heating and cooling rates that would result in good thermal contact and no Si droplet formation.

The ultimate cleaning temperature was limited by the maximum allowable current through the furnace. Although the power supply is capable of current output as high as 150 A, the leads and feedthroughs were limited to 90 A. In addition to the output current, the ultimate temperature was also dependent on the width of the Ta boat. A narrower boat would result in a higher temperature due to the reduced cross-sectional area for the current to flow through. However, the narrower the Ta boat and the higher the temperature, the more deformation would occur. At lower temperatures (1200 °C) there would be good thermal contact between the substrate and Ta boat, incomplete removal of the scratches. At higher temperatures (1800 °C), there would be complete removal of the scratches but increased deformation of the Ta boat. Therefore, it was necessary to find a balance between the Ta boat width, current output, and temperature that would result in good thermal contact and complete removal of the scratches.

The cleaning time is also an important variable because it needs to be adjusted to obtain complete, uniform etching. If the time is too short, then there will be incomplete removal of the scratches. If the time is too long, then the sample can be over etched.
resulting in surface roughening or degradation of the Ta boat. At the elevated temperature and corrosive hydrogen environment, the Ta boat will become brittle and eventually break. It is therefore necessary to prevent this from happening but also ensuring complete removal of the scratches.

The gas flow rate and composition are the final variables that can be adjusted. The gas composition can be a combination of hydrogen and argon. The argon acts as a diluent that can be used to reduce the relative amount of reactive hydrogen at the substrate surface and thus reduce the etch rate. The total gas flow rate can range from a few liters per minute up approximately fifty liters per minute (under standard temperature and pressure). Under all gas flow rates, the hydrogen was supplied at sufficient flow rates to eliminate mass transport limitations from the flowing gas to the substrate surface.

From the possible cleaning variables, it was necessary to find a balance that would result in a reproducible, effective cleaning procedure for the $6H$-SiC substrates. The optimized procedure would result in the reproducible and effective removal of residual oxygen and carbon contamination as well as the removal of the scratches. Further, the substrate surface needs to be smooth and uniform across the entire surface.

### 4.2.2 Heteroepitaxy of a MgO template layer

The hypothesis of using MgO as a template for heteroepitaxy is based on the close lattice match between the rocksalt structure of cubic MgO and the tetragonal structure of a wide range of perovskite functional oxides. Therefore, the successful integration of MgO on $6H$-SiC can then be used as a template layer for the subsequent heteroepitaxy of a variety of functional oxides with different functionality.
MgO heteroepitaxy was performed by MBE using a solid source magnesium source and a remote oxygen atom source. For all growths, the oxygen was supplied in excess, which resulted in a magnesium absorption controlled growth mechanism. However, it was still possible to vary the relative amount of atomic oxygen to molecular oxygen by varying the power to the atom source. In addition to the relative amount of oxygen to magnesium, the substrate temperature could be increased from room temperature up to ~900 °C. However, at elevated growth temperature, it is possible that the Mg desorption rate can exceed the Mg absorption rate and further over oxidize the 6H-SiC surface.

In order for the MgO to be an effective template for the subsequent heteroepitaxy, there are several requirements that must be met. The MgO film must be single crystalline, smooth, and have an abrupt, thermodynamically stable interface with the 6H-SiC. The single crystalline MgO is important in order for the lattice matched epitaxy to promote the integration of a variety of tetragonal perovskite ferroelectrics. The thermodynamically stable interface is important because complex functional oxide epitaxy often requires elevated temperatures for crystalline growth. Therefore, it is important that the MgO/6H-SiC interface not breakdown under subsequent growth conditions. Ultimately, the effectiveness of MgO as a heteroepitaxial template requires the ability of the MgO to promote the subsequent integration single crystalline functional oxides.

4.2.3 Heteroepitaxy of ferroelectric BTO

BTO is one of a variety of tetragonal perovskite ferroelectrics that is well lattice matched to MgO. Therefore, by successfully integrating single crystalline BTO on the
MgO would demonstrate the effectiveness of MgO as a heteroepitaxial template layer for a variety of tetragonal ferroelectrics.

BTO heteroepitaxy was performed by MBE using a solid source barium source, a titanium sublimator, and a remote oxygen atom source. Similar to the MgO growth conditions, oxygen was held in excess. However, because BTO is a ternary oxide, the Ti:Ba flux ratio needed to be adjusted in order to obtain the 1:1 film stoichiometry of BTO. In order to obtain crystalline BTO, elevated growth temperatures (> 500 °C) were necessary, which is typical for the crystallization of complex oxides.

In order for the successful heteroepitaxy of BTO, there are several characteristics that the BTO film must have. First, it must be single crystalline and smooth. This is because it will eventually be used as the starting surface for the subsequent deposition of BaM into a multilayered heterostructure. Second, and more importantly, it must be ferroelectric. If the BTO film is not ferroelectric, then it cannot be considered for use in a next-generation multifunctional heterostructure. Therefore, it is necessary to engineer a process capable of integrating high-quality, ferroelectric BTO on the MgO/6H-SiC.

4.2.4 Demonstration of a multilayered heterostructure

After complete characterization of the ferroelectric BTO/MgO/6H-SiC structure, the next step towards the realization of a next-generation multifunctional heterostructure is the subsequent integration of ferrimagnetic BaM. BaM heteroepitaxy was again performed by MBE using solid source barium and iron sources and a remote oxygen atom source.
The successful integration of BaM requires that the BaM be single crystalline, smooth, and have magnetic properties. In addition, success for the multifunctional heterostructure requires that the functional electric properties of the BTO be coupled to the functional magnetic properties of the BaM. However, demonstration of magnetolectric or magnetoelastic coupling is difficult. As a first step, this dissertation will demonstrate that the BTO is ferroelectric, and the BaM is ferrimagnetic.
5.0 Results and Discussion

The following section will discuss in detail the results and understanding of the research that was necessary for the advancement of this project and the ultimate goal of integrating complex functional oxides on wide bandgap semiconductors for next generation electronic devices. There are four major sections: 6H-SiC surface preparation, heteroepitaxial integration of MgO in 6H-SiC, integration of BTO on 6H-SiC by MBE, and multifunctional heterostructure on 6H-SiC.

5.1 6H-SiC surface preparation

In order to integrate multicomponent, complex, functional oxides on 6H-SiC, it was first necessary to establish a smooth, reproducible starting surface that would eventually promote an abrupt interface between the 6H-SiC substrate and oxide films. The SiC substrates were on-axis (±0.5°) 6H-SiC(0001). In most cases, the substrates were single side polished (0001) and epi-ready. However, some samples were purchased as double side polished in order to investigate the surface preparation of (0001) and (000\(\bar{T}\)), which correspond to Si-terminated and C-terminated surfaces, respectively.

5.1.1 As-received 6H-SiC preparation and characterization

Although there is an extensive amount of cleaning studies on 6H-SiC [107, 109, 113, 114, 145], very few focus on a thorough analysis with structural, morphological, and chemical characterization. Although 6H-SiC is readily available commercially, it is still
fairly expensive, ranging from approximately $700 up to $4,000 for one two-inch diameter wafer. The wide price range depends primarily on defect densities and surface finish. The least expensive wafers did not contain an epi-layer but rather a polished surface with scratches that were on the order of several microns deep. In addition to scratches, the surfaces contained residual oxygen and carbon contamination, as characterized by XPS and AES. Figure 5.1 below illustrates the RHEED and AFM characterization of the typical 6H-SiC starting surfaces.

**Figure 5.1**: Representations of a typical as-received, research grade, epi-ready 6H-SiC(0001) two-inch wafer. a) photograph of polished 6H-SiC(0001) orientation, b) RHEED pattern of degreased 6H-SiC(0001)-(1×1) surface, and c) AFM of 6H-SiC(0001) illustrating nanometer deeps scratch due to mechanical polishing.

Initial cleaning studies were performed on both the Si-terminated and C-terminated faces. Chemical characterization of the two orientations by AES (2 keV electron beam) and XPS (Al Kα x-rays, 1486.6 eV) after degreasing (see figures 5.2 and 5.3) indicated very similar starting surfaces with respect to the residual amount of carbon and oxygen surface contamination. The samples were initially degreased in heated solvents in order to remove the majority of residual carbon contamination. The elemental scans of Si(LMM) Auger transitions, figure 5.2 (b), indicate relatively more Si-O
bonding in the Si-terminated orientation than the C-terminated orientation and relatively more Si-C bonding in the C-terminated orientation. This is inferred from the differentiated peak shape and the relative intensities at ~70 eV (Si-O) and ~80 eV (Si-C). These bonding states are to be expected due to the surface termination of each orientation. For both orientation, the C(KLL) Auger transitions indicate mostly carbidic (Si-C) carbon, which is inferred from the characteristic W shape [146] of the differentiated spectra. AES data interpretation is often performed on differentiated spectra. This is primarily due to the pronounced effects that become more apparent after differentiation that would otherwise remain obscure. A comparison of a differentiated and non-differentiated survey scan is illustrated in appendix A.
Figure 5.2: AES characterization of the Si-terminated (red) and C-terminated (blue) orientations of as-received 6H-SiC. a) Differentiated survey scans illustrating the presence of Si, C, and O. b) Tight (elemental) scans of Si(LMM) Auger transition illustrating the differences in the local bonding environment. The Si orientation has relatively higher Si-O bonding compared to the C orientation, which has relatively higher Si-C bonding. c) Tight scans of C(KLL) Auger transition which show strong C-Si bonding for both orientations, which is inferred from the characteristic W shape.

XPS characterization (figure 5.3) was also used to characterize the as-received surfaces of the Si-terminated and C-terminated orientation of 6H-SiC. Similar to AES, the survey scans indicated on Si, C, and O. In order to extract useful bonding information, tight scans were collected around each of the observed photoemissions. Because the photoemission process is a primary, core level emission, the peak shape and
position are highly dependent on the local bonding environment from where the photoelectron originated. As illustrated in figure 5.3 (b), the C1s photoelectrons consists of both C-Si and C-O. This is indicated by the secondary peak at higher binding energy (~286 eV). The presence of C-O is more evident on the C-terminated orientation, due to the atomic termination of that orientation. The presence of C-O on the Si-terminated orientation (as well as apportion on the C-terminated orientation) is most likely due to residual contamination that was not removed during the degrease procedure. Figure 5.3 (c) illustrates the Si2p photoemission, but indicates similar bonding states for both orientations. The primary peak around 100.6 eV, is due to Si-C. However, the slight asymmetry at the higher binding energy is due to the presence of Si-O. However, due to the smaller chemical shift between Si-C and Si-O, compared to C-Si, and C-O, it is more difficult to immediately identify the two bonding states. After performing a background subtraction (Integrated Shirley method for inorganic, crystalline solids) and careful peak deconvolution (FWHM >1.2 eV and G/L of 80%) it is possible to distinguish between the various bonding states. From the elemental photoemission scans, the chemical composition was determined using default sensitivity factors.

Table 5.1 lists the atomic composition of the two orientations. The off stoichiometric ratio of Si:C is due to residual carbon contamination, atomic positioning within the crystal, and non-optimized sensitivity factors. A detailed description of the procedure used for compositional analysis can be found in appendix A.
Figure 5.3: XPS characterization (Al Kα x-rays) of the Si-terminated (red) and C-terminated (blue) orientations of as-received 6H-SiC. a) Survey scans illustrating the presence of Si, C, and O. b) Tight (elemental) scans of C1s photoemission illustrating the differences in the local bonding environment. The Si orientation has relatively lower C-O bonding compared to the C orientation. c) Tight scans of Si2p photoemission illustrating primarily Si-C bonding. The slight asymmetry at the higher binding energy is due to Si-O bonding, but is not as evident as the C-O bonding due to the smaller chemical shift.

Table 5.1: Compositional analysis of the Si-terminated and C-terminated orientation by AES and XPS.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Technique</th>
<th>Si</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)_{Si}</td>
<td>AES</td>
<td>24.6 ± 2.2%</td>
<td>67.3 ± 4.3%</td>
<td>8.2 ± 3.1%</td>
</tr>
<tr>
<td></td>
<td>XPS</td>
<td>44.5 ± 3.1%</td>
<td>47.4 ± 3.3%</td>
<td>8.1 ± 3.7%</td>
</tr>
<tr>
<td>(0001)_{C}</td>
<td>AES</td>
<td>23.6 ± 2.4%</td>
<td>70.4 ± 4.6%</td>
<td>5.9 ± 2.8%</td>
</tr>
<tr>
<td></td>
<td>XPS</td>
<td>33.7 ± 3.0%</td>
<td>58.0 ± 4.1%</td>
<td>8.3 ± 3.3%</td>
</tr>
</tbody>
</table>
In order to remove the residual contamination and scratches, a novel hydrogen cleaning procedure was used. The hydrogen cleaning procedure and custom built hydrogen flow furnace were based on the design by Ramachandran, *et al.* [108]. The 6H-SiC was placed on a Ta boat and heated (up to 1800 °C) under flowing hydrogen. For more details on the hydrogen cleaning procedure, refer to the experimental section. In order to optimize the hydrogen cleaning procedure, a series of systematic experiments were designed. The variables of interest included heating/cooling rates, substrate temperature, time of hydrogen exposure, gas flow rates, and Ar:H₂ gas ratio. Table 5.2 lists the limitations of each variable for the hydrogen flow furnace.

**Table 5.2:** System limitations for each independent variable of the hydrogen flow furnace. Note that temperature, heating rate, and cooling rate are not independent variable, but rather dependent on the current a width of the Ta boat.

<table>
<thead>
<tr>
<th>Variable (units)</th>
<th>Current (A)</th>
<th>Current precision (A)</th>
<th>H₂ flow rate (slpm)</th>
<th>Ar flow rate (slpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limits</td>
<td>90</td>
<td>2.5</td>
<td>0 - 15</td>
<td>0 - 12</td>
</tr>
</tbody>
</table>

Listed in the previous table, the only independent variables are the output current, the precision of the analog dial on the power supply, and the gas flow rates. Although the power supply is capable of currents as high as 150 A, the leads and power feedthroughs are limited to 90 A. Note that maximum temperature, heating rate, and cooling rate are not independent variables. Rather, they are dependent on the current and width of the Ta strip. The Ta strips were cut manually to width of approximately 0.5 inches, but there was always some variability and therefore no consistent correlation between current and temperature. However, at 90 A, the typical maximum temperature
was around 1800 ± 50 °C. The heating and cooling rates were also dependent on the current and width of the Ta boat. Further, the precision of the analog current readout on the power supply was limited to approximately 2.5 A. Therefore, the heating and cooling rates followed a stepped profile with increments of 2.5 A every X seconds, where X was varied to regulate the overall rates. Typically, when the optical pyrometer reading was above 600 °C, increments of 5 A corresponded to approximately 100 ± 10 °C. The lower limit of 600 °C, is due to the lower temperature limit of the pyrometer when operated in two-color mode. The gas flow rate limitations are due to the needle valve flow meters that were used to regulate the flow of each gas independently.

Due to the system limitations of temperature control, explained above, accurate heating and cooling rates were not quantitatively studied. However, during the course of the hydrogen cleaning experiments, the correlation between current and temperature remained fairly constant where 5 A corresponds to 100 ± 10 °C. Therefore, the heating and cooling rates were estimated based on the current/time stepped intervals.

During hydrogen cleaning, preliminary cleaning studies indicated that the Ta strips would deform when heated, even at temperatures as low as 600 °C, resulting in poor contact with the SiC and an unreliable, inadequate cleaning. Therefore, the strip was then bent into a boat shape. The formation of the boat was designed to relieve stress and minimize deformation of the Ta when current was supplied. An image of the Ta boat is included in figure 4.1 in section 4.1.1. To further minimize the deformation of the Ta boat, the heating rate was fixed at ~5 A every 30 seconds (~200 °C/min) based on visual observations during operation.
A similar situation was found for the cooling rate. Due to the high operating currents (up to 90 A) and reactivity of the hydrogen environment, the Ta boat became very brittle. When the current was removed, the Ta boat would often break. It was found that when the Ta boat broke at a high current (temperature), the sudden “quenching” of the SiC resulted in Si droplet formation on the surface. These droplets were observed by AFM and SEM, as well as the indication of an elemental Si-rich surface by XPS and AES. In order to prolong the life of the Ta boat and thus the slower cooling of the SiC, the current was reduced slowly at a rate of ~2.5 A every 30 seconds. This is equivalent to a cooling rate of ~100 °C/min. Although it was possible to increase the time interval, it was not possible to reduce the current intervals, due to the 2.5 A precision limit on adjusting the current. However, extending the time between steps did not have any impact on the life of the Ta boat. Rather, at the cooling rate of ~100 °C/min, the Ta boat lasted to ~20 A, which corresponds to a temperature below the 600 °C detection limit of the optical pyrometer when in two-color mode. At this point the power supply was simply turned off, the gas flow was turned off, and the sample was removed. When the Ta boat broke, the sample would inevitably fall to the bottom of the furnace. Unfortunately, it was impossible to prevent the sample from occasionally landing face down. Therefore, in the event of this happening, in order to minimize contamination, a piece of clean aluminum foil was placed on the bottom of the furnace before every cleaning.

In summary, because the deformation of the Ta would cause poor contact with the substrate and thus non-uniform heating, the heating and cooling rates were fixed to rates that maintained the integrity of the Ta boat, and thus sufficient contact between the Ta
and SiC. The strict requirements for maintaining the Ta integrity meant that the impact of various cooling and heating rates on SiC surface quality could not be tested. Therefore, the heating rate for all subsequent studies was held at 5 A every 30 seconds while the cooling rate was held at 2.5 A every 30 seconds. This corresponds to ~200 °C/min heating and ~100 °C/min cooling. Although the heating and cooling rates could be slowed down by increasing the time interval between each increment, these rates were found to be sufficiently slow enough maintain the integrity of the Ta boat, yet fast enough to minimize any unnecessary preparation time.

The individual effects of temperature and time had similar correlations regarding the effective removal of contaminants and scratches. At lower temperatures (< 1500 °C) the residual carbon (C-O in figure 5.2 (b)) was removed, and the formation of a silicate adlayer was formed. Details of the 6H-SiC surface reconstruction will be discussed later in section 5.1.2. However, the nanometer deep scratches remained visible by SEM and AFM. Similarly, when the time was shortened (< 20 minutes) a similar, ineffective cleaning resulted. By increasing the temperature (between 1600 °C and 1800 °C) and time (between 30 minutes and 60 minutes) complete removal of the scratches and undesired contamination could be obtained. The resulting 6H-SiC surface consisted of a smooth, atomically stepped surface with a silicate adlayer reconstruction (see section 5.1.2 for details).

The temperature and time were limited by a several factors, including the current limit of the feedthroughs (90 A) and the deformation of the Ta boat, as described previously. In addition, as the time was extended, even at temperatures around 1600 °C, the Ta became increasingly brittle and would eventually break apart. Therefore, the
sample would inevitably fall to the bottom of the furnace without the necessary cool down to prevent Si droplet formation. As a result, a balance was established between the operating temperature and the length of time held at that temperature. Ultimately, the standard cleaning procedure was run around 1700 ± 10 °C for 30 minutes.

Under the standard temperature and time conditions, the flowing gas composition and flow rates could be optimized in order to obtain a reproducible SiC starting surface that could be subsequently used to effectively integrate various oxide materials. Literature [107, 109, 113, 114] had focused on several different gas mixtures and flow rates ranging from a few liters per minute up to tens of liters per minutes (standard temperature and pressure). Typically, the total flow rates were designed to prevent mass transport limitations by supplying sufficiently high volumes of gas relative to the minimum amount needed to remove all contaminants. For a further explanation on the hydrogen etching mechanism, refer to sections 3.2.1 and 4.1.1. In addition, gas mixtures of argon and hydrogen were used in different volumetric flow ratios ranging from 0 to 2. In order to optimize the performance of the standard hydrogen cleaning procedure, the Ar:H₂ volumetric flow ratio was systematically varied from 0 to 2 and the total flow rate was systematically varied from 5 slpm to 15 slpm, based on the hydrogen gas flow rate limitation. Table 5.3 lists the conditions studied for Ar:H₂ flow ratio and total flow rate studies. Figure 5.4 illustrates the effects of Ar:H₂ and total gas flow rate on the surface morphology after hydrogen cleaning.
Table 5.3: A list of gas flow rates and volumetric flow ratios used for hydrogen cleaning of 6H-SiC. Blue represents a constant Ar:H₂ flow ratio and red represents a constant total gas flow rate. The letters A through I correspond to AMF characterization illustrated in figure 5.4.

<table>
<thead>
<tr>
<th>Run</th>
<th>Total flow rate (slpm)</th>
<th>H₂ flow rate (slpm)</th>
<th>Ar flow rate (slpm)</th>
<th>Ar:H₂</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.0</td>
<td>3.8</td>
<td>1.2</td>
<td>0.3</td>
<td>0.64</td>
</tr>
<tr>
<td>B</td>
<td>7.5</td>
<td>5.7</td>
<td>1.8</td>
<td>0.3</td>
<td>0.73</td>
</tr>
<tr>
<td>C</td>
<td>10.0</td>
<td>7.6</td>
<td>2.4</td>
<td>0.3</td>
<td>0.62</td>
</tr>
<tr>
<td>D</td>
<td>12.5</td>
<td>9.5</td>
<td>3.0</td>
<td>0.3</td>
<td>0.76</td>
</tr>
<tr>
<td>E</td>
<td>15.0</td>
<td>11.4</td>
<td>3.6</td>
<td>0.3</td>
<td>0.69</td>
</tr>
<tr>
<td>F</td>
<td>11.4</td>
<td>3.8</td>
<td>7.6</td>
<td>2.0</td>
<td>11.8</td>
</tr>
<tr>
<td>G</td>
<td>11.4</td>
<td>5.7</td>
<td>5.7</td>
<td>1.0</td>
<td>3.74</td>
</tr>
<tr>
<td>H</td>
<td>11.4</td>
<td>7.6</td>
<td>3.8</td>
<td>0.5</td>
<td>1.08</td>
</tr>
<tr>
<td>I</td>
<td>11.4</td>
<td>11.4</td>
<td>0.0</td>
<td>0.0</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Figure 5.4: AFM characterization and RMS roughness analysis of the effects of gas flow rate and flow ratio on the surface morphology of 6H-SiC. Blue represents a constant Ar:H₂ flow ratio and red represents a constant total gas flow rate. The letters A through I correspond to the parameters listed in table 5.3. The AFM
image with the green outline corresponds to the same cleaning procedure performed on the S-terminated orientation.

The RMS roughness plotted in figure 5.4 was determined from a single set of experiments and thus, no error is represented. However, selected conditions were repeated and were reproducible with RMS roughness within ± 10%. The AFM images represent hydrogen cleaning of the C-terminated orientation, but are also representative of similar results obtained in the Si-terminated orientation. Initial hydrogen cleaning experiments were conducted on the C-terminated orientation because it was possible to completely remove the residual oxygen contamination (below 1 at%, based on AES and XPS). However, further characterization and comparison between the Si-terminated and C-terminated orientations revealed that hydrogen cleaning of the Si-terminated orientation resulted in a better surface structure (RHEED) an improved MgO heteroepitaxy. These results will be discussed in further detail later. Similar trends were also observed for selected Si-terminated cleaning condition and did not warrant the complete, systematic study that was performed on the C-terminated orientation.

The primary difference in morphology between the Si-terminated and C-terminated orientations after hydrogen cleaning is the width of the steps. An effective cleaning was defined by the removal of residual contaminants (XPS and AES), the removal of scratches (SEM and AFM), and the formation of a smooth, atomically stepped surface (AFM). The average step width of several effectively cleaned C-terminated 6H-SiC substrates was 100 ± 7 nm, compared to Si-terminated 6H-SiC substrates, which was 265 ± 10 nm. The height of the steps for both orientations is very similar at 1.6 ± 0.2 nm, which corresponds to one unit cell height of 6H-SiC (1.5 nm). The difference in step
width may be attributed to the off-axis cut of the wafer. The off-axis tolerance of ± 0.5° is only valid for the Si-terminated orientation. If the C-terminated orientation were more off-axis, the then step density would increase. Based on the AFM images and the measured RMS roughness values, no correlation can be derived between the influence of the hydrogen gas flow rate and the resulting surface morphology. When the Ar:H₂ ratio was fixed at 0.3 (samples A – E), increasing total gas flow rate had little impact on the resulting morphology. The average RMS roughness between the five samples cleaned at an Ar:H₂ of 0.3 was 0.69 ± 0.14 nm. Considering the range of RMS roughness (0.45 – 11.8 nm) between the nine sample (A – I), but more importantly the range for the four samples that were held at a constant gas flow rate of 11.4 slpm (F – I), it is fairly safe to assume that the resulting RMS roughness error of 0.14 nm can be considered negligible. Therefore, by considering the five samples (A – E) as one sample, it is possible to evaluate the impact of the gas flow ratio, rather than individual gas flow rate, on the resulting surface morphology. Figure 5.5 illustrates that increasing the Ar:H₂ volumetric flow ratio result in significant surface roughening.
Figure 5.5: The surface roughness (RMS) of hydrogen cleaned 6H-SiC significantly increases with increased Ar:H₂ volumetric flow ratios. All other variables (temperature, time, heating, cooling) were held constant.

As the Ar:H₂ ratio is increased from 0 up to 2, the RMS surface roughness increases from 0.45 nm up to 11.8 nm, respectively. This indicates that as excess Ar is added to the gas mixture, the resulting cleaning/etching mechanism and surface morphology is transitioned from a stepped, layer-by-layer etching mechanism to an anisotropic etching mechanism that results in a disordered, rough surface. This may be due to the Ar acting as a diluent and limiting the available amount of hydrogen at the substrate surface, thus preventing a controlled and uniform etching mechanism. A second possibility to explain the increase in surface roughness with increased Ar:H₂ is the contribution of a physical etching component due to the significantly larger, inert argon atoms.

To further investigate the role of Ar in the etching mechanism, a Boltzmann’s energy distribution calculation was performed on the flow system in order to determine if
the roughening was a result of physical bombardment of the relatively large Ar atoms.

The Boltzmann’s velocity and energy distributions are represented by:

\[ f(v) = \frac{4 \sqrt{\pi}}{\sqrt{2 \pi k_B T}} \left( \frac{m}{2 k_B T} \right)^{3/2} v^2 \exp \left( \frac{-mv^2}{2 k_B T} \right) \]

Eqn. 5.1

Where:
- \( f(v) \) = probability that an atom will have velocity \( v \)
- \( m \) = mass of one atom (kg)
- \( k_B \) = Boltzmann’s constant (J/K or kg m²/sec²)
- \( T \) = absolute temperature (K)
- \( v \) = velocity (m/sec)

\[ KE(J) = \frac{1}{2} mv^2 \]

Eqn. 5.2

Where:
- \( KE \) = kinetic energy (J or kg m²/sec²)
- \( m \) = mass of individual atom (kg)
- \( v \) = velocity (m/sec)

From these two equations and energy distribution profile for Ar was plotted over a range of temperatures between 1400 °C and 2000 °C and localized velocity flow rates ranging from 0 – 2500 m/sec. From these equations, it is possible to estimate the local kinetic energy that the argon atoms have when they impact the heated 6H-SiC surface. Equation 5.1 can be used to plot the distribution profile of argon atoms over a range of velocities and temperatures. Equation 5.2 further relates the velocity of the argon atoms to a kinetic energy. Combining the two equations, it is possible to plot the energy distribution of the argon atoms at different temperatures. This plot is illustrated in figure 5.6 and is used to determine the distribution and probability that the argon has sufficient kinetic energy to physically etch the 6H-SiC substrate under high Ar:H₂ flow ratios. The left image represents typical volumetric flow rates for argon through the furnace. The
right image illustrates the entire energy distribution profile. The low kinetic energy of the argon atoms at the flow rates of interest indicates no physical contribution to the $6H$-SiC etching mechanism.

**Figure 5.6**: Boltzmann’s energy distribution for argon atoms flowing through the hydrogen furnace. The left image represents typical volumetric flow rates for argon through the furnace. The right image illustrates the entire energy distribution profile. The low kinetic energy of the argon atoms at the flow rates of interest indicates no physical contribution to the $6H$-SiC etching mechanism.

The velocities of the gas across the sample surface during the cleaning procedure were estimated by taking the volumetric flow rates of the Ar within the gas mixture and dividing it by the cross-sectional area of the furnace. Although this is not a quantitatively accurate velocity, it is assumed that it is within an acceptable range of the actual localized velocity. Under the conditions listed previously in table 5.3, the kinetic energy of the Ar atoms are on the order of $10^{-36}$ to $10^{-38}$ J (figure 5.6), which are at least sixteen orders of magnitude lower than the distribution maximum and significantly less than the bond strength of Si-C, which is $\sim 7.5 \times 10^{-19}$ J [147]. Therefore, the observed roughening effect
that is brought on by increasing the Ar:H\textsubscript{2} ratio is not due to the physical, kinetic bombard of the Ar atoms. Rather, the role of the Ar acts to reduce the availability of hydrogen that reaches the surface of the SiC, which further prevents the stepped, layer-by-layer etching mechanism that is observed for low Ar:H\textsubscript{2} flow ratios and pure H\textsubscript{2}.

Although the specific mechanism responsible for producing the stepped surface was not investigated further, it was important to define an operating window with the different processing variables that would produce a reliable, reproducible, smooth surface. For the subsequent integration of oxide films, all 6\textit{H}-SiC substrates were cleaned in the hydrogen furnace under a flow rate of 11.4 slpm pure H\textsubscript{2}, a heating rate of 200 \textdegree C/min (5 A every 30 seconds), a temperature around 1700 ± 10 \textdegree C, a time of 30 minutes, and a cooling rate of 100 \textdegree C/min (2.5 A every 30 seconds). Under these conditions, the resulting 6\textit{H}-SiC was smooth (RMS < 0.5 nm over 1 \textmu m\textsuperscript{2} area) with a stepped surface.

### 5.1.2 Hydrogen cleaned 6\textit{H}-SiC characterization

In addition to studying the effects of cleaning temperature, heating and cooling rate, cleaning time, Ar:H\textsubscript{2} flow ratio, and total flow rate on the surface morphology, a chemical and structural analysis by XPS, AES, and RHEED was performed. As mentioned previously, the surface of the as-received 6\textit{H}-SiC contained nanometer deep scratches and residual oxygen and carbon contamination. Once the standard hydrogen cleaning procedure had been proven to reliable result in the effective removal of the scratches and the formation of a smooth stepped surface, it was important to characterize the surface chemically by AES and XPS and structurally by RHEED. AES characterization and comparison of the two orientations before and after hydrogen
cleaning (figure 5.7) indicated the successful removal of oxygen for the C-terminated orientation, but not the Si-terminated orientation. Rather, hydrogen cleaning of the Si-terminated orientation resulted in an increase on Si-O bonding. This is indicated by the increase in intensity of the differentiated Si(LMM) spectra at 70 eV for the Si-terminated orientation (red) after hydrogen cleaning (bright red). The removal of oxygen on the C-terminated orientation (blue) allowed for an increase in the peak shape characteristic of Si-C around 80 eV. For both orientations, the C(KLL) Auger transition indicated an increase in carbidic carbon, as indicated by the characteristic W shape [146].
Figure 5.7: AES characterization and comparison of the Si-terminated and C-terminated orientation before and after hydrogen cleaning. a) Representative survey scans that indicate only Si, C, and O. Note the general change in peak intensities before and after hydrogen cleaning, due to the removal of contaminants and changes in bonding. b) Tight scans of Si(LMM) Auger transitions. The increase in Si-O (70 eV) is seen for the Si-terminated orientation and an increase in Si-C (80 eV) is seen for the C-terminated orientation. c) Tight scans of C(KLL) Auger transitions that indicate an increase in carbidic (C-Si) carbon for both orientations.

In addition to AES, XPS was used to more quantitatively characterize and compare the local bonding environments of the 6H-SiC for the two orientations before and after hydrogen cleaning. XPS is a powerful technique for analyzing bonding states because the photoemission of electrons is a result of primary, core level excitation.
Therefore, the specific kinetic energy of the excited electrons is more characteristic of its local bonding environment. Similar to the AES characterization of the C-terminated orientation, XPS revealed a significant decrease in residual oxygen (down to ~2 at%). In addition, tight scans of the C1s photoelectrons (figure 5.8 (b)) indicated primarily C-Si and C-H, indicating hydrogen termination of the surface. Tight scans of the Si-terminated orientation indicated the removal of C-O bonding (seen in the C1s spectra around 286 eV). Further, there is a slight increase in the asymmetry of the Si2p photoelectrons (figure 5.8 (c)) towards a higher binding energy. This asymmetry is due to Si-O bonding. Although oxygen was originally considered a residual contaminant, the presence of oxygen on the Si-terminated orientation is actually beneficial to the formation of a high quality surface reconstruction, which will be discussed later.
Figure 5.8: XPS characterization and comparison of the Si-terminated and C-terminated orientation before and after hydrogen cleaning. a) Representative survey scans that indicate only Si, C, and O. Note the general change in peak intensities before and after hydrogen cleaning, due to the removal of contaminants and changes in bonding. b) Tight scans of C1s photoemission. The decrease in C-O bonding is seen for both orientations. The C-terminated orientation results in a C-H terminated surface after hydrogen cleaning (bright blue). c) Tight scans of Si2p photoemission indicating primarily Si-C bonding for both orientations. For the Si-terminated orientation, The slight asymmetry at the higher binding energy is due to Si-O surface adlayer bonding.

The presence of the Si-O for the Si-terminated orientation after hydrogen cleaning, as indicated by both AES and XPS, is not characteristic of surface
contamination, but rather the formation of an adlayer. Further structural characterization of the adlayer will be discussed later. Compositional analysis of the adlayer by AES and XPS determined a stoichiometry between Si$_2$O$_3$ and Si$_3$O$_5$. However the variation in stoichiometry, is not due to mixed oxidation states, but rather poorly defined sensitivity factors. Without well-defined sensitivity factors for each of the two techniques, the absolute stoichiometry of the adlayer was not quantitatively determined. Due to the reproducibility in the formation of the adlayer during hydrogen cleaning of 6H-SiC(0001), the presence of Si-O bonding, and the consistency with literature, the adlayer is often referred to as a silicate adlayer reconstruction. Similar cleaning techniques and chemical analysis reported in literature [107, 109] indicate that the silicate adlayer for the Si-terminated orientation of 6H-SiC cannot be terminated by Si$_2$O$_3$, but rather the more stable stoichiometry of Si$_3$O$_5$ is obtained. In order to further characterize the silicate adlayer, as well as the structure of the both SiC orientations before and after hydrogen cleaning, RHEED was used.

The surface structure of each of the two orientations prior to hydrogen cleaning showed a diffuse hexagonal (1×1) pattern, shown in figures 5.9 (a) and 5.10 (a). The diffuse pattern is characteristic of random attenuation loss in the diffracted electrons and is most often associated with surface contamination due to the lack of crystal order in the adsorbed species. The hexagonal (1×1) pattern was determined by analyzing and collecting patterns at all angles 0° – 360°. A hexagonal pattern should consist of two, distinct, well aligned patterns each 30° apart. Due to the six-fold symmetry of the hexagonal substrate, the two distinct patterns should repeat every 60°. Figures 5.9 and 5.10 show the RHEED characterization of the two orientations (Si- and C-terminated,
respectively) before and after hydrogen cleaning. The designation of \(<1 \overline{1} 2 0>\) and \(<1 \overline{1} 0 0>\) indicate the two directions responsible for the repeating patterns and correspond to the directions normal to the \{11\overline{2} 0\} and \{1 \overline{1} 0 0\} planes of the 6H-SiC unit cell lattice. The direction of \(<1 \overline{1} 0 0>\) is rotated 30° from the \(<11 \overline{2} 0>\) direction. For a detailed description of lattice planes and directions, refer to appendix D.

**Figure 5.9:** Structural characterization by RHEED of Si-terminated 6H-SiC before top) and after (bottom) hydrogen cleaning. The \((1 \times 1)\) pattern characteristic of as-received 6H-SiC is transitioned to a silicate adlayer reconstruction with a \(\sqrt{3} \times \sqrt{3} R30^\circ\) structure. The adlayer structure is characterized by the formation of fractional Laue rings at \(L_{1/3}\) and \(L_{2/3}\). The AFM image is used to define the corresponding directions of the incident electron beam.
Figure 5.10: Structural characterization by RHEED of C-terminated 6H-SiC before top) and after (bottom) hydrogen cleaning. The (1×1) pattern characteristic of as-received 6H-SiC is maintained even after hydrogen cleaning. The AFM image is used to define the corresponding directions of the incident electron beam.

RHEED characterization of the two 6H-SiC orientations after standard hydrogen cleaning showed a significant difference in the surface crystal structure. The C-terminated orientation remained (1×1) after cleaning with an increased intensity of the rods and spots indicating the removal of amorphous, adsorbed surface species. The absence of any fractional Laue reconstruction rings in the pattern indicates that the surface structure remained intact, with an in-plane lattice spacing after hydrogen cleaning similar to the in-plane lattice spacing of the degreased structure before hydrogen cleaning.

Unlike the C-terminated orientation, the Si-terminated orientation reconstructed from the as-received (1×1) pattern to a $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ surface reconstruction after standard
This reconstruction was determined from the presence of two intermediate rings in the \(<1\overline{1} 0\) direction, designated \(L_{1/3}\) and \(L_{2/3}\), and the presence of additional rods and dots within the \(<1 \overline{1} 0 0\) pattern. The addition of these diffraction characteristics is associated with a reconstruction that is a result of the silicate adlayer formed during hydrogen cleaning. The \(\sqrt{3}\times\sqrt{3} R30^\circ\) designation is used to relate the atomic positioning of the reconstructed surface to that of bulk, non-reconstructed 6\(H\)-SiC.

A detailed discussion regarding the translation from real space to reciprocal space can be found in appendix B. Prediction and modeling of the \(\sqrt{3}\times\sqrt{3} R30^\circ\) reconstruction is discussed further in section 5.2.4 (figure 5.18) regarding the possible heteroepitaxial alignments of MgO(111) on the silicate adlayer reconstruction.

For example, bulk 6\(H\)-SiC(0001) has an in-plane lattice spacing (a) of 3.08 Å. In a (1×1) surface matrix, every Si atom on the surface is 3.08 Å from six surrounding Si atoms, where the six surrounding Si atoms make up the hexagonal structure. For a \(\sqrt{3}\times\sqrt{3} R30^\circ\) reconstruction, every Si atom is now \(a\times\sqrt{3}\) from six surrounding Si atoms. Thus, the in-plane lattice spacing in the reconstructed surface increases from 3.08 Å to \(~5.33\) Å. In addition, the larger hexagon of the adlayer is rotated 30° \((R30^\circ)\) from the hexagon of the bulk 6\(H\)-SiC structure. Figure 5.11 illustrates the reconstruction of the surface atoms from the bulk (1×1) structure to the \(\sqrt{3}\times\sqrt{3} R30^\circ\) reconstruction. The presence of the silicate adlayer, with its larger in-plane lattice spacing, is important to understanding the epitaxy of subsequent oxide film integration.
Figure 5.11: Schematic representation for the reconstruction of the $\sqrt{3} \times \sqrt{3} R30^\circ$ adlayer relative to bulk 6H-SiC. a) Top view of the simplest repeating unit of the 6H-SiC structure with appropriate atomic spacings. b) Top view of the hexagonal array for 6H-SiC. c) Designation of the silicon atoms (yellow) responsible for the $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction. d) Top view of the silicon atoms of the $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstructed hexagon. Note the $30^\circ$ rotation between the reconstructed hexagon and the bulk hexagon. e) Top view of entire $\sqrt{3} \times \sqrt{3} R30^\circ$ silicate adlayer reconstruction overlaid on 6H-SiC. f) Side view of entire $\sqrt{3} \times \sqrt{3} R30^\circ$ silicate adlayer reconstruction on 6H-SiC along the [1120] direction.

Epitaxial integration of functional oxides is a key component to the overall success of SiC as a next-generation semiconducting substrate. It is also necessary to
establish an abrupt and electrically effective interface between the SiC and subsequent layers. Increased surface roughness would be detrimental to the electron transport between the SiC substrate and the functional ferroelectric film, for example, due to an increase in interface defects including trapped states and charge accumulation. Therefore, the first step in ensuring an abrupt interface is to create an atomically flat substrate surface. As discussed previously, the standard ex-situ hydrogen cleaning procedure results in an atomically stepped, smooth surface. AFM characterization revealed a smooth surface with an RMS roughness of $0.45 \pm 0.02$ nm over a 1 $\mu$m$^2$ area. This roughness analysis includes the stepped features of the SiC surface, and is therefore not an accurate representation of the actual surface roughness. By selectively analyzing multiple step surfaces, the surface roughness was reduced to $0.26 \pm 0.02$ nm and better represents the actual surface roughness. However, due to AFM limitations and a tip radius of curvature around 10 nm, the surface atomic structure of the steps was not possible. Through collaboration with Dr. David Muller and Dr. Lena Fitting Kourkoutis at Cornell University, TEM characterization of hydrogen cleaned 6$H$-SiC(0001) was performed. Figure 5.12 is a strain contrast, cross-sectional TEM image of hydrogen cleaned 6$H$-SiC(0001). The TEM image clearly shows the six Si-C stacking layers responsible for the 6$H$-SiC polytype with an atomically flat surface. The diffuse region at the surface of the sample is due to the epoxy that was used to support the sample during preparation and ion milling. TEM characterization was not able to resolve the silicate adlayer. This may be due to electron beam damage, lack of long range order in the silicate adlayer, or sample preparation techniques.
Figure 5.12: Strain contrast, cross-sectional TEM image of hydrogen cleaned 6H-SiC(0001). The characteristic ABCACBA stacking sequence that makes up the 6H-SiC polytype is clearly visible. The substrate is atomically flat, but could not resolve the silicate adlayer reconstruction.

Thorough chemical, structural, and morphological characterization of the 6H-SiC starting surface indicates that ex-situ hydrogen cleaning is an effective technique for establishing a clean, crystalline, abrupt surface for the subsequent deposition of various oxides and functional materials. Although the hydrogen cleaning procedure has been optimized for both the Si-terminated and C-terminated orientations, the majority of oxide growths discussed in this dissertation focus on the Si-terminated orientation with the reproducible, high-quality $\sqrt{3}\times\sqrt{3} R30^\circ$ silicate adlayer reconstruction. This is in part due to the concept of forming an oxygen bridge between the SiC substrate and oxide films, as well as between alternating oxide layers. The concept of and oxygen bridge will be discussed further in the next section.
5.2 Heteroepitaxial integration of oxides on 6H-SiC

The development of a next-generation, multifunctional heterostructure requires the integration of high-quality functional oxides in wide bandgap semiconductors. The next two sections will discuss the progress towards integrating high-quality, ferroelectric BTO on 6H-SiC by the formation of an oxygen bridge, which can act to alleviate lattice mismatch and promote heteroepitaxy. Further, the approach used for the successful heteroepitaxy of BTO discussed in this dissertation is focused on the use of a high-quality, single crystalline MgO(111) template layer that is integrated between the 6H-SiC substrate and ferroelectric BTO film. The major focus of this section is towards the heteroepitaxial growth of high-quality MgO on 6H-SiC by MBE.

The heteroepitaxy of various complex, functional oxides on 6H-SiC depends upon many variables, including user-controlled processing parameters (e.g. temperature, flux ratios, growth rate) and intrinsic properties of the materials (e.g. lattice mismatch, thermal mismatch, reactivities). This work pursued the challenge of forming both an abrupt interface and an electrically effective interface between the functional oxide and the wide bandgap semiconductor through a simple oxide (MgO) to form an oxygen bridge. Through the use of MBE, it is possible to adjust the processing parameters in order to tune the desired crystalline and functional properties. This work also pursued the challenge of defining the parameter window and relative sensitivity of those parameters, and then linking the processing conditions to oxide film characteristics (chemistry, bonding, structure, morphology) and properties (impact on subsequent layer nucleation and growth, ferroelectricity, and dielectric behavior) for both the simple and complex oxides. This section first outlines the oxygen bridge approach, then documents the
investigation of MgO film growth and characterization, the use of MgO as an oxygen bridge to more complex oxides and the investigation of BTO film growth and characterization.

### 5.2.1 Oxygen bridge approach and challenges

Effective heteroepitaxial integration of functional oxides on the wide bandgap semiconductors SiC and GaN requires an approach that will overcome the large lattice mismatch challenges of integrating a cubic structure on a hexagonal substrate and create an abrupt interface with minimal electrical leakage. The concept of an oxygen bridge is based on the idea that oxygen, which is present in the silicate adlayer reconstruction of $6H$-SiC, MgO, and functional oxides, can be used as the common element to effectively integrate dissimilar oxide materials. MgO is an ideal candidate for the formation of an oxygen bridge because it is a binary oxide with a rock-salt structure that is well lattice matched with $6H$-SiC and a variety of tetragonal ferroelectrics. Further, the (111) orientation of MgO results in alternating layers of magnesium and oxygen. Therefore, it is possible to integrate high-quality MgO(111) on the $6H$-SiC(0001) $\sqrt{3}\times\sqrt{3} R30^\circ$ reconstruction by sharing the oxygen atoms of the silicate adlayer with the first layer of Mg through the formation of a Si-O-Mg bridge. Similarly, the MgO can be used as a heteroepitaxial template layer for the subsequent integration of tetragonal BTO(111) through the formation of an Mg-O-Ba (or Mg-O-Ti) bridge.

To illustrate the use of the MgO oxygen bridge, consider the case of BTO. BTO(111) has a Ba-to-Ba in-plane lattice spacing of $\sim5.66\text{ Å}$. Comparing this to the Si-to-Si in-plane lattice spacing in $6H$-SiC(0001) of $3.08\text{ Å}$, the resulting lattice mismatch is
~46% with the film in compression. This large mismatch is based on the spacing between each atom and its nearest neighbor for both the BTO(111) and 6H-SiC. Realistically, the BTO(111) cannot match atom for atom with SiC because of this large mismatch. By comparing the in-plane lattice spacings and structures of the BTO(111) and 6H-SiC, the lattice mismatch can be reduced to ~8.8% with the film in tension by relating one BTO lattice parameter to two 6H-SiC lattice parameters. This is a much more realistic possibility for the heteroepitaxy of BTO(111) on 6H-SiC(0001). However, as was mentioned in the previous section, the 6H-SiC(0001) has a $\sqrt{3}\times\sqrt{3} \ R30^\circ$ reconstruction. Taking the lattice spacing of the silicate adlayer into consideration, and the concept of an oxygen bridge between the BTO(111) and silicate adlayer, the lattice mismatch between BTO(111) and reconstructed 6H-SiC(0001) is ~5.9% in compression. The concept of an oxygen bridge to minimize lattice mismatch is based on the idea that oxygen is the one element that is consistent throughout the entire heterostructure, starting at the silicate adlayer, and extending through each oxide multilayer. Therefore, if the lattice spacing of oxygen in one layer closely matches the oxygen spacing in the adjacent layers, then it should be possible to fabricate a high quality heterostructure through the incorporation of an oxygen bridge. This concept can be applied to a variety of other oxide materials, and thus may enable a workable methodology for next-generation multifunctional devices.

One possible way to further minimize the lattice mismatch between the BTO and 6H-SiC and take advantage of the oxygen bridge concept is through the integration of a thin, crystalline, simple oxide template layer. MgO is a promising and potential candidate for use as a template layer/oxygen bridge because of its highly crystalline rocksalt structure and close lattice match to many tetragonal, perovskite, ferroelectrics. In
addition, MgO is a high dielectric oxide (~10) with a threshold voltage greater than 10 MV/cm [ADD YALE]. As a result, the performance and speed of the ultimate device will not be limited by the MgO interlayer, but rather the properties of the 6H-SiC or functional oxide layers.

As an example, the in-plane lattice spacing of MgO(111) is 2.98 Å (for Mg-to-Mg and O-to-O). When integrated on non-reconstructed 6H-SiC(0001) there is a ~3.4% tensile mismatch with an atom-to-atom epitaxy. When the $\sqrt{3} \times \sqrt{3}$ R30° silicate adlayer is considered, the mismatch increases to a ~10.5% compressive mismatch. However, comparison of the structure and spacings of the MgO(111) and $\sqrt{3} \times \sqrt{3}$ R30° reconstruction, the mismatch can be reduced to ~3.3% in tension if the pseudo-hexagon of MgO(111) were to rotate 30° relative to the $\sqrt{3} \times \sqrt{3}$ R30° reconstruction. By extension, and integration of BTO(111) on the MgO(111) through the concept of an oxygen bridge, results in a minimized lattice mismatch of ~4.4% in tension. The reduced theoretical mismatch between the MgO/6H-SiC as well as the BTO/MgO lends credence to the effectiveness of MgO as a heteroepitaxial template for the integration of BTO. This approach, too, can be expanded to a variety of other tetragonal, perovskite, ferroelectric oxides on 6H-SiC, and hence enable the next-generation of multifunctional devices.

The approach of the oxygen bridge pursued in this work either through the silicate adlayer or the MgO template, links the functional oxide to the hexagonal substrate through the pseudo-hexagonal (111) orientation of the cubic oxides. Because of the tetragonal perovskite structure of many functional oxide materials, the directional functional property effects of the oxides are the strongest (and hence the most amenable to tuning) in the (001) direction. Therefore, within the constraints of current device
architectures, the most desirable linking of the functional oxide film would be through the (001) orientation. However, the hexagonal structure of the 6H-SiC substrate and pseudo-hexagonal structure of the MgO(111), the resulting epitaxy for tetragonal ferroelectrics is also (111) oriented, which have poor ferroelectric properties relative to (001). As a result, there is a trade off between effective integration of tetragonal ferroelectrics with the wide bandgap semiconductor (requiring a (111) film orientation) and the alignment of the maximum ferroelectric effect (requiring a (001) film orientation). Addressing this tradeoff is beyond the scope of this dissertation, but will be discussed again in the recommendations section.

5.2.2 MgO/6H-SiC heteroepitaxy: Initial studies

Initial studies into the nucleation and growth mechanisms of MgO on 6H-SiC focused on the impact of flux ratios and substrate orientation. 6H-SiC substrates, both Si-face (0001) and C-face (000\(\overline{1}\)), were prepared by the standard hydrogen cleaning procedure discussed previously in section 4.1.1. MgO films were deposited on 6H-SiC at 140 °C with the remote oxygen atom source held constant at 90 W, 5.0×10\(^{-6}\) Torr (~1.8×10\(^{15}\) molecules O\(_2\)/cm\(^2\) sec), and an OED photomultiplier reading of 35 mV. The Mg:O flux ratio was varied by increasing the Mg flux (2.5×10\(^{13}\) – 3.6×10\(^{14}\) atoms/cm\(^2\) sec). In order to enable effective comparison from sample to sample, the magnesium fluence was held constant at ~1.5×10\(^{17}\) atoms/cm\(^2\). Therefore, by increasing the magnesium flux, it was necessary to decrease the deposition time in order to maintain the constant magnesium fluence. The MgO films grown on the two 6H-SiC orientations were characterized by AFM, RHEED, XPS, and AES.
For all films, XPS and AES characterization indicated stoichiometric MgO. This is not a surprise considering the MgO is a binary oxide, and oxygen was supplied in excess, resulting in the unlikelihood of magnesium metal deposition, and suggesting a Mg flux controlled growth mechanism. Figure 5.13 illustrates the effect of increasing Mg flux (Mg:O flux ratio) on the morphology (AFM) of the resulting MgO film for both the (0001) and (000\(\bar{1}\)) orientations. Although the corresponding RHEED images are not shown, the resulting surface crystal structure is listed along side the respective AFM image. For all of the MgO films, the thickness was calculated to be between 20 – 25 Å, based on the XPS signal attenuation of Si2p. The method used for estimating film thickness has an inherent error of 10% due to transport approximations, surface roughness, surface excitations, and surface refraction [148]. For a detailed explanation of thickness calculation, refer to appendix E.
Figure 5.13: The morphology and crystal structure of MgO is influenced by magnesium flux and substrate orientation. The left set corresponds to MgO grown on Si-terminated 6H-SiC, where increased Mg flux results in conformal, single crystalline MgO. The right set corresponds to MgO grown on C-terminated 6H-SiC, where an increase in Mg flux increases the crystallinity, but results in a poor morphology [149].

As the Mg flux was increased with all other parameters constant, the resulting film morphology and crystal structure was affected differently depending on the substrate orientation. When grown on the C-terminated (000 \bar{T}) orientation, the increase in Mg flux resulted in a less conformal film morphology. Although the film morphology was conformal at the lower Mg fluxes, the film crystal structure was amorphous. As the flux was increased, the film morphology transitioned to a highly three dimensional growth mechanism with polycrystalline RHEED features. An opposite effect was observed on
the Si-terminated (0001) orientation. At the low Mg flux, the MgO was non-conformal and polycrystalline. However, when the flux was increased, the MgO became highly single crystalline and conformal to the 6H-SiC stepped surface. It is necessary to note that because MBE is a line-of-sight deposition technique, it is not capable of uniform (conformal) film deposition on vertical or high aspect ratio features due to shadowing effects. The term conformal is used simply to describe the preservation of the underlying morphology, in this case the unit cell height stepped surface of the hydrogen cleaned SiC.

The difference in growth mechanisms on the two surfaces may be due to the differences in morphology and chemistry of the starting 6H-SiC orientations. The C-terminated orientation is a (1×1) surface structure consisting of carbon atoms, while the Si-terminated orientation is a $\sqrt{3}\times\sqrt{3} \, R30^\circ$ surface structure consisting of a silicate adlayer. It is possible that the existing presence of the oxygen in the silicate adlayer promoted the surface wetting of MgO during the initial nucleation and growth of the thin MgO films. This would result in a smoother, conformal, more crystalline film. The absence of oxygen on the carbon face would prevent the formation of an oxygen bridge between the substrate and MgO, possibly preventing the conformal, single crystalline growth that was observed on the Si-terminated orientation. The formation and importance of an oxygen bridge on 6H-SiC(0001) will be discussed later.

Since all of the MgO films were roughly the same thickness (20 – 25 Å), the increase in Mg flux can be directly related to an increase in MgO growth rate, as illustrated in figure 5.14 for films grown on both the (0001) and (000 $\overline{1}$) orientations. By increasing the Mg flux from $2.5\times10^{13}$ atoms/cm$^2$ sec to $3.6\times10^{14}$ atoms/cm$^2$ sec, the effective growth rate was increased from $\sim0.25$ Å/min to $\sim1.35$ Å/min. The linear
relationship between Mg flux and MgO growth rate indicates a magnesium absorption controlled mechanism that is not saturated and does not depend on the substrate surface. The error represented in the growth rate is indicative of sample variation between the two orientations as well as repeatability and does not include the inherent 10% error associated with the thickness calculations.

A magnesium absorption controlled growth mechanism is in contrast to the observed mechanism reported by Craft, et al. [84] and Yadavalli, et al. [122], discussed in section 3.3.1. This may be due to the use of atomic and molecular oxygen (supplied by the remote oxygen atom source) rather than molecular oxygen used by Craft, et al. and Yadavalli, et al., which would require extra energy to dissociate into free oxygen. The extra energy for dissociation of molecular oxygen was supplied by the elevated growth temperature of 650 °C [84] and resulted in an additional step in the MgO growth mechanism, which was potentially the limiting step. The magnesium absorption controlled mechanism is most likely due to the presence of free atomic oxygen at the surface and the low substrate temperature (140 °C), which reduces the desorption rates of Mg and O. If oxygen were the limiting factor for the growth rate of MgO, then increasing the Mg flux would have no impact on the growth rate of the MgO. Rather, at a substrate temperature of 140 °C, it would be expected that magnesium metal would be incorporated into the MgO film. This was not observed by XPS or AES; all films were stoichiometric MgO.
Figure 5.14: Under a constant oxygen (combination of O and O₂) environment and constant substrate temperature of 140 °C, an increase in magnesium flux linearly increases the MgO growth rate. This supports a magnesium absorption controlled growth mechanism. However, the non-zero intercept indicates a faster nucleation rate than growth rate. The magnesium absorption controlled growth mechanism was observed for both SiC orientations [88].

In addition to the observed magnesium absorption controlled growth mechanism, the slope of the line has a non-zero intercept. This indicates that the nucleation rate of MgO occurs much faster rate than the actual film growth rate. The nucleation is an important step in the overall growth mechanism of MgO because it can help understand the surface wetting of MgO on the 6H-SiC(0001) surface.

5.2.3 The role of oxygen on the nucleation of MgO

In order to investigate the nucleation of the MgO, various films were deposited on 6H-SiC(0001) under different nucleation conditions. The conditions included nucleating MgO at 140 °C with: 1) Mg flux of 1.0×10^{14} atoms/cm² sec with 35 mV oxygen plasma (i.e. standard growth process), 2) Mg flux of 1.0×10^{14} atoms/cm² sec with molecular oxygen, 3) Mg flux of 1.0×10^{14} atoms/cm² sec with 35 mV oxygen plasma for 1 minutes
followed by molecular oxygen for the remainder of the growth, and 4) exposure to 35 mV oxygen plasma for 1 minute to activate surface followed by Mg flux of $1.0 \times 10^{14}$ atoms/cm$^2$ sec with molecular oxygen. Sample 1 is designed as the standard reference for MgO film growth. Sample 2 was designed to study the impact of molecular oxygen on the nucleation and growth of MgO. Sample 3 was designed to see any effects of transition between oxygen species during nucleation and growth. Sample 4 was designed to evaluate a possible surface activation mechanism that was a result of exposure to the reactive atomic oxygen. Note that the oxygen plasma is generated remotely and the charged species are removed by ion deflection plates located at the end of the discharge tube. Therefore, only neutral O and O$_2$ are available for oxide growth. For more details on the remote oxygen source, refer to section 4.1.3.2.

For the four nucleation study experiments, the substrates were exposed to the same magnesium fluence regardless of oxygen species and exposure. With the exception of sample 2 (molecular oxygen), the three remaining MgO films deposited under the three different oxygen conditions yielded ~2.5 nm thick MgO films that were smooth (sub-nanometer roughness), single crystalline by RHEED, and conformal to the underlying 6H-SiC(0001) stepped surface. Sample 2, which was nucleated and grown using molecular oxygen, resulted in a rough (RMS = 5.2 ± 1.1 nm), three-dimensional (3-D) surface with an effective film thickness of 0.9 nm. Figure 5.15 illustrates the AFM images collected for the four different nucleation and growth conditions.

Considering the observed AFM morphology, surface roughness, and calculated thickness for Sample 2, it is apparent that the MgO film did not coalesce on the SiC surface. Rather, it formed random 3-D clusters that were approximately 7 ± 2 nm high.
This 3-D crystallite growth mode is consistent with other MgO growth modes observed on GaN by MBE using molecular oxygen as the oxygen source [84].

![Figure 5.15](image)

**Figure 5.15:** AFM characterization of MgO nucleated and grown under various oxygen environments [88]. For all samples, the magnesium fluence and substrate temperature was held constant. Figures (a) through (d) correspond to samples 1 through 4, respectively. a) O and O₂ at a photomultiplier reading of 35 mV, b) molecular oxygen, c) O and O₂ at a photomultiplier reading of 35 mV for 1 minute followed by 4 minutes of molecular oxygen, d) exposure to O and O₂ at a photomultiplier reading of 35 mV for 1 minute with no magnesium flux followed by 5 minutes of Mg and molecular oxygen.

By comparing the resulting MgO films obtained under conditions 1 and 2 (plasma vs. molecular) it is apparent that the presence of atomic oxygen is essential to the smooth, conformal growth of MgO on 6H-SiC(0001). Although the growth mechanism is dominated by the availability of magnesium at the surface (i.e. magnesium absorption controlled growth), the reactivity of the atomic oxygen appears to play a crucial role in the quality of the resulting MgO film. Further, by comparing condition 1 with conditions 3 and 4, the presence of atomic oxygen may only be necessary during the nucleation of MgO film growth. Sample 3 was nucleated with both magnesium and atomic oxygen for 1 minute, while the 6H-SiC(0001) surface of sample 4 was exposed to atomic oxygen without magnesium for 1 minute. The bulk of the MgO films for both samples were then grown using molecular oxygen. Under both conditions, the resulting MgO was similar is
crystal structure and morphology to the standard MgO. However, the surface roughness of samples 3 and 4 did increase from 0.50 ± 0.21 nm up to ~1.1 ± 0.6 nm. This indicates that conformal MgO can be grown using molecular oxygen, but results in a rougher film morphology and does require the presence of reactive atomic oxygen during the nucleation step.

The role of atomic oxygen during the nucleation of MgO appears to impact the initial wetting of MgO on the 6H-SiC surface. Although the $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ silicate adlayer reconstruction does contain oxygen that may be used for the formation of an oxygen bridge, it is a metastable surface that remains even after heating the SiC to over 600 °C in vacuum (~$10^{-9}$ Torr). Therefore, it is possible that the presence of atomic oxygen acts to activate the surface by encouraging the Si-O-Si bonds to break and further allowing the formation of a Si-O-Mg oxygen bridge. This possible mechanism can help explain why all MgO growths that were initially nucleated or exposed to atomic oxygen resulted in a conformal MgO film, while molecular oxygen resulted in a cluster growth mode. Figure 5.16 shows the proposed hypothesis of the nucleation reaction and the role of atomic oxygen in the nucleation of smooth, 2-D MgO on 6H-SiC(0001).
Figure 5.16: Proposed mechanisms for the nucleation of MgO in the presence of atomic oxygen (a) and molecular oxygen (b). The presence of atomic oxygen results in a 2-D nucleation and growth mechanism.

Using what was learned from the nucleation and growth mechanism studies, the production of high-quality, smooth, single crystalline MgO on 6H-SiC(0001) was achieved. For the remainder of the studies, only 6H-SiC(0001) was used. This is due to the more consistent and uniform hydrogen cleaning of this surface, as well as the ease of integrating high-quality MgO compared to the C-terminated orientation.
5.2.4 MgO growth mechanism and physical properties

Within (111) oriented ionic crystalline MgO, the atomic-level structure is composed of alternating layers of magnesium and oxygen. Due to the nature of the (111) orientation of ionic rock-salt structures, the alternating layers of oppositely charged magnesium and oxygen result in a dipole moment perpendicular to the surface. In order to minimize this instability, the surface cannot truly be terminated by a layer of oxygen or magnesium. Much research has been conducted to understand the true surface termination of MgO(111) [134, 136, 137, 150]. Early work suggested the surface became faceted into neutral {100} planes [134, 136]. However, more recent research has reported that faceting is not a favorable means of stabilization, but rather MgO(111) surface terminations of $\sqrt{3} \times \sqrt{3} R30^\circ$, $2\sqrt{3} \times 2\sqrt{3} R30^\circ$, or $2 \times 2$ reconstructions are predicted to be more favorable for minimizing electric dipoles [137-139, 150, 151]. Although these surface reconstructions are electrically stable, they often require high temperatures (>800 °C) to form. Further research combining experimental and theoretical studies supported a hypothesis for an OH-terminated MgO(111)-(1×1) surface, which is more energetically favorable than the complex surface reconstructions and results in a surface termination that is more stable than the non-polar MgO(100) surface [150, 152].

Considering the bulk, physical properties of a crystalline MgO lattice, the atom-to-atom spacing of MgO(111) is 2.98 Å and results in a hexagonal structure. When overlaid onto the $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction of the 6H-SiC(0001), there are two possible epitaxy alignments. Figure 5.17 illustrates the two epitaxy alignments for MgO/6H-SiC that result in the lowest lattice mismatch. In one alignment (blue), the atoms that make up the hexagonal structure of the MgO(111) surface align with the hexagonal structure of the
6H-SiC silicate adlayer reconstruction. In this arrangement, the lattice mismatch is around 10.5% with the film in compression. The second alignment (red), the hexagon of the MgO(111) is rotated 30° from the reconstructed hexagon of the 6H-SiC, resulting in a lattice mismatch around 3.3% with the film in tension. The XRD inset illustrates that only the 6H-SiC substrate and (111) oriented MgO were detected, confirming the single crystalline orientation of the RHEED pattern. The inset includes the (00012) diffraction peak for the substrate and the (222) diffraction peak for MgO because the (0006) and (111) diffraction peaks overlap and do not clearly illustrate the epitaxial relationship. While the θ-2θ XRD scan does confirm the (111) orientation of the MgO film and the epitaxy of the heterostructure, it cannot determine which out of plane atomic alignment illustrated in figure 5.17 (a) is actually occurring.
Figure 5.17: The epitaxy alignment possibilities for single crystalline MgO(111) on 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ reconstruction. a) MgO(111) can be in tension (red) with a 3.3% mismatch or in compression (blue) with a 10.5% mismatch. b) XRD $\theta$-2$\theta$ scan illustrating only pseudo-hexagonal epitaxy of MgO.

One possible means of determining which epitaxy alignment is preferred is through the use of RHEED. For a hexagonal structure, there is an inherent 6-fold symmetry. This symmetry can be translated into two distinct directions. In the case of 6H-SiC, they are $<1\bar{1}00>$ and $<11\bar{2}0>$, while for MgO they are $<1\bar{1}0>$ and $<11\bar{2}>$. The difference in nomenclature is due to the hexagonal unit cell for 6H-SiC (a, b, c, d) and the cubic unit cell for MgO (a, b, c). By translating the real-space lattice meshes of the reconstructed 6H-SiC(0001) and MgO(111) into reciprocal space, it is possible to model the expected RHEED patterns for the two angles of symmetry. Figure 5.18 shows the translation steps for the $\sqrt{3} \times \sqrt{3}$ $R30^\circ$ reconstruction of the 6H-SiC(0001) and the expected...
RHEED patterns for the 6H-SiC substrate and relates it to the actual RHEED patterns that were obtained for the 6H-SiC and MgO at the two angles of symmetry.

Figure 5.18: RHEED characterization of the epitaxial alignment of MgO on 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction. a) Schematic representation of 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction in real space. b) Schematic representation of the reciprocal space translation of 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction. c) Predicted RHEED pattern for 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction and the actual observed RHEED pattern. d) RHEED pattern for MgO(111) deposited on the 6H-SiC(0001) surface illustrating the preferred tensile epitaxial alignment.

In the modeled RHEED images of the 6H-SiC surface, the blue diffraction spots are the diffraction spots generated from the bulk 6H-SiC lattice mesh. The green diffraction spots are a result of the $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction. It should be expected that the intensity of the green spots would be less than those of the blue. This is due to the
overall amount of atoms that are available for the constructive diffraction of electrons. Comparing the modeled RHEED patterns to the actual RHEED patterns, it is easy to determine which symmetry angle the RHEED electron beam is incident, as illustrated in the actual images.

When MgO is deposited on the 6H-SiC, the RHEED pattern changes. By comparing the observed MgO RHEED patterns with modeled RHEED images of a (111)-(1×1) pattern (model not shown) it was found that MgO prefers the second epitaxy alignment with a 3.3% tensile mismatch. Due to the absence of any reconstruction rings or intermediate diffraction spots in the MgO RHEED patterns (unlike the 6H-SiC RHEED patterns) it is safe to assume that the MgO(111) is not reconstructing into a more complex geometry. Similarly, the absence of chevrons in the MgO RHEED pattern indicates that faceting is also not occurring.

Through careful characterization of the MgO films by XPS and RHEED, there is evidence of an OH-terminated (1×1) surface. A 10 nm MgO(111) film was deposited on hydrogen cleaned 6H-SiC(0001) at a substrate temperature of 140 °C. A thickness of 10 nm was chosen to ensure that the oxygen O1s photoelectron signal was originating from only the MgO film and not the silicate adlayer on the 6H-SiC, since 10 nm is greater than the attenuation depth of electrons originating from oxygen at the interface. The resulting RHEED pattern indicated similar 3-D characteristics as the 2 nm MgO films and maintained a pattern characteristic of MgO(111). XPS characterization of the film indicated one Mg2p photoelectron peak, but two O1s photoelectron peaks. The primary O1s peak, associated with MgO, was located at a binding energy around 530 eV. The secondary peak was located at a binding energy ~2 eV higher and was designated as the
OH surface state, in close agreement with Lazarov, et al. [152]. Taking into account sampling volume, the relative intensity of the OH peak to the MgO peak was calculated to be 0.11, indicating an effective monolayer coverage slightly more than one. The monolayer coverage of OH greater than 1 is most likely due to the 3-D features observed by RHEED, which would increase the overall surface area and therefore increase the amount of available sites for OH termination.

Angle resolved XPS (ARXPS) was used to determine if the OH is in fact a surface termination. The 100 Å MgO film was analyzed by XPS at four different take-off angles: 90°, 60°, 45°, and 30°. By decreasing the take-off angle from 90° to 30°, XPS becomes much more surface sensitive decreasing from 9.3 nm (90°) to 4.7 nm (30°). Figure 5.19 illustrates the ARXPS results for the OH/MgO ratio, taken from the O1s spectra, at the four different take of angles.

**Figure 5.19:** ARXPS comparison of the OH/MgO ratio determined from the O1s photoelectron spectra indicating the OH surface termination of MgO films.
The ARXPS analysis demonstrates that the relative amount of OH:MgO increases as the take off angle is lowered from 90° to 30°. Although the absolute change in the two deconvoluted O1s peaks at the different angles may have a large error associated with it (as high as 10%), by taking the relative ratio of the two peaks for each angle, the error can essentially be reduced to only a few percent by eliminating any variability and inconsistency in geometry. The increase in the ratio along with the observed RHEED patterns support the hypothesis of a hydrogen-stabilized MgO(111)-(1×1) surface structure.

During MgO growth at 140 °C, there is an apparent transition in the RHEED pattern of the MgO(111). During the initial few layers of growth (up to a few nanometers), the RHEED pattern indicates a smooth, semi layer-by-layer growth mode with some small 3-D features, as is evident by the slight intensity variation in the Laue rods in the zeroth Laue zone. As the film thickness is increased (up to 10 nm), the 3-D features in the RHEED pattern becomes more distinct with evidence of twinning, as is evident by presence of double spots within the zeroth Laue zone.

Figure 5.20 illustrates the enhanced twinning and 3-D features as MgO film thickness is increased, and schematically represents the twinned atomic structure. A representation of the twinning is highlighted in the inserted red box within the RHEED images. Note that the RHEED images have been cropped to only illustrate the zeroth Laue zone. The enhancement of the twinned feature indicates that as the film thickness increases, no single MgO atomic registry is preferred. The cross-sectional schematics illustrate the different atomic stacking sequences that are responsible for the twinned structure. The ball model represents a more 3-D illustration of how the different stacking
sequences or atomic registries could align. Although only two registries are represented, there are a total of 8 different arrangements that are possible within the (111) orientation of MgO. Due to the inherent nature of (111) oriented rock-salt structure, no atomic registry is preferred. As the MgO nucleation sites begin to coalesce on the surface, the combination of the misaligned registries results in a twinned MgO film with small 3-D features. The thicker the MgO film, the more pronounced these features become, ultimately resulting in a highly twinned 3-D surface. However, although the MgO crystallites do dominate the RHEED pattern, AFM characterization of the thick (50 nm) MgO films still reveals smooth (sub nanometer roughness), macroscopic conformal growth with the 3-D feature too small to resolve by AFM due to the tip radius of curvature of 10 nm.
Figure 5.20: Characterization of the twinned MgO(111) crystal structure. a) RHEED images illustrating the onset and pronounced twinned features as MgO film thickness increases [49]. The red box highlights the diffraction characteristic associated with a twinned structure. b) Cross-sectional schematic illustrating the stacking sequence of ideal, un-twinned MgO(111). c) Cross-sectional schematic illustrating the stacking sequence of twinned MgO(111). d) Schematic representation of two possible stacking sequences that are responsible for twinned MgO. Each ball (red and blue) represents a different Mg-O stack and rotational symmetry.

As illustrated in figure 5.20, the RHEED patterns indicate a twinned structure in the appearance of doublet spots in the zeroth Laue zone as the film thickness increases.
from 2 nm to 35 nm. Further, the two angles of symmetry (<1\overline{1}0> and <11\overline{2}>) from figure 5.20 (d) still result in two distinct RHEED patterns. When the MgO film thickness increased above 50 nm, there was an apparent in-plane rotation within the MgO film that was observed by RHEED. Once the in-plane rotation occurred, the two distinct RHEED patterns taken along the <1\overline{1}0> and <11\overline{2}> incident angles became identical. By manually superimposing the distinct RHEED patterns together from thinner (10 nm) MgO films (i.e. simulating a mixed 30° in-plane rotation of the MgO), it was realized that the 50 nm MgO had undergone a 30° in-plane rotation. Because the two angles of symmetry for the pseudo-hexagonal structure of MgO(111) are 30° apart, the resulting RHEED pattern for the 50 nm MgO(111) film consisted of diffraction characteristics resulting from a mix of the two incident angles (<1\overline{1}0> and <11\overline{2}>).

This is illustrated in figure 5.21 where the two typical RHEED patterns for the <1\overline{1}0> and <11\overline{2}> incident angles of a 10 nm MgO film were superimposed to result in a mixed diffraction pattern. The green circles represent diffraction maxima common to both angles of symmetry, while the red and blue circles are representative of <1\overline{1}0> and <11\overline{2}>, respectively. By identifying the positions of the diffraction maxima in the processed image and comparing it to the observed RHEED patterns for the 50 nm MgO film, the resulting patterns matched.

However, because the processed image (figure 5.21 (c)) is actually a twinned single crystal, the intensity maxima are not distorted spherically. For the 50 nm MgO film, the 30° in-plane rotation also results in degree of polycrystalline features, which is evident in the spherical elongation of the diffraction maxima in figure 5.21 (f) and (g). Since little difference is observed between the two incident angles for the 50 nm MgO
film, it is safe to qualitatively state that there is no remaining preferred atomic arrangement or rotation. Thus, although the 50 nm MgO film remained (111) oriented, the out-of-plane alignment resulted in mixed rotations. This is important to consider when integrating a subsequent oxide on the MgO. The mixed in-plane rotation could prevent subsequent heteroepitaxy due to mixed lattice spacings and surface structure. Note that the 30° in-plane rotation does not result in a fully polycrystalline RHEED pattern. Rather, the MgO is still fully (111) oriented with a mix of only 30° and 60° symmetry, but no other intermediate angles.

Figure 5.21: RHEED characterization of MgO(111) with a simulated 30° in-plane rotation (a – c) and observed 30° in-plane rotation for 50 nm MgO (f and g). a) RHEED pattern of 10 nm MgO(111) along <1\bar{1}0> incident angle, b) RHEED pattern of 10 nm MgO(111) along <11\bar{2}> incident angle, c) superimposed image of RHEED patterns along the <1\bar{1}0> and <11\bar{2}> incident angles of 10 nm MgO(111), d) identification of diffraction locations for superimposed image, e) identification of diffraction locations for 50 nm MgO(111), f) RHEED pattern of
50 nm MgO(111) along <1\overline{1}0> incident angle, and g) RHEED pattern of 50 nm MgO(111) along <11\overline{2}> incident angle.

As indicated by RHEED, the growth of MgO(111) appears to follow a 3-D growth mechanism, but maintain a smooth (RMS = 0.60 ± 0.07 nm) almost 2-D like surface. Traditionally, a 3-D growth mode is accredited to the Volmer-Weber growth mode. However, the RHEED pattern of the initial few layers of MgO indicate an apparent layer-by-layer wetting of the surface prior to the formation of the 3-D, twinned features. If the initial growth mechanism does in fact follow a 2-D layered growth mode, then the overall resulting growth mechanism of the MgO would follow the Stranski-Krastanov. In order to further investigate the possible growth mode, cross-sectional TEM characterization was performed through collaboration with Dr. David Muller and Dr. Lena Fitting Kourkoutis at Cornell University. Figure 5.22 shows a strain contrast, cross-sectional TEM image of the MgO/6H-SiC interface.
Figure 5.22: Cross-sectional TEM characterization of 20 nm MgO/6H-SiC(0001) indicating the transition from a 2-D growth mode to a 3-D columnar growth mode occurring at a thickness ~ 5 nm. Typical RHEED patterns are inserted to illustrate the transition from the higher quality, thin MgO (< 5 nm, red box), to thicker 3-D MgO (20 nm, blue box). The 3-D features are ~ 3 nm in size and below the detection limit of AFM (tip radius of curvature of 10 nm). The observed horizontal lattice fringes of 6H-SiC and MgO correspond to the out-of-plane lattice spacings of 6H-SiC(0001) and MgO(111), respectively [49].
Cross-sectional TEM characterization of the MgO/6H-SiC interface of a 20 nm MgO film indicates an initial, higher quality MgO layer that is approximately 5 nm thick. Within this thickness range, the corresponding RHEED pattern remains characteristic of a relatively smooth, layered structure, as indicated by the presence of vertically elongated diffraction spots. The remaining thickness above the 5 nm region consists of 3-D columnar grains that are approximately 3 nm in diameter and extend through to the surface of the MgO film. When the growth mode transitions from 2-D to 3-D columnar, the characteristic RHEED pattern becomes indicated the onset of a twinned, 3-D structure. The distinct spotty RHEED pattern becomes dominated by electron transmission through the 3 nm MgO grains rather than surface diffraction. The combination of in-situ RHEED and ex-situ TEM suggest a Stranski-Krastanov growth mode for MgO(111) on 6H-SiC(0001), as schematically illustrated in figure 5.23.

**Figure 5.23**: schematic representation of the Stranski-Krastanov growth mode of MgO(111) on 6H-SiC. The initial nucleation and growth follows a 2-D growth mode, which transitions to a 3-D growth mode at a MgO thickness of 5 nm.
In summary, the nucleation and growth of MgO(111) on 6H-SiC follows a Stranski-Krastanov growth mode. The initial onset of 2-D nucleation for MgO(111) on the $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ reconstructed 6H-SiC requires the presence of atomic oxygen. The 2-D growth mode (at 140 °C) can be extended up to thicknesses of ~ 5 nm before transitioning to a 3-D columnar growth mode. The columnar features are approximately 3 nm in size. Further, as the MgO film thickness increased to 50 nm, there was an observed 30° in-plane rotation, which resulted in a mixed in-plane structure, but preservation of the (111) out-of-plane orientation.

In order to more accurately and quantitatively characterize the interfaces between the 6H-SiC, 2-D MgO, and 3-D MgO, high resolution TEM needs to be implemented. However, this was not possible due to charging effects and beam damage that were observed in the initial attempts.

Although MgO(111) is inherently twinned, it may be possible to minimize the degree of twinning and in-plane rotation by increasing the energy within the crystal lattice. The simplest way of doing so is the addition of thermal energy. In addition to investigating the effect of thermal energy on the crystal structure, it is also important to investigate the thermal stability of the MgO/6H-SiC interface for understanding interface stability during subsequent high-temperature functional oxide depositions.

5.2.5 Thermal stability and interface breakdown

In order for the MgO to be an effective template for functional oxide heteroepitaxy and future device applications, the MgO film and MgO/SiC interface must be thermally stable without any interface breakdown during subsequent functional oxide
final deposition and device processing steps. Initial thermodynamic calculations indicate
that in the absence of any excess atomic species (namely atomic oxygen), the MgO/SiC
interface should remain thermodynamically stable over all practical temperatures (up to
1000 °C) [147].

A series of experiments was designed to test the chemical, structural, and
morphological stability of the MgO/SiC structure. In the first set of experiments, ~20 Å
of MgO(111) was deposited on hydrogen cleaned 6H-SiC(0001) at a substrate
temperature of 140 °C, a magnesium flux of 1.0×10^{14} \, \text{cm}^{-2} \, \text{s}^{-1}, an oxygen chamber
pressure of 5.0×10^{-6} \, \text{Torr}, and a photomultiplier reading of 35 mV. These MgO films
were then exposed to four different post-deposition exposure conditions: 1) heated to 740
°C in vacuum (1.0×10^{-9} \, \text{Torr}) for 90 minutes, 2) heated to 650 °C in molecular oxygen
(5.0×10^{-6} \, \text{Torr}) for 60 minutes, 3) heated to 650 °C in a light oxygen plasma (5.0×10^{-6}
Torr, 35 mV) for 60 minutes, and 4) heated to 650 °C in a harsh plasma (5.0×10^{-6} \, \text{Torr},
125 mV) for 60 minutes. RHEED was used real-time to monitor the crystal orientation of
the MgO films during growth and during post-deposition exposures. Table 5.4 lists the
different exposure conditions that were investigated.

Table 5.4: A list of temperature and oxygen exposure conditions for evaluating the
stability of the MgO/6H-SiC interface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>O₂ Pressure (Torr)</th>
<th>Photomultiplier (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-post</td>
<td>90</td>
<td>740</td>
<td>1.0×10^{-9}</td>
<td>0</td>
</tr>
<tr>
<td>2-post</td>
<td>60</td>
<td>650</td>
<td>5.0×10^{-6}</td>
<td>0</td>
</tr>
<tr>
<td>3-post</td>
<td>60</td>
<td>650</td>
<td>5.0×10^{-6}</td>
<td>35</td>
</tr>
<tr>
<td>4-post</td>
<td>60</td>
<td>650</td>
<td>5.0×10^{-6}</td>
<td>125</td>
</tr>
</tbody>
</table>

The four as-deposited MgO films were grown to an average thickness of 20.3 ±
2.9 Å. The ± 2.9 Å does not include the 10% error associated with the thickness
calculations. Rather, it is indicative of the error associated with thickness variation between the four samples, which were grown to a target thickness of 20 Å.

XPS characterization of the four as-deposited MgO films indicated that they were stoichiometric with an average composition of MgO$_{1.07\pm0.18}$. After each post-deposition exposure, XPS analysis indicated that the chemistry for all of the MgO films (samples 1-post, 2-post, 3-post, and 4-post) was stable with no change in bonding state of the Mg2p peak and no indication of magnesium peroxide, magnesium metal, or magnesium silicide. Thus, although the thickness of the MgO film and the interface oxide states can change under specific post-deposition exposure conditions as discussed below, the MgO film present after the exposure conditions tested remains stoichiometric and single crystalline with a (111) orientation.

After exposure to oxygen at elevated temperature (samples 2-post, 3-post, and 4-post) the O1s and Si2p photoelectron peaks indicated the formation of a SiO$_x$ layer. Figure 5.24 qualitatively illustrates the appearance of the SiO$_x$ layer as indicated by the Si2p XPS spectra. The peak intensities in figure 5.24 have not been normalized, and thus illustrate the additional signal attenuation of the silicon in bulk SiC through the SiO$_x$ layer formed during post-growth exposure conditions. RHEED indicated the crystalline MgO(111) pattern was maintained on the surface during all exposures. Thus, it is reasonable to assume that the SiO$_x$ is forming at the MgO/SiC interface and does not influence the crystal structure of the MgO film. Following this assumption, the additional attenuation of the Si2p peak after exposure was used to help calculate the thickness of the SiO$_x$ layer. The SiO$_x$ thicknesses were calculated to be 2.5 nm, 17.0 nm, and 22.1 nm for
samples 2-post, 3-post, and 4-post, respectively. Detailed explanation of the thickness calculation is discussed in appendix E.

The post-exposure MgO/SiOx/SiC layered structure is most evident in samples 3-post and 4-post. The SiOx layer is composed of two different oxidation states of the silicon. The left most peak, with a binding energy around 103.3 eV is associated with SiO2, while the middle peak, with a binding energy around 102.1 eV, is associated with SiO. The binding energy position and intensity of the newly formed SiOx is different from the silicate adlayer (figure 5.24 (a) and (b)) and is composed mixed intermediate oxide states of SiO and SiO2.

![Figure 5.24: XPS tight scans of Si2p spectra for the four MgO samples that were exposed to different temperature and oxygen conditions. The increase in SiOx indicates a breakdown at the MgO/6H-SiC interface [48].](image)

Sample 1, which was heated to 740 °C for 90 minutes at 1.0×10⁻⁹ Torr with no oxygen exposure, showed a slight decrease in MgO film thickness of less than 0.2 Å. This change in thickness is within the error of the thickness calculation itself and is not
considered significant. In addition, the attenuated signal originating from the silicate adlayer remained unchanged after exposure. This illustrates the thermal stability of the MgO/SiC interface when heated in vacuum.

The MgO film of sample 2, which was heated to 650 °C under molecular oxygen at a pressure of $5.0 \times 10^{-6}$ Torr for 60 minutes, decreased in thickness by 2.6 Å. This is a 15% decrease in MgO thickness compared to the as-deposited film, which is outside the 10% calculation error and is a repeatable trend when heating 20 Å MgO films in molecular oxygen to temperatures above 650 °C. There is also a slight attenuation change in the bulk Si2p, which suggests a small increase in SiO₅ formation. The change in peak intensities suggests an equivalent SiO₅ thickness increase around 2.5 Å. Based on the qualitative comparison between samples 1-post and 2-post, illustrated in figure 5.24 (a) and (b), the increase in SiO₅ is not visibly obvious. However, the relative amount of SiO₅ to SiC increases from 0.07 (1-post) to 0.12 (2-post) indicating an increase in SiC attenuation. Comparison of the SiC peak intensities for samples 1-post and 2-post further indicates a 21% attenuation, which is due to the presence of the thin SiO₅ layer formed after exposure to molecular oxygen (2-post). The combined decrease in MgO, increase in SiO₅, and additional SiC attenuation supports a possible etching mechanism with interface breakdown during oxygen exposure at 650 °C.

When exposed to 740 °C in vacuum (1.0×10⁻⁹ Torr) there was no observed removal of MgO or interface breakdown indicating a thermodynamically stable interface, which was expected based on thermodynamic calculations [147]. However, exposure to molecular oxygen at 650 °C did result in interface oxidation and etching of MgO. This indicates an etching/formation mechanism that requires high temperature and the
presence of molecular oxygen, which further suggests the possibility of activating the molecular oxygen by dissociating it into atomic oxygen species.

To further test for a possible etching mechanism, samples 3 and 4 were heated to 650 °C and exposed to oxygen plasma of 35 mV and 125 mV, respectively, at 5.0×10⁻⁶ Torr for 60 minutes. After plasma exposure, both samples indicated an overall loss in MgO thickness as well as a significant increase in SiOₓ formation. Sample 3, which was exposed to a 35 mV plasma, indicated a MgO thickness loss around 6.4 Å and a SiOₓ formation around 17 Å. Sample 4, which was exposed to a 125 mV plasma with a higher atomic oxygen content than the plasma exposed to sample 3, indicated a MgO thickness loss around 8.1 Å and a SiOₓ formation of 22 Å.

A comparison of the calculated MgO and SiOₓ thicknesses before and after treatment is illustrated in figure 5.25. The error bars displayed represent the inherent 10% error associated with the thickness calculation. The thicknesses are representative of MgO and SiOₓ thicknesses that were formed during MgO deposition and after exposure treatment. The relative intensity and thickness that is associated with the silicate adlayer, and the error associated with it based on repeatability from sample to sample, has been removed from the data. This is not to indicate that the silicate adlayer has remained untouched, but rather used to illustrate the significance of the additional oxidation that resulted after the high temperature (650 °C) and oxygen exposure.
Figure 5.25: Thickness comparison of the MgO loss and SiO\textsubscript{x} formation after exposure to various elevated temperature and oxygen conditions. The decrease in MgO and increase in SiO\textsubscript{x} supports and etching/formation mechanism that requires available atomic oxygen and high temperatures [48].

Although heating in vacuum for 90 minutes did not change either the film thickness or composition, as the intensity of oxygen exposure conditions increased (with “intensity” defined by the amount of reactive atomic oxygen as measured by the photodiode reading) the overall thickness of the MgO film decreased and the formation of SiO\textsubscript{x} increased. This suggests a possible etching/formation mechanism where the presence of available oxygen, especially atomic oxygen, at elevated temperatures causes the formation of SiO\textsubscript{x} at the interface and etching of MgO. The atomic oxygen could be supplied by the remote oxygen atom source or the cracking of O\textsubscript{2} at the hot surface. The cracking of O\textsubscript{2} significantly reduced the rate of MgO etching and SiO\textsubscript{x} formation relative the generation of atomic oxygen by the remote oxygen atom source. This demonstrates the importance of atomic oxygen on the etching/formation mechanism.
Although the MgO film after exposure remained stoichiometric, crystalline, and without evidence of metallic Mg, the AFM surface roughness measurements on the plateaus of the stepped films revealed measurable surface roughening with increased active oxygen exposure, suggesting increased etching. The as-deposited MgO films had an average RMS roughness over five sampling areas of 0.27 ± 0.02 nm. The sample heated in vacuum (sample 1-post) had an average RMS of 0.38 ± 0.03 nm and the sample annealed under the 125 mV plasma (sample 4-post) had an average RMS of 0.66 ± 0.05 nm. For all surface roughness measurements, the RMS errors are statistical errors from multiple areas on repeated samples and do not represent any error in absolute resolution. Further, in order to accurately represent any change in surface roughness, the roughness analysis was selectively performed along the step surfaces and did not incorporate the entire stepped morphology.

It is important to note that the etching of the film by reactive oxygen is also temperature dependent. Four samples were used to evaluate the effect of substrate temperature on the breakdown of the interface. Initially, 20 Å MgO(111) was deposited on the four 6H-SiC(0001) substrates at 140 °C. Each sample was then exposed to the harsh oxygen plasma, with a photomultiplier reading of 125 mV, for 60 minutes at different temperatures. The temperatures of interest included the initial growth temperature 140 °C, and various higher temperatures indicative of typical PLD, CVD, or MBE functional oxide deposition conditions: 400 °C, 525 °C, and 650 °C. The degree of interface breakdown increased with increasing temperatures, as shown in figure 5.26 by the increase in SiO$_x$ formation with increased substrate temperature. Figure 5.26 incorporates the SiO$_x$ formation as an accumulation of both SiO and SiO$_2$, beyond the
original silicate adlayer, at binding energies of 102.1 eV and 103.3 eV respectively. However, it is important to note that with the exception of the sample exposed to oxygen at 650 °C, the SiOₓ layers consists of only SiO. The SiOₓ composition for the sample at 650 °C was approximately 14.0 Å SiO and 8.1 Å SiO₂. Interestingly, no SiO₂ formation was observed for the other three samples.

![Figure 5.26](image)

**Figure 5.26:** MgO/6H-SiC interface breakdown increases significantly with increased temperature, indicating a kinetically controlled formation mechanism. The SiOₓ formation is dependent on both available atomic oxygen and temperature [48].

The Huttig temperature where surface mobility becomes significant is defined as 1/3 of the melting point. The Huttig temperatures, which are defined as 1/3 of the melting point and corresponds to the temperature where surface mobility is sufficient enough to undergo agglomeration, for MgO and SiC are 943.3 °C and 910 °C respectively. These temperatures are significantly higher than the temperatures used in this study. Thermodynamic calculations using changes in the Gibbs free energy for the formation of SiOₓ from SiC and MgO constituents [147] suggest a thermodynamically stable MgO/SiC interface, where silicon bound to carbon will not preferentially bond with
oxygen already bound to magnesium for all temperatures used in this study. This indicates that the formation of the SiO$_x$ layer is not a result of Si scavenging O atoms from the MgO film.

Interface stability was supported experimentally when sample 1 was heated to 740°C for 90 minutes and did not show any increase in SiO$_x$ nor loss of MgO. If silicon could scavenge oxygen from MgO, sample 1-post would have formed a SiO$_x$ layer of a thickness comparable to the other heated samples. This is consistent with other stable interfaces between silicon-based semiconductors and magnesium oxides [88, 131, 153] as well as the importance of oxygen and high temperature for the oxidation of SiC [132, 133, 135].

The formation of a SiO$_x$ interface requires the presence of active oxygen to breakdown the MgO/SiC interface. In addition, the thermodynamic calculations show that unbound O provides a thermodynamic driving force for breakdown of the otherwise stable MgO/SiC system [147]. This suggests that atomic oxygen must first become available at the MgO/SiC interface in order to initiate SiO$_x$ formation. Since the SiO$_x$ interface forms readily during exposure to atomic oxygen at elevated temperatures, it is possible that active oxygen reaches the interface along grain boundaries in the MgO to initiate the formation of SiO$_x$ at the interface resulting in a layered MgO/SiO$_x$/SiC structure.

One hypothesized scenario is listed in mechanisms 1 through 4 [48], once the unbound O reaches the MgO/SiC interface.

$$\text{SiC}_\text{(s)} + 2\text{O}_\text{(g)} \rightarrow \text{SiO}_\text{(s)} + \text{CO}_\text{(g)} \quad (1)$$

$$\text{SiO}_\text{(s)} + \text{MgO}_\text{(s)} \rightarrow \text{SiO}_2\text{(s)} + \text{Mg}_\text{(s)} \quad (2)$$
This hypothesized mechanism explains the stability of the interface when annealed under vacuum, as active oxygen is not available at the interface. It explains the minimal interface breakdown during molecular oxygen exposure where the O$_2$ is not active, compared to the light (35 mV) and harsh (125 mV) plasma containing unbound O species. The hypothesis accounts for the appearance of SiO and SiO$_2$ in the Si$_2$p XPS spectra as well as the loss of MgO through the desorption of magnesium metal as a vapor at the high temperatures (step 3). Although the formation of SiO$_2$ is thermodynamically favored over SiO [147], it is likely that under many processing conditions, the availability of atomic oxygen at the interface is insufficient to account for the total formation of SiO$_2$. This would require the SiO to scavenge oxygen from the MgO film, per step 2. This secondary oxygen scavenging step can account for the experimentally observed increase in interface breakdown between the two plasma exposures, where the harsh plasma (i.e. more available atomic oxygen) showed greater interface breakdown and increased loss of MgO film thickness.

From figure 5.25 and 5.26, the increase in interface breakdown is influenced by both the availability of atomic oxygen and substrate temperature. Figure 5.26 indicates a kinetically controlled mechanism where the availability of atomic oxygen at the interface is in excess and the rate of interface breakdown is kinetically controlled by substrate temperature. This is indicated by the exponential increase in SiO$_x$ formation as the temperature was increased from 140 °C to 650 °C under a constant oxygen environment (125 mV). Figure 5.25, which illustrates the formation of SiO$_x$ at 650 °C to increasing
atomic oxygen in the vacuum environment, indicates that the rate of interface breakdown is influenced by the availability of atomic oxygen at the interface. Although the observed contributions of both temperature and atomic oxygen support a kinetically controlled mechanism, it is not possible to rule out the influence of the diffusion rate for atomic oxygen along MgO grain boundaries.

Through collaboration at North Carolina State University with Dr. Jon-Paul Maria and Mark D. Losego, the thermal stability of MgO/6H-SiC was further tested by heating a thick (38 nm) MgO film up to 790 °C for 30 minutes in air. Although the film was too thick to characterize the MgO/6H-SiC interface by XPS, GADDS and XRD was used to characterize the stability of the crystal structure and orientation before and after heating. For both the as-deposited and heated samples, GADDS and XRD characterization indicated only 6H-SiC(0001) and MgO(111). The preservation of the MgO(111) diffraction peak after heating combined with the absence of any additional diffraction peaks lends credence to the hypothesis that in addition to the stability of the MgO/6H-SiC interface, the MgO crystal structure is also thermally stable. This is an essential aspect that must be met in order to ensure the stability and performance of the ultimate device heterostructure.

5.2.6 Temperature impact on the surface structure of MgO(111)

Real-time RHEED monitoring of the MgO film heated in vacuum (sample 1-post) indicated a slight 3-D to 2-D transition after reaching 650 °C. When the heated sample was cooled to room temperature, the more 2-D RHEED pattern was maintained. A typical RHEED pattern for a MgO film deposited at 140 °C is represented in figure 5.27.
The RHEED pattern is characteristic of MgO(111) taken along the <1\bar{1}0> azimuth and shows some 3-D characteristics, as indicated by the intensity spots located in the zeroth Laue zone (L₀). During the temperature exposure step of sample 1 to 740 °C in vacuum, the 3-D RHEED characteristics were observed to transition to 2-D characteristics when the substrate temperature reached 650 °C. The film maintained the (111) orientation throughout the high-temperature exposure. The transition to 2-D characteristics is indicated by the smoother streaks in the zeroth Laue zone, represented in figure 5.27. This apparent RHEED transition at 650 °C was observed for all four samples that were exposed to different temperature and oxygen conditions. If the observed RHEED transition is a true representation of a smoother surface, this could be of significant importance for the use as a template layer for functional oxide integration, where it is important to establish an abrupt interface.

To further explore this transition to a more 2-D surface, a 20 Å MgO(111) was deposited on 6H-SiC(0001) at 140 °C followed by rapidly heating the sample to 650 °C at 1.0×10⁻⁹ Torr. AFM characterization was performed on the 20 Å MgO(111) film after heating, and was compared to another 20 Å as-deposited film (i.e. without post-deposition heating). Based on the 3-D characteristics observed by RHEED, it was expected that the as-deposited film would show higher surface roughness compared to the heated sample. The average surface roughness from five locations on the as-deposited MgO(111) and the heated MgO(111) was measured to be 0.27 ± 0.02 nm and 0.26 ± 0.03 nm, respectively. Thus no measurable difference in surface roughness was observed within the resolution limitations of the AFM.
As discussed in section 3.3.1, the actual surface structure of (111) orientated MgO is widely debated. One relaxation mechanism that can alleviate the dipole moment is surface reconstruction or faceting. However, *in-situ* RHEED characterization of the as-deposited and heated MgO films does not support either a surface reconstruction or faceting. Rather, the RHEED pattern is characteristic of a (111)-(1×1) surface structure and XPS supports an OH terminated surface.

If the surface is terminated by OH, then the smoothing effect observed in RHEED suggests the relative amount of OH should drop after the MgO films were heated and transitioned to a streaky RHEED pattern. To test this, a 10 nm MgO film was deposited at 140 °C and then annealed to 650 °C at 1.0×10⁻⁹ Torr for two minutes in order to transition to the more 2-D surface. The 10 nm film was used for its higher surface roughness (0.65 ± 0.05 nm versus 0.44± 0.03 nm for a 2 nm MgO film) in order to maximize surface area for OH attachment and thus maximize the potential change in OH concentration on the surface after the 2-D transition. The more 2-D RHEED pattern remained even after the
film had cooled to room temperature. XPS characterization of the ratio of OH to MgO, as indicated by the O1s peak (figure 5.28), indicated an OH:MgO ratio of 0.22 for the as-deposited MgO and 0.07 for the film heated to 650 °C in vacuum (1.0×10⁻⁹ Tor. The significant decrease in the relative amount of OH is most likely due to a surface smoothing effect that was observed in RHEED. The presence of OH after heating the sample is due to the smoother MgO surface and less surface area for OH termination sites, rather than a surface reconstruction.

In addition, a second sample was deposited to a thickness of 10 nm at a 650 °C growth temperature in order to maintain a smooth 2-D surface during growth and then to evaluate the surface termination after cooling. XPS characterization of the film indicated a relative OH to MgO ratio of 0.06 as calculated from the O1s peak. The additional decrease in the relative ratio from 0.07 for the heated MgO film to 0.6 for the high temperature deposited MgO film may be associated with the smoother 2-D surface that was maintained during film growth. Figure 5.28 illustrates the O1s photoelectron spectra for the 10 nm low temperature MgO, annealed MgO, and 10 nm high temperature MgO. XPS characterization of all the films discussed indicate a MgO(111)-(1×1) OH terminated film.
Figure 5.28: XPS characterization of the O1s spectra and corresponding RHEED pattern for MgO films [48, 49]; a) as-deposited MgO, b) MgO deposited at 140 °C then heated to 650 °C in vacuum (1.0×10⁻⁹ Torr), and c) MgO deposited at 650 °C. The decrease in OH and streakier RHEED patterns indicate a smoother MgO surface when heated or deposited at 650 °C.

It is currently unclear if the decrease is 3-D features is related to a decrease in grain boundaries or only surface smoothing. Although AFM characterization and surface roughness analysis was performed, the smoother surfaces that were observed by RHEED could not be resolved by AFM due to the 10 nm radius of curvature of the AFM tip. High resolution TEM is needed to understand this difference, and is a recommendation for future work. If the MgO film deposited at 650 °C does in fact have fewer grain boundaries, then this may help better understand the contribution of oxygen diffusion along grain boundaries, which is being considered for future in-depth understanding of the interface breakdown mechanism. Although the MgO film deposited on the 6H-SiC at 650 °C was too thick to observe any interface breakdown by XPS, similar high
temperature growths have been performed with MgO thicknesses around 20 Å. Interestingly, although the substrate was shuttered from the line-of-site of the oxygen source, even at substrate temperature of 650 °C and an oxygen environment of 5.0×10^{-6} Torr and 35 mV there was no evidence by XPS or RHEED of surface oxidation prior to growth. This may be due to the thermodynamically favored formation of MgO compared to SiO. Although SiO_2 is thermodynamically favorable over both SiO and MgO, it does require bonds to be broken within the silicate adlayer of the SiC. Therefore, it is not too surprising that the formation of MgO is favorable given the availability of atomic magnesium and atomic oxygen at the surface.

Understanding the conditions that contribute to the breakdown of the MgO/6H-SiC interface and the quality of the MgO film is important for consideration of subsequent functional oxide integration, which could require elevated temperature (greater than 650 °C) and the presence of atomic oxygen. Therefore, it is necessary to determine a range of processing conditions that can be used for functional oxide integration without compromising the integrity of the MgO film or MgO/6H-SiC interface.

MgO films and the MgO/6H-SiC interface have been proven to be stable under exposure to temperature and oxygen conditions that will be required for the deposition of subsequent functional oxides. However, for all stability studies, the MgO films remained in the UHV environment. An additional stability study was performed to test the stability of the MgO surface after being removed from the UHV system and exposed to air. This is important for the consideration of collaboration with other universities, where the samples will need to be exposed to air for several days while being sent. MgO films were
exposed to air for up to two weeks and then reanalyzed by XPS, AES, and RHEED. Although the two week exposure time was chosen, exposure for extended (months) periods of time would most likely behave similarly. Chemical analysis indicated that after exposure to air, there was an increase in oxygen (~10%) and carbon (~15%) surface contamination. Further, the RHEED pattern became diffuse due to attenuation losses through the adsorbed surface contamination, but remained (111)-(1×1). The high quality MgO surface could be recovered and the surface contaminants removed by heating the sample to 650 °C for 30 minutes. Although the minimum temperature and time for the successful removal of the surface contaminants was not determined or optimized, real-time RHEED observations indicated that 30 minutes at 650 °C was sufficient to reestablish a sharp RHEED pattern. Heating the film in order to remove surface contamination is not an issue due to the fact that the elevated temperature would be necessary for the subsequent growth of the functional oxides, and it is believed that the streaky pattern comes from a smoother yet still stoichiometric and single crystalline surface. XPS and AES characterization after heating indicated the removal of the adsorbed surface contaminants and the recovery of stoichiometric MgO. The recovery procedure of the MgO surface after exposure to air for up two weeks allows for collaborative studies where the MgO films could be grown by MBE on 6H-SiC in the Interface Engineering Laboratory at Northeastern University and then shipped to collaborating universities nationally or internationally.
5.2.7 MgO/6H-SiC band bending and offsets

Band bending and band offsets are important for understanding heterojunction band discontinuities, Schottky-barrier heights, and interface band bending [60-62]. Characterization of the valence band and conduction band offsets for the MgO/6H-SiC interface were performed with high resolution XPS spectral scans using Al Kα radiation. For each measurement, at least two sets were performed in order to ensure repeatability and reliability of the data. Prior to the data collection of each sample, calibration was performed using Au4f7 and Cu2p3 spectral positions and a ΔeV of 848.67 eV. Three different sample sets were used and each set consisted of hydrogen cleaned 6H-SiC(0001), 5 nm MgO(111), and 10 nm MgO(111). For each data set, XPS survey scans were collected, as well as elemental scans (Si2p, C1s, O1s, Mg2p, Mg1s) and valence band maxima (VBM).

The valence band offset (ΔEV_B) was calculated using the equation:

\[ ΔE_{VB} = (Si_{2p} - VBM)_{SiC} - (Mg_{2p} - VBM)_{10nm MgO} - (Si_{2p} - Mg_{2p})_{5nm MgO} \]  

Eqn. 5.3

The VBM spectra were collected over the binding energy range from 25 eV to -5 eV. The VBM value was determined by determining the zero intercept of the slope of the curve. In order to ensure accurate calibration, a charge reference was determined for each sample by measuring the ΔeV between the C 1s and Si2p photoelectron peaks (183.2 eV) for the hydrogen cleaned 6H-SiC and 5 nm MgO sample sets, and the ΔeV between the Mg1s and Mg2p (1253.6 eV) for the 5 nm and 10 nm MgO sample sets. Both charge references were used for the 5 nm MgO sample sets in order to ensure similarity between the two charge reference checks. The charge references were designed to cover a wide enough energy range (at least 100 eV) to reliably determine any shifting in the scale.
factor. Note that the scaling between the specific peaks must be accurate in order to reliably determine band offsets, but the absolute position of each peak is not relevant. This is because and constant shift in the spectra would affect each peak equally and would therefore be cancelled out. For example, consider the XPS analysis of the 10 nm MgO. If the scaling is correct where $\Delta E_{\text{VBM}} = 1253.6$ eV, but the absolute peak positions are shifted by 0.75 eV, then the second term in the $\Delta E_{\text{VB}}$ equation should be rewritten as $((\text{Mg} \text{2p} – 0.75) – (\text{VBM} – 0.75))$, which becomes, $(\text{Mg} \text{2p} – \text{VBM} – 0.75 + 0.75)$ or $(\text{Mg} \text{2p} – \text{VBM})$. Therefore, provided the scaling and charge references are accurate, there is no need to be concerned with absolute peaks positions. Figure 5.29 illustrates typical XPS survey scans for the three sample sets. For each sample set, there was no appreciable shift in the spectra.
Figure 5.29: XPS characterization used to determine the band offsets at the MgO/6H-SiC interface. a) Survey scan used to determine scaling and charge reference, b) valence band spectra illustrating the difference in valence states of 6H-SiC (red), 5 nm MgO (blue), and 10 nm MgO (green), and c) demonstration of precise VBM determination for 6H-SiC based on the method developed by Kraut, et al. [60, 61] and refined by Chambers, et al. [62].

In the absence of any charging, the elemental peak positions and VBM values were precisely (± 0.05 eV) determined for each sample set. Table 5.5 lists the binding energies that were extracted from the XPS analysis.
Table 5.5: List of binding energies determined by core level emissions and VBM spectra collected by XPS. These values were used to determine the band offsets at the MgO/6H-SiC interface.

<table>
<thead>
<tr>
<th>Sample set</th>
<th>Si2p (eV)</th>
<th>Mg2p (eV)</th>
<th>VBM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6H-SiC</td>
<td>101.01 ± 0.02</td>
<td>N/A</td>
<td>1.58 ± 0.05</td>
</tr>
<tr>
<td>5 nm MgO</td>
<td>101.04 ± 0.03</td>
<td>49.83 ± 0.03</td>
<td>2.39 ± 0.05</td>
</tr>
<tr>
<td>10 nm MgO</td>
<td>N/A</td>
<td>50.30 ± 0.02</td>
<td>3.58 ± 0.05</td>
</tr>
</tbody>
</table>

The errors listed in the table for the Si2p and Mg2p photoelectron peaks are indicative of sample-to-sample variation, while the error listed for the VBM is more representative of an error in determining the slope intercept. To more accurately determine the VBM values, each sample was fit several times by the method developed by Kraut, et al. [60, 61] by linearly fitting the valence band edge to a zero-intercept with the background. The values presented in the table represent the average and standard deviation of the fittings. Substituting these values into the valence band offset equation 5.3 resulted in a ΔEVB = 1.50 ± 0.09 eV. This calculated value, in conjunction with bulk MgO and 6H-SiC bandgap energies, corresponds to a conduction band offset of ΔECB = 3.27 ± 0.09 eV. A schematic representation of the MgO/6H-SiC band diagram is illustrated in figure 5.30.
Figure 5.30: Simplified band structure of the MgO/6H-SiC interface. The majority of the offset is seen in the conduction band, with an offset of 3.27 eV. The large conduction band offset makes it ideal for high frequency switching applications due to reduced tunneling currents.

For the simplified band diagram illustrated in figure 5.30, the 6H-SiC used was heavily doped n-type (nitrogen) substrates. As a result, the Fermi level, represented by the dashed line in figure 5.30, should be expected to shift towards the conduction band in the 6H-SiC band structure. This is due to the addition of available electrons resulting from the doping. The dopant concentration was measured to be $\sim3.5\times10^{17}$ cm$^{-3}$, as determined from Hall measurements conducted at Yale University (Dr. Charles Ahn, Dr. Fred Walker, and Agham-Bayan Posadas). The vendor specifications for the dopant concentration were between $9\times10^{14} - 1\times10^{19}$ cm$^{-3}$. The band offsets are a result of the mismatch in bandgap energies between the substrate and the film. If 6H-SiC had been an intrinsic semiconductor (little to no doping), then the Fermi level would essentially be midway between the valence band and the conduction band. Then, by aligning the Fermi
level of the substrate and MgO film, the band offsets would be equally distributed between the valence band and conduction band offsets. However, since the 6H-SiC is n-type with the Fermi level shifted toward the conduction band, the majority of the bandgap mismatch will be absorbed in the conduction band.

Although no literature reports of the band diagram for the MgO/6H-SiC system could be found, MgO/GaN band offsets for n-type GaN have been reported to be $\Delta E_{\text{VB}} = 1.2$ eV, $\Delta E_{\text{CB}} = 3.2$ eV by Craft, et al. [59] and $\Delta E_{\text{VB}} = 1.06$ eV, $\Delta E_{\text{CB}} = 3.30$ eV by Chen, et al. [63]. Thus the band offsets represented in the previous figure are comparable to other MgO band offsets reported in literature. Although the measured $\Delta E_{\text{VB}}$ for the MgO/SiC offsets are several tenths of an eV higher than in the MgO/GaN system, this is to be expected. Considering that both the GaN and 6H-SiC are n-type, the Fermi levels in both semiconductors are shifted towards the conduction band. Therefore, the majority of the difference in the bandgap energies between the 6H-SiC and GaN is seen in the valence band. So when MgO is integrated on the two different substrates, the majority of the difference in offsets should be seen in the $\Delta E_{\text{VB}}$ with little change observed in the $\Delta E_{\text{CB}}$. Although the major difference in band structures between MgO/GaN and MgO/6H-SiC is observed in the valence band offset, this has no practical implication device applications. Rather, major interest is in the conduction band offset [64]. Narrow conduction band offsets would result in creased tunneling current, which would be detrimental to the high-frequency polarization switching of a ferroelectric – wide bandgap semiconductor device [59, 64]. Due to the current limitations in the fabrication of high-quality, next-generation heterostructures, the minimum acceptable conduction band offset has not yet been established.
5.3 Potential applications for MgO/6H-SiC heterostructure

MgO has the potential for a wide range of applications due to its physical properties, optical properties, and dielectric properties, in addition to being an oxygen-bridge template to a variety of different perovskite ferroelectrics and hexagonal ferrites. The MgO(111)/6H-SiC(0001) structure was characterized and tested for two applications: a next generation metal oxide semiconductor field effect transistor (MOSFET) device, and a template for functional oxide integration on SiC.

5.3.1 MgO/6H-SiC MOSFET

MOSFET devices are devices that are used to amplify or switch electric signals. Their basic design consists of an n- or p-type semiconductor channel, a source/drain, and a gate oxide. The current benchmark for MOS devices is based on the natively grown oxide SiO₂ on Si. However, in high-frequency high-power applications, the Si-based MOSFET begins to break down. Refer to table 2.1 in section 2.1.2 for a comparison of properties between Si and 6H-SiC. In order to meet the increasing demands of the electronics industry, which requires high-power and high-frequency devices, a new materials system is necessary to replace silicon based technology. The solution is to develop new generation of gate oxides whose dielectric properties are capable of accommodating the frequency and power potentials of wide bandgap semiconductors. Although the surface of 6H-SiC can be oxidized to form a SiO₂ dielectric layer, the electrical properties of SiO₂ would limit the performance of the device. Rather, new gate oxide materials need to be developed with electrical properties that meet or exceed the demands of the MOSFET for next generation devices.
MgO is a suitable candidate for use as an alternative gate dielectric for SiC. This is due to its large bandgap (7.8 eV), high dielectric constant (~10), large band offsets with 6H-SiC, and high thermal stability; all of which are necessary characteristics for next-generation MOSFETs [64]. Recently Stodilka, et al. [128] reported on the use of MgO(111) as a gate dielectric on 6H-SiC(0001). The authors reported a breakdown field of 3.5 MV/cm. The cause of breakdown was attributed to the highly textured MgO crystallite morphology. It is hypothesized that the breakdown field value could be greatly increased by improving the epitaxy and crystallinity of the MgO film.

Through collaboration with Dr. Charles Ahn, Dr. Fred Walker, and Agham-Bayan Posadas at Yale University, twenty-seven MgO/6H-SiC devices were fabricated and tested. The MgO films were deposited on hydrogen cleaned 6H-SiC(0001) by MBE to thickness of 2.7 nm, 5.5 nm, 10.4 nm, and 20.5 nm. The film thicknesses were determined by x-ray reflectivity. For electrical measurements, aluminum pads (50 µm, 83 µm, and 150 µm diameters) were deposited to thicknesses of 50 nm. For the bottom contact, the SiC was scratched with a diamond tip scribe and coated with InGa eutectic alloy. Both the top and bottom contacts resulted in ohmic contacts, as determined by current-voltage (I-V) measurements on bare 6H-SiC and MgO substrates.

The MgO/6H-SiC structure was characterized by C-V hysteresis and leakage current (breakdown voltage). The capacitance was measured using an Agilent E4980A precision LCR meter and leakage was measured using a Keithley 4200 Semiconductor Characterization System. For all capacitance characterization, a typical depletion (negative bias) and accumulation (positive bias) was observed, which is consistent with the profile expected from an n-type semiconductor. C-V curves were also obtained at 300
°C where there was no observed temperature dependence. Figure 5.31 illustrates the C-V characterization for the 20.5 nm MgO film collected at four different frequencies (1 kHz, 10 kHz, 100 kHz, and 1 MHz). These results indicate that MgO has is a potential alternative gate dielectric for 6H-SiC.

**Figure 5.31:** C-V curves for MgO/6H-SiC parallel plate capacitor [129]. a) Characteristic depletion (negative bias) and accumulation (positive bias) curve for an n-type capacitor, b) hysteresis behavior with a width of ~0.8 V. The combination of frequency dependence and hysteresis behavior indicate the presence of interface state.

The capacitance characterization also indicated a hysteresis behavior where the reverse sweep was ~0.8 V wide (figure 5.31 (b)). In addition, there was some frequency dispersion within the accumulation region of the capacitance curve as seen by the offsets in the positive bias of figure 5.31 (a). These two anomalies indicate the presence of trapped interface states. The density of the interface states was estimated by the ac conductance method [154] to be \(6.2 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}\) at a trap energy 0.2 eV below the
conduction band. Although the measured interface density is not ideal, it is comparable to those reported for both SiO₂ and other alternative dielectric materials on SiC [30, 128]. In order to optimize the capacitance properties of the MgO/6H-SiC structure, it will be necessary to reduce the interface density by at least an order of magnitude, based on current SiO₂/Si interface state calculations [24].

The dielectric constant of the MgO structure was determined by modeling the capacitor as a parallel plate capacitor. This method is described by the following equations.

\[ C = \frac{\kappa \varepsilon_0 A}{d} \]  
\[ \frac{C}{A} = \frac{\kappa \varepsilon_0}{d} \]

Where:
- \( C \) = capacitance
- \( \kappa \) = dielectric constant
- \( \varepsilon_0 \) = permittivity of free space (1)
- \( A \) = area of the plates
- \( d \) = plate separation/dielectric thickness

This equation assumes that the measured structure is an ideal parallel plate capacitor containing only one dielectric material. Therefore, by plotting the area of the capacitance versus the inverse of the plate separation (i.e. dielectric layer thickness), the slope of the curve represents the dielectric constant. However, most real parallel plate capacitors are not ideal, but rather consist of a series capacitor of multiple dielectric layers. A series capacitor can arise from defects at interfaces, unwanted reaction phases, contact voids, and the internal capacitance of the machine. Therefore, the capacitance equations can be rewritten to account for the series capacitor.
Similar to the ideal parallel plate model, the dielectric constant and series capacitance element can be extracted from the previous equation by plotting the inverse capacitance versus the dielectric layer thickness ($D$). The slope of the curve is directly related to the dielectric constant, while the non-zero intercept is representative of the series capacitance element. The series capacitance equations (equations 5.6 – 5.8) represent a two-component series capacitor, but the equation can be extended to include any number of dielectric layers. However, if multiple undesired and unexpected dielectric layers are present, it is difficult to distinguish between their individual contributions. Rather, their effects are combined into the generic non-zero intercept term. This is a limitation of both the characterization technique and the equations used to represent the series capacitor.

The series capacitance equation for a parallel plate capacitor was used to determine the dielectric constant of MgO. Four MgO film thicknesses of 2.7 nm, 5.5 nm, 10.4 nm, and 20.5 nm were used. The inverse capacitance versus MgO thickness plot is illustrated in figure 5.32.
**Figure 5.32**: Inverse capacitance curve used to determine the dielectric constant of the MgO. The slope of the line is directly related to the dielectric constant (equation 5.8). The non-zero intercept indicates a series capacitor and the equivalent of 1.3 nm of SiO₂ [129].

From figure 5.32, the dielectric constant of MgO was calculated to be \(~10\) (equation 5.8), which is consistent with the expected dielectric constant of single crystalline MgO [155]. The non-zero, y-intercept corresponds to series capacitance component of approximately 1.3 nm of SiO₂. Although there are several possibilities for this series capacitance, its value is expressed as an effective SiO₂ thickness. The most likely cause of this series capacitance is due to the presence of the $\sqrt{3} \times \sqrt{3}$ R30° silicate adlayer that results after the *ex-situ* hydrogen cleaning. Precise XPS characterization and thickness calculations of the silicate adlayer were performed based on an estimated sampling depth of 8.3 nm, which was calculated based on the kinetic energy of the Si2p photoelectron generated by Al Kα incident x-rays and the density of SiC [148]. Using a known sampling volume, and assuming that all of the oxygen detected by XPS was on
the surface of the SiC, the resulting silicate adlayer thickness was calculated to be ~1.2 nm. These thickness calculations have an inherent error around 10%, but the calculated value of 1.2 nm ± 10% is in close agreement with the 1.3 nm that was observed in the inverse capacitance fit. Thus, the non-zero intercept and series capacitance that was observed in figure 5.32 is due to the silicate adlayer and MgO acting as two distinct dielectric layers.

Based on the previously discussed MgO characterization (crystal quality, interface stability, large band offsets, capacitance, dielectric constant), MgO has the necessary properties for use as an alternative gate dielectric on SiC. To further support the integration of MgO on SiC for MOSFET devices, it is necessary that the MgO be able to meet or exceed the operating voltages and breakdown of the SiC substrate. In order to maximize the operating potential and performance of the SiC based device, it is important that the electrical properties of the substrate be the limiting factor. If the substrate is capable of performing at high frequencies and high voltages, but the dielectric layer fails, then the overall performance of the device is not realized and a new dielectric material should be considered.

In addition to the capacitance and frequency characterization of the MgO/6H-SiC structure, it is important to determine the breakdown voltage, which is important for establishing the threshold voltage that can be applied before the structure collapses and leakage current occurs. The breakdown voltage of the MgO/6H-SiC structure was evaluated by measuring the leakage current of twenty-seven parallel plate capacitors, where the MgO was 2.7 nm thick. A typical leakage current versus voltage curve for a single device is shown in figure 5.33. At a negative bias, the leakage current is being
measure through the \(6H\)-SiC bottom contact of the capacitor and is therefore disregarded for device characterization because it does not represent the properties of the structure, but rather only the semiconductor. However, at appositive bias, the current is being measured at the MgO contact and is therefore characteristic of the MgO leakage properties. As the applied electric field is increased from 0 MV/cm to \(~12\) MV/cm, there is a fairly linear relationship. This is characteristic of the dielectric, insulating properties of the MgO film following Ohm’s Law where \(V = IR\). Once the voltage threshold has been reached, the insulating properties of the MgO begin to breakdown, resulting in a drastic decrease in resistance and increase in current flow. This voltage is referred to as the breakdown voltage.

![Graph showing current density vs. electric field](image)

**Figure 5.33:** Typical leakage current measurement for an MgO/\(6H\)-SiC parallel plate capacitor. Histogram analysis of the breakdown statistics for the twenty-seven capacitors found the median breakdown voltage at 12 MV/cm [129].
The inset in figure 5.33 is a histogram analysis of the breakdown statistics for all twenty-seven devices. The median breakdown field was found to be 12 MV/cm, where nine of the twenty-seven devices failed. Further, seventeen of the twenty-seven devices failed at electric fields greater than or equal to 12 MV/cm. The low leakage and high breakdown field is attributed to the high crystalline quality of the MgO that was epitaxially grown on the 6H-SiC.

5.3.2 MgO as a heteroepitaxial template layer

The primary interest in the high quality MgO layer, regarding this dissertation, is for use as a heteroepitaxial template for the integration of various functional oxides; specifically tetragonal ferroelectrics. Initial investigation into the effectiveness of MgO as a heteroepitaxial template was performed through collaboration with Yale University (Dr. Charles Ahn, Dr. Fred Walker, and Agham-Bayan Posadas) and North Carolina State University (Dr. Jon-Paul Maria, and Mark Losego). One 2.5 nm MgO(111)/6H-SiC(0001) sample was sent to Yale University where BTO was deposited by PLD. Two hydrogen cleaned 6H-SiC(0001), one 2.5 nm MgO(111)/6H-SiC(0001), and one 10 nm MgO(111)/6H-SiC(0001) samples were sent to North Carolina State University where BST was deposited by PLD. As discussed in section 5.2.6, the stability and recovery of samples exposed to laboratory air was tested prior to shipping samples across the country, and no unrecoverable damage to the surface was revealed.
5.3.2.1 PLD grown BTO on MgO/6H-SiC template

The first attempt to integrate BTO on the MgO/6H-SiC template was performed through collaboration with Yale University. Initially, a 2.5 nm MgO(111)/6H-SiC(0001) sample was grown by MBE at 140 °C. The sample was shipped overnight to Yale University where the sample was immediately put under vacuum. The total exposure time to air was less than 36 hours. Once under vacuum (10^{-7} – 10^{-6} Torr) the sample was heated to 650 °C to remove excess contamination and to establish a stable growth temperature for the subsequent BTO deposition. Approximately 40 nm BTO was then deposited by PLD on the MgO/6H-SiC template.

![AFM and XRD characterization of BTO deposited on 2.5 nm MgO/6H-SiC.](image)

**Figure 5.34:** AFM and XRD characterization of BTO deposited on 2.5 nm MgO/6H-SiC. The resulting film was 3-D with an RMS of 2.6 nm over a 1 µm² area but only (111) oriented, demonstrating the effective heteroepitaxy of BTO on MgO/6H-SiC.

XRD characterization (figure 5.34) of the BTO/MgO/6H-SiC heterostructure indicated only (111) oriented BTO, but also contained diffraction peaks originating from the 6H-SiC substrate. The 2.5 nm MgO film was too thin to detect by XRD. AFM characterization of the BTO film indicated 3-D grains roughly 90 nm in size and a RMS
roughness over a 1 µm² square of 2.6 nm. Although the BTO surface is rough, relative to the MgO and 6H-SiC roughnesses of ~ 0.45 nm, the absence of any mixed orientation in the XRD scans lends credence to the potential of MgO(111) to align the growing film and promote heteroepitaxial integration of BTO on 6H-SiC.

5.3.2.2 PLD grown BST on MgO/6H-SiC template

A more complete collaborative investigation into the effectiveness of MgO as a heteroepitaxial template layer was performed at North Carolina State University, where thick BST (~300 nm) was grown by PLD on three different starting surfaces. The first was hydrogen cleaned 6H-SiC(0001) with a √3×√3 R30° surface reconstruction, the second was 2.5 nm MgO(111)/6H-SiC(0001), and the third was 10 nm MgO(111)/6H-SiC(0001).

Similar to the collaboration at Yale University, all of the substrates were prepared and shipped overnight to North Carolina State University and placed back under vacuum within 36 hours. All substrates were then heated to 650 °C for 30 minutes in order to remove excess surface contamination prior to BST growth by PLD.

General area diffraction detection system (GADDS) characterization of the series of BST films indicated similar results to that observed in the initial collaborative study at Yale University. When BST was integrated on the MgO(111) templates, the resulting BST film was (111) oriented. This was observed for both the 2.5 nm thick MgO and the 10 nm MgO. ϕ-scans (not shown) of the epitaxial BST/MgO/6H-SiC indicated a twinned, 6-fold symmetry for the BTO similar to the twinned structure of the MgO(111). When BST was deposited on 6H-SiC(0001) directly, the resulting diffraction pattern indicated
an amorphous film. Efforts were made to crystallize the BST/6H-SiC by annealing the film to 900°C in a nitrogen environment. The resulting x-ray diffraction pattern (GADDS) indicated a slight improvement in the alignment of BST(111), but also contained polycrystalline rings and reaction phases. Thus, an MgO template layer is essential for the epitaxial integration of BST(111) on 6H-SiC.

![Figure 5.35: Characterization and demonstration of the effectiveness of MgO as a heteroepitaxial template for BST on 6H-SiC. Column (a) represent BST deposited on 6H-SiC, which resulted in an amorphous 3-D film. Column (b) represents BST deposited on 2.5 nm MgO/6H-SiC, which resulted in only (111) oriented BST with macroscopic conformal growth to the stepped 6H-SiC surface but small 3-D...](image-url)
features. Column (c) represents BST deposited on 10 nm MgO/6H-SiC, which also resulted in only (111) oriented BST with macroscopic conformal growth to the stepped 6H-SiC surface but small 3-D features. The top row is the GADDS image, the middle row is the θ-2θ line profile along the dotted blue line, and the bottom row represents the corresponding surface morphology. The single RHEED image is characteristic of BST(111).

AFM characterization of the three BST films indicated a 3-D grainy growth mechanism for all cases. For BST/6H-SiC, the surface roughness was ~16 nm and consisted of large grains 100 – 150 nm in size. However, when BST was deposited on the MgO template (both 2.5 nm and 10 nm) The film morphology was much smoother with RMS values of ~0.29 nm and ~0.45 nm for 2.5 nm MgO and 10 nm MgO, respectively. Further, although the BST was several nanometers thick, the general morphology of the BST revealed the preservation of the underlying stepped surface of the 6H-SiC. In addition to promoting the heteroepitaxy of BST(111), the use of an MgO template layer results in a smoother, more conformal BST film. A smooth surface will be necessary for establishing an abrupt interface between the adjacent functional oxide layers.

RHEED images of the two epitaxial BST films deposited on the 2.5 nm and 10 nm MgO template layers were identical and characteristic of a (111) oriented tetragonal perovskite, which supports the (111) oriented diffraction pattern that was observed by GADDS. A typical RHEED pattern for the BST(111) is illustrated in figure 5.35. The interpretation of the RHEED patterns characteristic (111) oriented tetragonal structures will be discussed in further detail in section 5.4.2.

From the more complete collaborative study regarding the successive integration of MgO(111) as a template layer on 6H-SiC, there is strong evidence that MgO can
effectively promote the heteroepitaxy of a various perovskite ferroelectrics. Further, it appears that only a thin layer (2.5 nm) is required to promote heteroepitaxy. From these initial studies, an experimental plan was developed for understanding the growth parameters and property characterization for the heteroepitaxy of ferroelectric BTO on 6H-SiC by MBE through

5.4 Integration of BTO on 6H-SiC by MBE

In the previous section, preliminary heterostructures were integrated on 6H-SiC with and without an MgO template layer by PLD. Although PLD has the advantage of depositing thick (several hundred nanometers) films in relatively short periods of time, it does not have the same level of control as MBE. This is due to fact that PLD requires the use of pre-fabricated sputtering targets, and pressures in the millitorr range. Typically, the stoichiometry of a target is the same, or similar to, the desired stoichiometry of the film. As a result, it is not possible to dynamically adjust individual flux species real-time, without alternating between multiple targets. However, in an MBE system, each elemental flux is controlled independently and the processing pressure during growth is typically 5.0×10⁻⁶ Torr. The independent control of species flux and lower growth pressure eliminates gas-phase reactions, minimizes contamination rates, and allows atomic level control of the nucleation and growth mechanisms of the oxide films.

The ultimate goal of BTO deposition was to integrate high-quality, smooth, single crystalline BTO with ferroelectric properties on the MgO/6H-SiC template by MBE. The challenges that needed to be addressed included establishing appropriate operating conditions for the heteroepitaxy of stoichiometric BTO, characterization of the crystalline
properties of BTO, characterization of the ferroelectric properties of BTO, and establishing a smooth (sub-nanometer roughness) surface for the subsequent integration of BaM into a multifunctional heterostructure.

5.4.1 Establishing operating conditions window

BTO was deposited by MBE using a solid source effusion cell for barium, a Ti-ball sublimator for the titanium, and a remote oxygen atom source for oxygen. Due to the low vapor pressure of titanium, the implementation of a Ti-ball is an affordable alternative to a high temperature effusion cell. However, precise control over the titanium flux is restricted due to the limitations of the Ti-ball power supply, which is fixed at 0.5 A intervals. As a result, tuning of the flux conditions to obtain stoichiometric BTO was performed by adjusting the Ba flux, which was supplied by a traditional effusion cell.

Unlike traditional effusion cells, which can be controlled to within ± 1 °C, the Ti-ball is limited to 0.5 A intervals with no temperature readout. Figure 5.36 demonstrates the use of the Ti-ball for depositing titanium at different currents. As the current to the Ti-ball was increased, the Ti flux increased exponentially. However, determination of the actual Ti-flux was limited to vendor supplied data representing the relationship between current and mass loss of titanium. Therefore, the Ti-ball current was varied to obtain a stoichiometry close to that of BTO, followed by the tuning of stoichiometry by adjusting the Ba flux. For all initial BTO films designed to narrow down the stoichiometry window, the barium flux, oxygen species, and substrate temperature (650 °C) were held constant. By varying the power supply current to the Ti-ball, the stoichiometry (Ba:Ti ratio) could be roughly set. However, the exact stoichiometry fell between the current
setting of 40.5 A and 41 A. Since the power supply is limited to intervals of 0.5 A, the Ba flux had to be adjusted in order to obtain a Ba:Ti ratio of 1:1. As seen by XPS, the titanium rich films result is shoulder towards the lower binding energy side that corresponds to excess TiO.

![Graph](image)

**Figure 5.36:** a) Determination of a rough operating window for obtaining stoichiometric BTO by varying the Ti flux, which is limited to 0.5 A intervals on the power supply. Stoichiometric BTO lies between operating currents of 40.5 A and 41 A. b) XPS characterization of the BTO films indicates a lower binding energy shoulder for titanium rich films, which corresponds to excess TiO.

In the case of MgO, one species (oxygen) could be supplied in excess while the second (Mg) would be the rate determining species. In the case of the ternary oxide BTO, both Ti and Ba oxidize readily to form TiO\(_2\) (tetragonal) and BaO (rock-salt), and thus it is not clear that one single species can be the rate limiting species. Therefore it is necessary to find a balance between the three independent flux variables in order to
obtain stoichiometric, tetragonal BTO. Due to the complexity of the ternary oxide, there is a narrow operating window in which stoichiometric, tetragonal BTO can be obtained. If the Ba:Ti ratio deviates from stoichiometric, the crystal structure of the resulting film is affected greatly. Illustrated previously in figure 5.36, XPS characterization of BTO films grown with an excess titanium flux results in a mixture of TiO₂ (BTO) and TiO. This excess TiO further affects the crystal structure of the film, as illustrated in figure 5.37.

Figure 5.37: RHEED characterization of the crystal structure of BTO films grown on MgO/6H-SiC with various Ba/Ti stoichiometric ratios, as determined by XPS. As the Ba/Ti ratio deviates from 1.0 the resulting crystal structure becomes polycrystalline (Ba/Ti = 1.2 or 0.8) or amorphous (Ba/Ti = 1.4 or 0.6).

Stoichiometric BTO (Ba/Ti = 1.0) results in the characteristic 3-D RHEED pattern that is discussed later in section 5.4.2. BTO films that were slightly off-stoichiometric with Ba:Ti ratios that were slightly Ti rich (0.8) or Ba rich (1.2) result in highly polycrystalline films. If the Ba:Ti ratio was varied further off the desired stoichiometry, the resulting film was amorphous.

Once the desired stoichiometry was obtained, it was possible to continue the investigation into the effectiveness of MgO(111) as an effective heteroepitaxial template. Based on the appropriate growth conditions established from the previous figure, BTO
was deposited at 650 °C on hydrogen cleaned 6H-SiC(0001) and 2.5 nm MgO(111)/6H-SiC(0001). Similar to the collaborative study conducted with North Carolina State University, it was found that even a thin (2.5 nm) MgO layer was both effective and necessary for the heteroepitaxial integration of BTO on 6H-SiC. Figure 5.38 illustrates the *in-situ* RHEED characterization of the BTO growth.

**Figure 5.38**: RHEED sequences used to characterize the effectiveness of MgO(111) as a template layer for the heteroepitaxy of BTO(111) [48]. a) RHEED sequence of amorphous BTO deposition on 6H-SiC without a MgO template layer. b) RHEED sequence of heteroepitaxy of BTO on 6H-SiC with a 2.5 nm MgO template layer. c) XRD θ-2θ scans illustrating only (111) oriented BTO.
When BTO was deposited at 650 °C and 0.5 nm/min by MBE on hydrogen cleaned 6H-SiC(0001) with the $\sqrt{3}\times\sqrt{3} R30^\circ$ surface reconstruction, the resulting BTO was amorphous (figure 5.38 (a)). When deposited on a 2.5 nm MgO(111) template layer, the resulting BTO was crystalline, but exhibited highly 3-D RHEED feature similar to those observed by RHEED for the epitaxial BST(111) films grown by PLD at North Carolina State University (figure 5.35)). The consistency between the results discussed for PLD grown BST and MBE grown BTO on 6H-SiC and MgO/6H-SiC, indicates the importance, and effectiveness of MgO as a heteroepitaxial template for tetragonal ferroelectrics. AFM characterization of the 4 nm BTO film deposited on the MgO template layer indicated 3-D grains ~50 nm in size, but with a surface roughness of ~0.82 nm over a 1 µm² area. Although the 3-D features contribute to a surface morphology with sub-nanometer roughness, it will still be necessary to establish a smoother, 2-D surface for the subsequent integration of BaM. However, the integration of a MgO template layer has demonstrated the potential for the heteroepitaxy of tetragonal ferroelectrics on 6H-SiC. The processing conditions can be tuned further to establish higher-quality, single crystalline BTO.

5.4.2 Interpretation of BTO RHEED pattern

The characteristic RHEED patterns of the PLD-deposited BST and BTO that were shown in the figures 5.35 and 5.38, appear to be similar and are unique to (111) oriented tetragonal ferroelectrics. Interpreting the RHEED patterns are important to understanding the growth mechanisms by MBE. In order to decipher the RHEED pattern and relate it to the crystal structure of the tetragonal perovskites, it is first necessary to understand the
nature of the (111) orientation of the tetragonal perovskites. Similar to (111) oriented MgO, BTO has a similar atomic stacking sequence that results in a pseudo-hexagonal structure. However, since BTO has a tetragonal structure, the resulting hexagon is distorted in one direction. This is because the c:a lattice ratio is 1.011 (4.038 Å/3.998 Å).

Similar to the discussion previously in section 5.2.4 regarding the RHEED interpretation of MgO(111) pattern, BTO(111) is inherently twinned due to the six-fold symmetry within the crystal structure. However, it should be noted that the distorted hexagon of BTO(111) does not have a true six-fold symmetry, but rather a two-fold symmetry. The six-fold symmetry is a result of non-preferential rotation of the pseudo-hexagon, where the two-fold symmetry is characteristic of two planes of symmetry and is designated by lines 1 and 2 in figure 5.39 (b). Figure 5.39 compares the true six-fold symmetry of MgO(111) to the rotational six-fold symmetry of BTO(111). Note that the distorted hexagon of BTO(111) has been exaggerated (figure 5.39 (b)) in order to more clearly represent the rotational symmetry.
Figure 5.39: schematic representation of; a) 6-fold symmetry of the pseudo-hexagonal structure of MgO(111), and b) pseudo 6-fold symmetry of BTO(111). The numbered lines represent the planes of symmetry.

Based on the simplified rotational model of figure 5.39, the pseudo six-fold symmetry is due to a combination of the three symmetric 60° rotations and the two lines of symmetry that are characteristic of the pseudo-hexagonal structure of BTO(111). Extending the simplified in-plane rotational model to a 3-D crystalline mesh model, can help address the unique 3-D RHEED pattern that was observed for both BTO and BST. The distinct spots within the zeroth Laue zone are typical of a 3-D surface where the RHEED pattern is dominated by electron transmission rather than surface diffraction. Figure 5.40 illustrates a model of the rotational symmetry within the BTO 3-D lattice and the corresponding RHEED interpretation. Note that the 3-D lattice mesh for a tetragonal
crystal in real space is essentially identical to the 3-D lattice mesh in reciprocal space (figure 5.40 (d) and (e)). The difference between the real space and reciprocal space is the distance between each atom and a 30° rotation. Representation of a real space to reciprocal space transposition is illustrated in figure 5.18. Further details regarding the transposition from real space to reciprocal space can be found in appendix B. The 3-D lattice model, illustrated in figure 5.40 (d) and (e), is representative of the reciprocal space translation of BTO(111). Due to the 90° lattice angles and near-symmetric crystal structure (a = b ≠ c, but c/a= 1.011) of the perovskite structure, the transposition between real space and reciprocal space results in near identical crystal lattice meshes.

**Figure 5.40**: Interpretation of RHEED pattern characteristic of BTO(111). a) Characteristic RHEED pattern taken along the <110> incident angle. b) Larger
image of the zeroth Laue Zone illustrating transmission dominated pattern. c) Identification of diffraction maxima. d) Reciprocal space model of BTO(111) illustrating two possible 60° rotational options. e) Correlation between the characteristic RHEED pattern of BTO(111) and the corresponding reciprocal space model. The reciprocal space model in part (e) is a combination of the two models illustrated in part (d).

The first step to understanding and interpreting the BTO RHEED pattern was to focus on the zeroth Laue zone (L₀) and the specific locations of the diffraction maxima (figure 5.40 (a) – (c)). As indicated on the close up image of L₀ (figure 5.40 (b)), the zones (-1,0), (0,0), and (1,0) indicate the Laue rods that correspond to the lattice spacing of the BTO surface hexagon and the shared lattice mesh for all rotations of symmetry (designated by the green atoms in the model of figure 5.40 (c)). These atoms have an in-plane, mirrored symmetry about the (0,0) Laue rod for every 60° rotation and exist in every third row of atoms. However, the 3-D lattice mesh model (figure 5.40 (d)) illustrates that the two rows of atoms (red and blue) between the layers of green atoms are not symmetric about the (0,0) Laue rod. This asymmetry is a result of the distorted hexagon of the (111) oriented perovskite. Although the BTO crystals are all (111) oriented, the 60° rotational symmetry results in a combination of 60° in-plane rotations with no preferred alignment. As a result, the BTO lattice mesh consists of a combination of rotations. When these mixed rotations are added together, the resulting lattice mesh is an identical match to the observed RHEED patterns at both RHEED angles (figure 5.40 (e)). Although the characteristic BTO RHEED pattern is a result of mixed 60° in-plane rotations, the crystal structure of the BTO remains (111) oriented (figure 5.38). The similarities between the modeled reciprocal 3-D lattice mesh of BTO(111) and the
observed RHEED patterns indicate that the unique RHEED pattern is characteristic of BTO(111) (or any tetragonal perovskite) and is dominated by electron transmission through the twinned BTO crystals.

5.4.3 BTO epitaxy alignments

Similar to the epitaxy models discussed previously for MgO(111) on 6H-SiC(0001), there are several epitaxy possibilities that minimize lattice mismatch between the BTO(111) and either the MgO(111) or the 6H-SiC(0001). For BTO(111) integration on MgO(111) or 6H-SiC(0001), the lattice mismatches were minimized using the O-to-O lattice spacing of 2.83 Å for BTO(111). Note that this is an average lattice spacing between the oxygen atoms due to the elongation and asymmetry of the BTO(111) pseudo-hexagon. The implication of using the average lattice spacing is discussed at the end of this section.

Figure 5.41 illustrates the two lattice-matched possibilities for BTO(111) on MgO(111)/6H-SiC(0001) and BTO(111) on 6H-SiC(0001) with a $\sqrt{3} \times \sqrt{3} R30^\circ$ surface reconstruction. In both cases, the minimum compressive and tensile mismatches are represented. The minimum mismatches for BTO/6H-SiC are 6.2% and -7.9% (figure 5.41 (a)). The mismatches are reduced to 5.7% and -5.3% for BTO/MgO/6H-SiC (figure 5.41 (b)). The negative sign represents a tensile mismatch, while positive represent compressive.
Figure 5.41: Epitaxy alignments for BTO(111) on 6H-SiC (a) and MgO/6H-SiC (b). For all epitaxy alignments, the green atoms represent tensile mismatch and the yellow atoms represent compressive mismatch. The direction references are relative to the surface structure of either 6H-SiC (a) or MgO (b).

The two epitaxy alignments for BTO(111) on reconstructed 6H-SiC(0001) (figure 5.41 (a), yellow and green) consist of a 6.2% compressive mismatch (yellow), where the hexagon of the BTO aligns with the hexagon of the reconstructed 6H-SiC, and a 7.9% tensile mismatch (green), where the hexagon of the BTO is rotated 30° from the hexagon of the reconstructed 6H-SiC. As indicated by RHEED, BTO epitaxy was not observed on the reconstructed 6H-SiC(0001). As no chemical breakdown or diffusion of the interface was observed by XPS, this suggests that for both of these epitaxial alignments, the
mismatch between the film and substrate was too great to promote aligned, crystalline film growth. This is also consistent with the lack of epitaxy that was observed for the BST/6H-SiC and performed through collaboration at North Carolina State University (figure 5.35).

When integrated on the MgO(111) template layer (figure 5.41 (b)), the mismatch between the O-O of BTO(111) and the substrate (O-O of MgO(111)) is reduced to 5.7% compressive (yellow), with a 30° rotation of the hexagon, and 5.3% tensile (green), with no rotation. Based on these calculated values, the most favorable alignment is the 5.3% tensile mismatch. This epitaxy alignment results in both the minimum mismatch value and favorable mismatch type (tensile) for perovskite oxides. Comparing the RHEED patterns of BTO to the corresponding RHEED patterns of MgO prior to growth, it was observed that BTO(111) does prefer to tensile mismatch of 5.3%. This epitaxy was determined by the comparing the RHEED patterns taken along the <11̅0> and <11̅2> incident angles of the MgO(111) template and the corresponding BTO pattern along the same incident angles. The results indicated an out of plane epitaxy where BTO{11̅0} is parallel to MgO{11̅0}. Therefore, the pseudo-hexagon of BTO(111) aligns with the hexagon of MgO(111).

The represented lattice constants and mismatches for MgO(111) and BTO(111) are based on bulk crystal properties at room temperature and do not take into account thermal expansion at elevated deposition temperatures. Considering the thermal expansion coefficient of MgO > BTO > 6H-SiC, the actual tensile mismatch between BTO and MgO would be expected to increase during heating, while the compressive mismatch would decrease. Regardless, the observed BTO epitaxy followed option 2 of
the modeled BTO/MgO/6H-SiC alignment with a tensile mismatch. Therefore, the overall epitaxy of the heterostructure followed \( \text{BTO}\{111\}||\text{MgO}\{111\}||\text{6H-SiC}\{0001\} \) and \( \text{BTO}\{1\overline{1}0\}||\text{MgO}\{1\overline{1}0\}||\text{6H-SiC}\{11\overline{2}0\} \). Note that the use of \( \{hkl\} \) is applied as a family of planes which include all individual (hkl) planes. A detailed discussion of lattice planes and direction can be found in appendix D.

Understanding the in-plane and out-of-plane epitaxial alignments is important for demonstrating the effectiveness of forming an oxygen bridge between the adjacent oxide layers. BTO(111) has an elongated pseudo-hexagonal surface structure due to the elongated c-axis of the tetragonal crystal structure. This results in different atom-to-atom in-plane lattice spacings of 5.65 Å and 5.68 Å (for Ba-to-Ba) or 2.82 Å and 2.84 Å (for O-to-O). Figure 5.39 (b) illustrates the different atom-to-atom spacings that results from the elongated pseudo-hexagon of BTO(111). Since there is no apparent preferred rotation within the BTO, the in-plane lattice spacing discussed are an average of the two; 5.67 Å for Ba-to-Ba and 2.83 Å for O-to-O. In addition, the lattice matching models represent BTO(111) as a pure hexagon with the aforementioned average lattice spacing. In reality, there is an equal number of O-O spacing with a lattice of 2.82 Å and 2.84 Å. Although there is less than a 1% difference in the lattice spacing, it is possible that this had an impact on the heteroepitaxy of BTO resulting the 3-D morphology and growth mode, which will be discussed later. Further, due to the uniformly mixed 60° in-plane rotation inherent to BTO(111), it is impossible to determine the exact bridging between the MgO and BTO. However, due to the small (less than 1%) difference in the O-O spacings of BTO(111), the range of tensile mismatch (figure 5.41 (b), green) ranges from 4.9% to 5.7%. This may have a significant impact on the interface bridging between the BTO and
MgO. In order to fully characterize the BTO/MgO bridging mechanism, it will be necessary to perform high-resolution, cross-sectional TEM on the BTO/MgO interface. This was not available at the time, but will be included in the recommendations for future work.

5.4.4 Film thickness, temperature, and growth rate effects on BTO/MgO/6H-SiC

In order for the BTO/MgO/6H-SiC heterostructure to be of any practical use, the BTO must be high-quality and of a sufficient thickness (tens to hundreds of nanometers) to obtain usable ferroelectric functionality. The characteristic RHEED pattern of BTO(111) was observed to occur very early on in film deposition, within the first few monolayers of growth. This is due to the onset of mixed 60° in-plane rotation and twinning. Similar the appearance of the 3-D RHEED pattern observed with thick MgO, real-time monitoring of the BTO RHEED pattern revealed evidence of a smooth wetting layer during the nucleation and initial stages of film growth. However, unlike the gradual 2-D to 3-D RHEED transition for the MgO system, the transition in the BTO system was very abrupt, occurring between 1 and 3 nm (figure 5.42 (a) and (b)). Figure 5.42 illustrates the sudden transition form a smooth streaky RHEED pattern to the 3-D transmission pattern and the corresponding surface morphologies. All BTO films were deposited at 650 °C at a growth rate of 0.5 nm/min.
Figure 5.42: AFM and RHEED characterization of BTO deposited on MgO/6H-SiC at 650 °C at a rate of 0.5 nm/min [49]. The images correspond to different BTO thicknesses of: a) 1 nm, b) 3 nm, c) 10 nm, and d) 60 nm.

The nucleation and initial growth (up to 1 nm) of BTO(111) on MgO(111)/6H-SiC(0001) maintains the macroscopic conformal features of the stepped surface of the underlying 6H-SiC surface. At a thickness of 1 nm, the corresponding RHEED pattern is streaky and characteristic of a smooth, layered surface. With an RMS surface roughness of 0.46 nm, the 1 nm BTO film is very similar in morphology to both the 6H-SiC and MgO(111) where the RMS roughness is dominated by the steps. The smooth nucleation and wetting of BTO on the MgO surface may be due to the initial formation of the oxygen bridge between the MgO and BTO. This bridging mechanism could result in a smooth uniform initial layer of BTO before the onset of the inherent 60° in-plane rotation and twinning, which is indicated by the spotty, transmission dominated RHEED pattern (figure 5.42 (b) – (d)).

At a BTO film thickness of 3 nm (figure 5.42 (b)), the transmission dominated 3-D RHEED pattern characteristic of the mixed 60° in-plane rotation and twinning is
obtained. The corresponding AFM data indicate the loss in macroscopic conformity, but maintenance of the smooth (RMS 0.50 ± 0.03 nm) surface. The stepped surface morphology that has previously dominated the surface characterization remains faint, but no longer contributes to the surface roughness measurement. Therefore, the increase in roughness from 0.46 ± 0.02 nm to 0.50 ± 0.03 nm is relatively significant and a result of actual surface features.

As the film thickness was increased further to 10 nm and 60 nm (figure 5.42 (c) and (d), respectively), the surface roughness and 3-D features became more apparent by AFM. Although there is an increase in 3-D features between the 3 nm and 10 nm BTO films, the corresponding RHEED patterns are very similar. This indicates that the transmission dominated RHEED pattern of BTO(111) occurs even for a relatively smooth surface (RMS = 0.50 ± 0.03 nm, figure 5.42 (b)) with less defined 3-D features. The characteristic, transmission dominated RHEED pattern of BTO(111) remains for the duration of BTO growth (up to 60 nm), indicating a 3-D growth mode that results in non-ideal surface morphology for subsequent functional oxide integration.

The diminished RHEED pattern that is associated with the 60 nm BTO film (figure 5.42 (d)) is due to less ordered grains than the 10 nm BTO film (figure 5.42 (c)) with some random rotations (i.e. other rotations in addition to the inherent 60° in-plane rotations). This would result in an attenuation of the crystalline 3-D pattern and a slight increase in the formation of polycrystalline diffraction rings. This is observed in figure 5.42 (d), by the diminished intensity and spherical elongation of the diffraction spots. Continued deposition of BTO at 650 °C beyond 60 nm, resulted in a gradual transition to a polycrystalline film. The increase in polycrystallinity is due to a lack or ordered in-
plane rotation within the BTO film. This same random in-plane rotation was observed for MgO on 6H-SiC (figure 5.21). Maintaining single crystalline BTO will be necessary for promoting the subsequent heteroepitaxy of hexagonal BaM.

Because BTO is a ferroelectric, there is a minimum grain size in which the ferroelectric properties are maintained. Below this size, the BTO becomes paraelectric. Deng, et al. [37] reported ferroelectric properties for BTO grain ~20 nm in size and films 4 nm thick. In order to ensure that the grain size is large enough to maintain ferroelectric properties as well as maintain crystallinity, the deposition conditions need to be optimized to maximize film grain size while maintaining a smooth surface for abrupt interface integration of continued heteroepitaxial integration.

Because of increased surface mobility, it was hypothesized that depositing BTO at higher substrate temperatures would help maintain film crystallinity for extended thicknesses and increase grain size. An increase in surface mobility would result in larger and fewer nucleation sites. When BTO was deposited under the same flux conditions, but an increased substrate temperature of 750 °C, the morphology of the resulting BTO consisted of much larger grains, with increased surface roughness, but the same characteristic 3-D RHEED pattern. Figure 5.43 illustrates the effect of substrate temperature on the film morphology by comparing the AFM images and RHEED patterns for films grown under identical conditions except for substrate temperature.
Figure 5.43: AFM and RHEED characterization of 60 nm BTO(111) deposited on MgO/6H-SiC at 650 °C (a) and 750 °C (b). The increase in substrate temperature increased surface mobility resulting in larger and fewer nucleation sites [49].

Both BTO films presented in figure 5.43 are approximately 60 nm thick. As expected, increasing the deposition temperature resulted in the nucleation and growth of much larger grains (average size of 75 nm). The characteristic RHEED pattern of single crystalline BTO(111) remained sharp up to 60 nm when deposited at 750 °C, indicating improved control over the random in-plane rotation that is responsible for onset of polycrystallinity. However, the larger grains associated with BTO growth at 750 °C (figure 5.43 (b)) resulted in an increase in surface roughness from 0.73 ± 0.05 nm (figure 5.43 (a)) for BTO at 650 °C to 1.39 ± 0.08 nm. The increase in grain size could help ensure that the BTO film maintained ferroelectric properties, but the increase in surface roughness is detrimental to the eventual integration of a multifunctional and multiferroic layered structure. Therefore, further refinement of the BTO processing conditions was required in order to obtain a smooth, crystalline BTO film that was sufficiently thick.

Besides substrate temperature, other processing variables that were varied in order to determine their relative impact of growth mechanisms and hence film composition and morphology were flux species (O₂ vs. O) and growth rate. Preliminary investigations
revealed that increasing the atomic oxygen content by increasing the power to the remote oxygen atom source, and thus OED reading, had no impact on the resulting film morphology. Increasing the relative amount of atomic oxygen from an OED reading of 35 mV to 125 mV resulted in an increase in TiO$_2$ formation and a TiO$_2$ rich BTO film, as determined by the Ti2p photoelectron peak from XPS. This is most likely due to the preferred oxidation reaction of TiO$_2$ (-888.8 kJ/mol) compared to BaO (-520.3 kJ/mol).

In order to account for the impact of atomic oxygen on the change in film chemistry, the Ba flux had to be increased accordingly. Once the chemistry was reestablished, no variation was observed in the film morphology or crystal structure. This indicates that the growth mechanism of BTO is not simply dependent on the Ti and Ba flux (or flux ratio), but also the relative amount of available atomic oxygen. It is possible that under lower O:O$_2$ (35 mV) conditions, the formation of TiO$_2$ is limited by the availability of atomic oxygen, but balanced with the formation of BaO. As the O:O$_2$ is increased (to 125 mV), the higher reactivity of TiO$_2$ relative to BaO results in an imbalance in the individual oxidation rates of Ti and Ba, further resulting in a TiO$_2$ rich BTO film.

When the individual fluxes were increased to balance the changes in O versus O$_2$ content, this produced an increase in growth rate, and the resulting BTO morphology was greatly improved. At a substrate temperature of 650 °C, the growth rate of BTO was doubled from 0.5 nm/min to 1 nm/min. Figure 5.44 compares 60 nm BTO(111) deposited at 0.5 nm/min (35 mV) and 1.0 nm/min (125 mV) and illustrates the improved surface morphology (AFM) and crystal structure (RHEED) obtained at the higher growth rate and O:O$_2$. 
Figure 5.44: AFM and RHEED characterization of 60 nm BTO(111) deposited at; a) 0.5 nm/min and 35 mV oxygen plasma, and b) 1.0 nm/min and 125 mV oxygen plasma. The increase in growth rate is due to the increase in TiO$_2$ formation at the increased oxygen plasma, and appropriately increasing the Ba flux to reestablish stoichiometry.

When BTO was deposited at the increased growth rate of 1.0 nm/min (figure 5.44 (b)), the resulting film morphology became smoother (RMS $0.48 \pm 0.03$ nm versus $0.73 \pm 0.05$ nm) and conformal to the underlying stepped surface of the 6H-SiC. The macroscopic stepped surface was maintained for films in excess of 100 nm, and the 2-D growth mode transition to 3-D grains was delayed for thicknesses up to 300 nm. The improved 2-D growth mode of BTO(111) is likely due to the increase in available oxygen during the nucleation and growth of BTO, which allows for the increased oxidation rate of TiO$_2$ and BaO. This is similar to the oxygen effect that was observed for 2-D growth of MgO (section 5.2.4).

Although the smooth, stepped surface of the 60 nm BTO film is preferred for the eventual integration into a multifunctional and multiferroic heterostructure, the thickness of the BTO must be further increased to >100 nm in order to obtain sufficiently high ferroelectric properties. This is due to configuration limitations in the P-E hysteresis
looper that was typically used to characterize ferroelectric properties of bulk ferroelectric or films in excess of 500 nm. With the increased growth rate, high-quality, conformal BTO(111) was grown to a thickness of 300 nm in order to characterize the ferroelectric properties of the BTO/MgO/6H-SiC structure. Electrical characterization will be discussed in the following section.

The nature of BTO, as well as other tetragonal perovskites, results in an inherently twinned structure when grown in the (111) orientation. Similar to the MgO growth mechanism presented previously, BTO appears to follow the same Stranski-Krastanov growth mode as MgO, where there is an initial 2-D layer-by-layer growth (up to 1 nm) followed by a transition to a 3-D growth mode, as characterized by RHEED. The 3-D surface morphology could be controlled and varied by adjusting substrate temperature, O:O\textsubscript{2} ratio, and growth rate. However, the transition to a 3-D growth mode and the onset of 3-D features (AFM and RHEED) appears unavoidable.

5.5 Electrical characterization of BTO/MgO/6H-SiC

Although the ferroelectric properties of (001) oriented BTO are preferred over the (111) orientation, the pseudo-hexagonal structure of the (111) orientation can be used for the subsequent integration of hexagonal ferrites (BaM) into a multifunctional heterostructure. The first step in evaluating the practicality of BTO(111) for use in a multifunctional heterostructure is the characterization of its ferroelectric properties. Ferroelectricity is a result of a spontaneous and remnant dipole polarization in the BTO crystal lattice. The physical displacement of the atoms results in an electric potential across the material. This dipole moment is theoretically maximized in the c-axis or (001)
orientation of BTO. However, measurable polarization can still occur in the (111) direction.

To characterize the ferroelectric properties of the BTO(111)/MgO(111)/6H-SiC(0001) structure, two techniques were employed. The first was a qualitative measure of the electric domains (electric force microscopy, EFM) and the second was a quantitative measure of the polarization (polarization-electric field hysteresis, P-E).

5.5.1 Electric force microscopy

EFM characterization was performed on a 60 nm BTO(111) deposited at 650 °C at a growth rate of 1 nm/min. The resulting BTO morphology was a smooth (RMS = 0.48 ± 0.03 nm) stepped surface. Figure 5.45 illustrates the qualitative EFM characterization that was collected at a tip offset height (Δz) or 25 nm and various bias voltages of -10 V, -5 V, 0 V, 5 V, and 10 V.

![EFM characterization of 60 nm BTO(111) deposited on MgO/6H-SiC. a) morphology of BTO consists of stepped surface conformal to the underlying 6H-SiC, b) EFM with -10 V bias, c) EFM with a -5 V bias, d) EFM with 0 V bias, e) EFM with 5 V bias, f) EFM with 10 V bias.](image)

* For all micrographs (1 μm²) z-scale: 0 – 70 a.u.
Δz = 25 nm

Bias: -10 V → +10 V

**Figure 5.45**: EFM characterization of 60 nm BTO(111) deposited on MgO/6H-SiC. a) morphology of BTO consists of stepped surface conformal to the underlying 6H-SiC, b) EFM with -10 V bias, c) EFM with a -5 V bias, d) EFM with 0 V bias, e)
EFM with 5 V bias, f) EFM with 10 V bias. For all EFM images, the z-scale was fixed at 0 – 70 a.u. and a tip offset ($\Delta z$) of 25 nm.

From the initial trace across the surface, the resulting morphology consists of a stepped surface (figure 5.45 (a)) as expected and discussed previously for these film growth conditions. During the retrace, different voltage biases were applied and run sequentially from -10 V to +10 V in intervals of 5 V. As illustrated in figure 5.45, at the higher applied biases (figure 5.45 (b) at -10 V and figure 5.45 (f) at +10 V) there is evidence of a stripped domain that appears to follow the stepped morphology of the AFM image. As the bias is reduced to -5 V and +5 V, (figure 5.45 (c) and (e), respectively) the clarity and resolution of the stripped domains begins to fade. This is due to the reduced electrostatic interaction between the remnant domain charge of the BTO film and the lower bias of the scanning probe. Further, when the bias is completely removed, there is no evidence of domains. This is due to the absence of any charged interaction between the BTO film and scanning probe. The absence of any features also indicates that the technique is working properly by maintaining a fixed distance ($\Delta z = 25$ nm) from the surface and subtracting the topology from each retrace scan.

When the scanning probe is biased positively it will be attracted to a negatively polarized domain. When the bias is reversed, the tip will be repelled from the same negatively polarized domain. The series of EFM scans indicates the presence of striped BTO domain features. That is, the dipole moments of BTO(111) film form an alternating positive-negative structure that corresponds to the stepped surface morphology of the film. The dipole moments are static and make up the striped features observed in figure 5.45 (b) – (f). These domains become more pronounced as the voltage bias between the
scanning probe and sample is increased. If the series of images identify actual BTO domains, then the images collected at -10 V and +10 V biases should be inverse images of each other.

Visual inspection of the EFM images is inadequate for characterizing the deflection inversion. In order to more accurately characterize the inversion, a line profile was performed through the Q Port SPM Analysis Software v.1.0.0. A line profile was manually selected and automatically superimposed onto the series of EFM images. By fixing a line in the software, the precise position of the displayed line profile was the same for each scan. Figure 5.46 represents the line profile that was performed for the EFM scans collected at voltage biases of -10 V (blue) and +10 V (red).

**Figure 5.46**: Line profile scans of BTO(111) comparing the domain structure at bias voltages of +10 V (red) and -10 V (blue). Because the BTO domains are static, opposite bias voltages should result in inverse line profiles.

The precise position of the line profiles in figure 5.46 is the same for both images and is held constant by the software used for data processing. The inset arrows illustrate
the deflection inversion when opposite tip biases are applied. Although the deflection inversion is not well defined across the entire line scan, it does demonstrate that the EFM scans are a qualitative characterization of the stripped domains within the BTO(111) film. Even though the observed polarized domains are not well defined and uniform across the entire scan area, their presence does indicate that the BTO is ferroelectric. Since all ferroelectric materials are inherently piezoelectric, the properties of the BTO suggest the film can be optimized and integrated into a BaM/BTO/MgO/6H-SiC heterostructure with magnetoelectric and magnetoelastic properties.

The striped domain features follow the stepped morphology of the BTO film. This is likely due to the formation of natural grain boundaries that form vertically along each step edge. Although the lattice matching and epitaxy have been addressed for the BTO/MgO/6H-SiC interfaces, there still remains a mismatch within the BTO film itself. This mismatch occurs normal to the surface along the step edges. It is possible that the vertical mismatch formed along the step edge is responsible for the alternating domain polarization from step to step, due to the discontinuity on the horizontal atomic positioning. A schematic representation of the grain boundary formation and mismatch is illustrated in figure 5.47, where there is a represented discontinuity within the horizontal lattice fringes of the oxide film.
Figure 5.47: Schematic representation of the horizontal discontinuity (vertical mismatch) for oxide integration of 6H-SiC that results from the different out-of-plane lattice spacing between the 6H-SiC, MgO, and BTO.

Figure 5.47 schematically represents a horizontal discontinuity that is expected for both MgO/6H-SiC and BTO/MgO, resulting in a vertical, out-of-plane mismatch. This discontinuity and mismatch is due to the difference in out-of-plane lattice spacing between 6H-SiC, MgO, and BTO. The expected vertical offset between horizontal atomic planes for MgO/6H-SiC is \(~0.44\) Å. Each horizontal atomic plane for MgO(111) is \(~2.43\) Å, which corresponds to a vertical mismatch of \(~18\)% for BTO/MgO, the expected vertical offset is \(~0.68\) Å. Each horizontal atomic planes for BTO(111) is \(~2.32\) Å, which corresponds to a vertical mismatch of \(~30\)% . Note that these calculations assume a perfect 2-D layer-by-layer structure and incorporate the preservation of a 15 Å step height (one unit cell height of 6H-SiC). Based on the large vertical mismatch within the BTO horizontal planes, it is possible that the inherent grain boundaries that form along the step edges are responsible for the observed stripped domain structure.
5.5.2 P-E hysteresis characterization

P-E hysteresis loops were measured using a Radiant Technologies, Inc. Precision LC Materials Analyzer in the Center for Microwave Magnetic Materials and Integrated Circuits at Northeastern University. Accurate film thickness and contact area are necessary for precise quantification of the ferroelectric (polarization) properties. Although the actual film thickness was not known, the thickness was estimated based on a four point growth calibration using substrate signal attenuation in XPS. Similar growth calibrations with MgO were characterized by TEM and confirmed that the actual MgO film thickness was within ±10% of the estimated film thickness. Therefore, it was assumed that the BTO film thickness is 300 ± 30 nm thick. The error associated with thickness has been considered throughout the characterization of the ferroelectric properties of the BTO(111) film. The electric field values reported, which are dependent on film thickness, represent the values associated with a thickness of 300 nm. Conveniently, the ±10% thickness error corresponds to a ±10% error for all reported applied field values.

For P-E hysteresis measurements, a top contact of Cu with a diameter of 1.5 mm was sputtered onto the BTO through a shadow mask. The bottom contact was fabricated by scratching the bottom the 6H-SiC with a diamond tip scribe and using an InGa eutectic alloy to create an ohmic contact, similar to the process used for C-V characterization of MgO/6H-SiC capacitors (section 5.3.1). P-E hysteresis was performed at various switching frequencies ranging from 0.01 kHz up to 1 kHz. Sweeping voltage
was applied starting at zero volts, sweeping to positive voltage, sweeping to negative volts, and then back to zero volts.

The P-E hysteresis loops for 300 nm BTO(111) on MgO/6H-SiC is illustrated in figure 5.48 and was collected at a frequency of 0.3 kHz. As an electric field is applied, the ferroelectric domains within the BTO begin to align, resulting in an increase in polarization. Therefore as the applied field is swept towards a positive bias, the dipole moments align vertically towards the Cu top contact. When the bias is reversed and a negative electric field is applied, the dipole moments of the BTO align vertically in the opposite direction. However, at a negative bias, the measured polarization is not representative of the ferroelectric BTO, but rather the dielectric properties of the 6H-SiC. A schematic representation of the structure is also included. The initial polarization offset is due to an initial voltage soak for 100 ms, per standard procedure in order to initially polarize the domains.

**Figure 5.48:** a) P-E hysteresis characterization of 300 nm BTO(111) on MgO/6H-SiC. At positive electric field, the polarization is characteristic of ferroelectric BTO, while the negative electric field is characteristic of the dielectric properties of 6H-SiC.
b) Close-up of the onset of leakage. The black solid line exaggerates the effect. c) Schematic of BTO/MgO/6H-SiC heterostructure.

The basic principle behind P-E hysteresis is as follows. First, a voltage is applied across the structure and held for a fixed duration. For the case in figure 5.48, this soak time was 100 ms. The voltage is then removed and the surface charge is measured at the top contact. The higher the polarization potential at the contact/film (or contact/substrate) interface, the higher the resulting surface charge. This process is repeated for every voltage step increment up to the manually defined voltage setpoint. For example, if the setpoint voltage is 10 V with increments of 0.1 V/step, then there are \((4\times10)/0.1 = 400\) steps. The multiple of 4 comes from \(0 \rightarrow +10 \rightarrow -10 \rightarrow 0\).

The P-E hysteresis loops in the figure 5.48 are asymmetric in that the electric field width is larger for the positive voltage bias (ferroelectric BTO contribution) relative to the negative voltage bias (dielectric SiC contribution). The asymmetry is due in part to the different contacts that were used. One contact was a direct ohmic contact between the Cu pad and the BTO film. However, the second contact was essentially a MgO/SiC/InGa contact. Although the InGa/SiC contact is ohmic, the MgO/SiC structure essentially acts as a dielectric layer that cannot effectively store a charge. This is observed in the linear and symmetric shape observed in the negative applied field for all applied voltage biases. Therefore, the only region that is characteristic of ferroelectric BTO is in the positive applied electric field region.

Typical hysteresis loops for ferroelectric materials have a distinct “S” shape characteristic of the polarization of the ferroelectric domains saturating, and shown in figure 2.7 in section 2.4.1. In the hysteresis loop representative of the BTO/MgO/6H-SiC
structure, there is an apparent lack of saturation, which is also characteristic of an additional dielectric response. For a dielectric, the apparent polarization will continue to increase with applied field and never saturate. However, for a ferroelectric, if too high of an electric field is applied, the polarization begins to drop off as a result of leakage and electrical breakdown. This effect can be partially observed in figure 5.48 (b) for the 10 V hysteresis loop (orange) where the final polarization of 4.3 μC/cm² at an applied field of 550 kV/cm is slightly less than the polarization of 4.5 μC/cm² at 450 kV/cm. This slight rounding effect is characteristic of a combination of leakage current and a dielectric contribution, most likely resulting from the MgO/6H-SiC. Table 5.6 lists the extracted values for maximum polarization (P_max), remnant polarization (P_rem), and coercive field (C_E) that were obtained for the four applied voltages of 7.5 V, 8.5 V, 9.5 V, and 10 V. The maximum polarization corresponds to the maximum number of ferroelectric domains that aligned when an electric field was applied. Remnant polarization corresponds to the number of ferroelectric domains that remained aligned when the applied field was removed. Coercive field corresponds to the applied field necessary to depolarize all remnant domains.

**Table 5.6:** List of important ferroelectric properties that were extracted from P-E hysteresis characterization of BTO/MgO/6H-SiC at various voltage biases.

<table>
<thead>
<tr>
<th>Applied Voltage (V)</th>
<th>P_max (μC/cm²)</th>
<th>P_rem (μC/cm²)</th>
<th>C_E (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>3.5</td>
<td>1.0</td>
<td>110</td>
</tr>
<tr>
<td>8.5</td>
<td>4.0</td>
<td>1.2</td>
<td>139</td>
</tr>
<tr>
<td>9.5</td>
<td>4.3</td>
<td>1.4</td>
<td>169</td>
</tr>
<tr>
<td>10</td>
<td>4.5</td>
<td>1.5</td>
<td>179</td>
</tr>
</tbody>
</table>

In order to validate the functionality of the BTO/MgO/6H-SiC structure, it is necessary to compare the electrical properties that were measured by P-E hysteresis with
the electrical properties of BTO(111) reported in literature, compiled in table 5.7. The polarization and coercive properties of the BTO/MgO/6H-SiC structure are similar to the properties of BTO(111) reported in literature [44, 45, 101], indicating that the ferroelectric properties of the structure represented in figure 5.48 are comparable to the current functionality performance of BTO(111). However, it is important to note that the structures in literature are not integrated into functioning substrates and can therefore not be considered for device applications.

Table 5.7: Comparison of ferroelectric properties of the BTO/MgO/6H-SiC structure with ferroelectric properties of BTO(111) reported in literature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( P_{\text{rem}} ) (( \mu \text{C/cm}^2 ))</th>
<th>( C_E ) (kV/cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTO/MgO/6H-SiC</td>
<td>1.5</td>
<td>179</td>
<td>N/A</td>
</tr>
<tr>
<td>BTO/LNO/STO</td>
<td>0.1</td>
<td>89.6</td>
<td>[45]</td>
</tr>
<tr>
<td>BTO/Pt/TiO(_2)/SiO(_2)/Si</td>
<td>1.87</td>
<td>150</td>
<td>[101]</td>
</tr>
<tr>
<td>BTO/Nichrome*</td>
<td>5.4</td>
<td>200</td>
<td>[101]</td>
</tr>
</tbody>
</table>

* Nichrome is brand name for a nickel-chromium alloy (Ni\(_{0.8}\)Cr\(_{0.2}\))

As mentioned previously, at high applied fields (figure 5.48 (b)), there is an apparent onset of leakage. The electrical properties of the MgO/SiC structure can accommodate significantly higher electric fields than the BTO due to the dielectric properties of MgO and semiconducting properties of 6H-SiC. As a result, the observed leakage effect will appear before any saturation effects. Therefore, P-E hysteresis can was only performed at electric fields that did not result in BTO leakage. However, once leakage occurs, the structure and ferroelectric properties of the BTO collapse. Therefore, given the limited number of sputtered contact (two), P-E characterization was performed at voltage below the breakdown of the BTO structure prior to leakage measurements.

Leakage current is a measure of how much current can flow through the structures under a given applied field. Leakage measurements were collected independent of
frequency, but rather the current flow was measured after a 1000 ms soak at each applied voltage. This is a limitation of the equipment where it is not possible to adjust the frequency of leakage measurements. Although indication of leakage effects began at applied fields around 500 kV/cm (figure 5.48 (b)), they were not distinct until ~700 kV/cm. Figure 5.49 illustrates a more accurate evaluation of the leakage current and breakdown voltage. The leakage current is determined from this figure as the sudden increase in current flow. The voltage at which this occurs is referred to as the breakdown voltage and is designated by the red dashed line at ~700 kV/cm. The negative applied field corresponds to the leakage through the 6H-SiC and is not characteristic of the BTO film.

Figure 5.49: Leakage measurement for BTO/MgO/6H-SiC. The breakdown voltage (red dashed line) corresponds to an applied field of ~700 kV/cm.

From figure 5.49 the leakage effects that contribute to the P-E measurements in figure 5.48 can be determined across the entire range of applied electric fields of interest
(0 – 550 kV/cm). Leakage contribution is important to consider in order to quantify the ferroelectric properties of the BTO(111). This is because ferroelectric hysteresis circuits do not directly measure the polarization of the material. Rather, they measure the remnant switched charge \( Q \) after the applied voltage bias has been removed. For an ideal, insulating, ferroelectric, the charge is defined by the following equation.

\[
Q = 2P_r A \quad \text{Eqn. 5.9}
\]

Where:
- \( Q \) = measured switched charge
- \( P_r \) = remnant polarization
- \( A \) = electrode area

However, for most real circuits, there is an additional term that accounts for leakage current. This is seen in equation 5.10.

\[
Q = 2P_r A + \sigma E_a t \quad \text{Eqn. 5.10}
\]

Where:
- \( \sigma \) = electrical conductivity
- \( E_a \) = applied field
- \( t \) = measuring time

The addition of this second term is due to the leakage current that the material experiences when an electric field is applied. Therefore, it is essential to account for this additional loss when trying to understand the true ferroelectric contribution to the P-E hysteresis (figure 5.48). It is important to note that all the values presented in tables 5.6 and 5.7, including those reported in literature [45, 101], are representative of hysteresis loops that resemble a lossy dielectric and do not take into account the leakage current. It is the presence of this dielectric component that is responsible for and is the dominating factor of the hysteresis loop shape, and hence the values reported for the remnant
polarization, maximum polarization, and coercive field are not accurate representations of the actual ferroelectric contribution.

In order to characterize the true ferroelectric properties of the BTO/MgO/6H-SiC structure, it is necessary to separate the dielectric contribution (MgO and SiC) from the ferroelectric contribution (BTO). Figure 5.50 represents the hysteresis loop for the 300 nm BTO(111) film at a bias voltage of 10 V after the leakage current has been removed. The represented hysteresis curve represents only the ferroelectric contribution of the BTO(111) film. Unlike the hysteresis represented in figure 5.48, the ferroelectric contribution resembles more of an “S” shape (figure 2.7), which is characteristic of ferroelectric saturation. However, there is a distinct narrowing of the coercive field and lowering of the remnant polarization. This is due to the poor ferroelectric nature of (111) oriented BTO.

Figure 5.50: P-E hysteresis illustrating only the ferroelectric contribution of the BTO/MgO/6H-SiC structure. The positive applied field corresponds to polarization measurements obtained on the top Cu electrode. The negative applied field remains characteristic of MgO/6H-SiC.
Reevaluation of the ferroelectric properties with the dielectric losses removed reveals a much lower remnant polarization (~0.13 μC/cm²) and coercive field (~20 kV/cm). However, the overall shape of the hysteresis loop is more characteristic of a ferroelectric material, as indicated by the “S” shape. This characteristic shape was not present for applied voltages below 10 V (figure 5.48), indicating insufficient applied fields to saturate the ferroelectric domains.

Further, by removing the leakage current and dielectric contributions, there is evidence of polarization saturation that occurs when the applied field is greater than ~600 kV/cm as seen by plateau region at the higher applied fields. Figure 5.51 illustrates the $P_{\text{max}}$ for the 300 nm BTO(111) film at different applied fields and switching frequencies of 0.3 kHz (blue) and 0.02 kHz (red). The figure shows a saturated polarization of ~4.7 μC/cm² that is independent of frequency. The lack of frequency dependence indicates that the observed ferroelectric contributions are accurate representations of the ferroelectric BTO. Note that figure 5.51 is different from figures 5.48 and 5.50 in the sense that the polarization is not measured as the applied field is not swept. Rather, the figure represents the polarization that was measured under the specific applied field. Therefore, there is no hysteresis behavior.
Figure 5.51: Determination of saturated polarization of BTO(111) deposited on MgO/6H-SiC after the removal of all dielectric and leakage contributions.

If the BTO/MgO/6H-SiC heterostructure were a true dielectric, then varying the switching frequency should have a significant impact of the dielectric loss. The similarities in the $P_{\text{max}}$ values between the two switching frequencies in figure 5.51, along with the apparent saturation around 4.7 $\mu$C/cm$^2$, indicate the adjusted polarization values are characteristic of the ferroelectric component of the BTO/MgO/6H-SiC heterostructure. Although the adjusted remnant and coercive values are significantly lower than the non-adjusted values, as well as the values reported in literature, they do represent only the ferroelectric properties. The literature values that are presented in table 5.7 were obtained from BTO(111) films that were deposited on conducting, non-functional substrates and do not account for leakage effects. Therefore, the characterization of these literature structures can only be used as a general reference for BTO(111) properties and not a device structure reference. The experimental values obtained for the BTO/MgO/6H-SiC structure are characteristic of the entire structure, not
just BTO(111), and the BTO(111) was integrated with a functional semiconductor substrate, rather than a metal. Thus direct comparison with literature values is problematic. However, the successful demonstration of measurable and quantifiable ferroelectric properties of the BTO/MgO/6H-SiC heterostructure contributes to the realization of a next-generation, multifunctional heterostructure on 6H-SiC.

5.6 Multifunctional oxide heterostructure on 6H-SiC

Although the properties of (111) oriented ferroelectrics are inherently poor relative to (001) oriented ferroelectrics, the pseudo-hexagonal structure of the (111) surface can be utilized to integrate hexagonal ferrites into a multifunctional, multiferroic heterostructure where the properties can be effective enough to be utilized in next generation devices. In order to test the feasibility and concept of a multilayered functional oxide heterostructure, barium hexaferrite (BaM, BaFe$_{12}$O$_{19}$) was deposited by MBE on the BTO/MgO/6H-SiC structure.

BaM is a hexagonal, ferrimagnetic material with a magnetoplumbite crystal structure, high magnetic anisotropy (17 kOe), high permeability, and high susceptibility. These intrinsic properties make BaM an ideal candidate for next-generation microwave devices and multilayered heterostructure integration. However in order to optimize the magnetic properties of BaM in the multilayered heterostructure, it is necessary to obtain BaM(001) out of plane.

BTO(111) was initially grown to a thickness of ~60 nm at 650 °C and a growth rate of 1 nm/min on MgO/6H-SiC. Under these conditions, the resulting BTO morphology consisted of the smooth (RMS = 0.48 ± 0.03 nm), stepped surface. The
thinner BTO layer was chosen in order to maintain a 2-D surface in which to deposit the BaM. BaM was then deposited by MBE at 750 °C at a growth rate of ~1.2 nm/min to a thickness of ~170 nm. The oxygen was supplied at a background pressure of 7.0×10⁻⁶ Torr, a forward plasma power of 200 W, and a corresponding OED reading of 320 mV. These processing conditions were chosen based on preliminary deposition studies of BaM grown directly on MgO(111) substrates and MgO/6H-SiC, which resulted in crystalline, stoichiometric BaM.

Figure 5.52: Surface morphology characterization by AFM of; a) ferroelectric BTO(111) template layer, b) subsequent BaM layer, and c) zoomed in image of BaM surface.

Figure 5.52 illustrates the AFM characterization of a representative BTO morphology and the actual BaM morphology. AMF characterization of the BaM/BTO/MgO/6H-SiC heterostructure indicates a distinct change in surface morphology between the BTO/MgO/6H-SiC (figure 5.52 (a)) and the BaM (figure 5.52 (b)). The BTO(111) template layer consist of a smooth (RMS = 0.41 ± 0.04 nm) stepped surface, while the BaM surface is significantly more rough (RMS = 3.05 ± 0.15 nm) with
no preservation of the underlying stepped surface. The resulting morphology of the BaM consisted of asymmetric 3-D features approximately 8 nm high.

RHEED and XRD characterization of the BaM crystal structure revealed a polycrystalline film with mixed orientations. The mixed orientations were observed by the presence of the randomly oriented (107) diffraction peak (not shown). The polycrystallinity is mostly likely a result of the poor epitaxy alignment between the BaM and BTO lattice. The in-plane O-to-O spacing of BTO(111) (~2.83 Å) compared to BaM(0001) (2.94 Å), results in a lattice mismatch of ~3.7% in compression. This is different from the tensile film strain in both the MgO/6H-SiC and the BTO/MgO/6H-SiC structures based on the oxygen bridge heteroepitaxy approach. Although the compressive mismatch between the BaM and BTO is similar in magnitude to the tensile strains in the BTO/MgO (5.3 % tension) and MgO/6H-SiC (3.3% tension) alignments, it is possible that the nature of the BaM(0001) epitaxy is promoted with minimal tensile mismatch.

Research has shown that high quality BaM could be grown by PLD on MBE grown MgO/6H-SiC, where the lattice mismatch between BaM and MgO is 1.4% in tension [47]. Further, other research groups have deposited BaM on BST(100)/MgO(100) by PLD [17-19]. BST and BTO have identical crystal structures and very similar lattice spacing and therefore similar mismatch between these ferroelectrics and the BaM. Although Heindl, et al. [17] report that that the BaM was only (001) oriented, the discussion of the AFM and VSM characterization contradicts this claim. The reported AFM and VSM indicate an acicular crystal structure (needle-like with random orientation) and no magnetic anisotropy. This is very similar to the experimental results
illustrated in figures 5.52 and 5.53 where there is no evidence of a hexagonal crystal structure or preferred anisotropy.

**Figure 5.53**: VSM characterization of BaM/BTO/MgO/6H-SiC heterostructure. Magnetization in the parallel (red) and perpendicular (blue) directions are similar in shape, indicating a lack of uniaxial anisotropy.

VSM characterization of the BaM/BTO/MgO/6H-SiC structure in figure 5.53 indicates that there is no magnetic anisotropy within the BaM film. This is seen by the similar shape in hysteresis for the perpendicular magnetization (blue line) and parallel magnetization (red line). Magnetic anisotropy is defined as a directional dependence of a material’s magnetic properties. Single crystalline BaM has a high magnetic anisotropy in the [001] direction. An ideal BaM film would be (001) oriented and have a high magnetic anisotropy perpendicular to the film surface. This would result in a distinct, well defined S-shape in the perpendicular VSM hysteresis loop. Likewise, the parallel magnetization would result in a diagonal, straight line. In the absence of any well defined anisotropy, which can arise from randomly oriented crystallites, there is little distinction between the magnetization directions.
The combination of AFM, XRD, and VSM characterization of the BaM film integrated on BTO/MgO/6H-SiC shows a polycrystalline BaM film with no preferred orientation and poor magnetic properties. However, the results of the preliminary investigation do indicate that the BaM film does have functional magnetic properties and that there is promise for the integration of a functional oxide, multilayered heterostructure on 6H-SiC. Further investigation and focus is necessary into the specific nucleation and growth mechanisms of BaM on BTO in order to optimize the magnetic properties and functionality of the heterostructure. In addition, further characterization is required to demonstrate any magnetoelectric or magnetoelastic coupling effects between the two functional films.
6.0 Conclusions

The goal of this dissertation was to demonstrate the successful integration and characterization of functional oxides and oxide heterostructures on 6H-SiC. In order for success, specific objectives needed to be completed. These objectives included: effective cleaning and preparation of the starting 6H-SiC surface, heteroepitaxial integration of various functional oxides on the 6H-SiC, integration of multilayered heterostructure, and the characterization of the functional properties of the oxide layers. Each oxide layer needed to be of high quality and have a smooth surface, which would act as an abrupt interface when integrated with the subsequent deposition of an additional functional oxide. The successful demonstration of a multilayered heterostructure on SiC would contribute to the progress towards the development and optimization of a next-generation, multifunctional device.

6H-SiC surface preparation was successfully accomplished by ex-situ hydrogen cleaning in a custom build hydrogen flow furnace. The processing conditions were optimized for both the Si-terminated and C-terminated orientation in order to obtain a reproducible, smooth, surface with no residual scratches or undesired surface contamination. The standard hydrogen cleaning conditions for both orientations was optimized at a flow rate of 11.4 slpm pure H₂, a heating rate of 200 °C/min (5 A every 30 seconds), a temperature around 1700 ± 10 °C, a time of 30 minutes, and a cooling rate of 100 °C/min (2.5 A every 30 seconds). Under these conditions, the resulting 6H-SiC was smooth (RMS < 0.5 nm over 1 μm² area) with a uniformly stepped surface. The resulting steps of the C-terminated orientation were 100 ± 7 nm wide and 1.6 ± 0.2 nm high. The
steps for the Si-terminated orientation were 265 ± 10 nm wide and 1.6 ± 0.2 nm high. The step height is due to the height of a single 6H-SiC unit cell (1.5 nm). After hydrogen cleaning, the C-terminated orientation resulted in a (1×1) structure that was C-H terminated with less than 2 at% residual oxygen contamination. The Si-terminated orientation consisted of a high-quality $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ silicate adlayer reconstruction with a stoichiometry of Si$_3$O$_5$. The silicate adlayer is stable up to 600 °C when heated in vacuum ($\sim$10$^{-9}$ Torr). Although the hydrogen cleaning procedure has been optimized for both the Si-terminated and C-terminated orientations, the majority of oxide growths discussed in this dissertation were deposited on the Si-terminated orientation with the reproducible, high-quality $\sqrt{3}\times\sqrt{3}$ $R30^\circ$ silicate adlayer reconstruction. This was due to the formation of an oxygen bridge between the SiC substrate and oxide films, which aided in the heteroepitaxy of high-quality, single crystalline oxides.

High-quality, single crystalline MgO(111) was successfully deposited on 6H-SiC(0001) by MBE. The MgO was found to have a magnesium absorption controlled growth mechanism. The smooth (RMS < 0.5 nm over a 1 µm$^2$ area), conformal growth mechanism of MgO on 6H-SiC(0001) was attributed to the presence of atomic oxygen at the surface during the nucleation and growth. The surface structure of the MgO films consisted of an OH stabilize (1×1) structure. The conformal morphology of the MgO films was maintained for thicknesses up to 38 nm. However, the inherent nature of MgO resulted in a high twinned structure, the degree of which could be controlled by heating up to 650 °C. The MgO/6H-SiC interface was determined to thermodynamically stable with no interface breakdown at temperatures up to 740 °C in vacuum ($\sim$10$^{-9}$ Torr) for 90 minutes and up to 790 °C in air for 30 minutes. This is important for integration into a
multifunctional heterostructure that requires subsequent deposition temperature as high as 650 °C.

The MgO/6H-SiC band offsets were calculated from XPS measurements of the valence band maximum to be 3.27 eV for the conduction band and 1.50 eV for the valence band. These offsets are comparable to band offsets for similar interfaces between MgO and n-type wide bandgap semiconductors. The large band offsets make the MgO/6H-SiC structure ideal for integration into a MOSFET device. Dielectric and capacitance characterization of the MgO/6H-SiC structure indicated a dielectric constant of ~10, which is typical of bulk single crystalline MgO, and a median breakdown voltage of 12 MV/cm. The large dielectric constant and breakdown voltage make the MgO/6H-SiC structure ideal for next-generation dielectrics and MOSFETs.

Single crystalline MgO(111) has also been proven to be both effective and necessary for the heteroepitaxial integration of tetragonal single crystalline BTO on 6H-SiC(0001). Without the use of the MgO template layer, the resulting BTO was amorphous. Integration of a high-quality, thin (~2 nm) MgO(111) layer between the 6H-SiC(0001) and BTO, resulted in the deposition of single crystalline BTO(111), thus demonstrating the concept of an oxygen bridge and the use of MgO(111) as a heteroepitaxial template.

The high-quality, single crystalline BTO(111) that was integrated on MgO/6H-SiC was shown to have functional ferroelectric properties. EFM revealed the formation of striped domains that align with the stepped structure of the underlying 6H-SiC substrate. The BTO(111) was demonstrated ferroelectric hysteresis with a saturated polarization
around 4.7 µC/cm², a remnant polarization around 0.13 µC/cm², and a coercive field around 20 kV/cm.

Demonstration of a BaM/BTO/MgO/6H-SiC multifunctional heterostructure was fabricated by MBE. The resulting structure has ferroelectric properties from the BTO layer and ferrimagnetic properties from the BaM layer. However, the ferrimagnetic BaM film deposited on the BTO/MgO/6H-SiC structure lacks the high uniaxial anisotropy that makes it an ideal candidate for next-generation microwave devices. No demonstration or characterization of magnetoelectric or magnetoelastic coupling between the BTO and BaM was performed, but will be required for actual multifunctionality of the heterostructure.

This study and conclusions demonstrate the potential for next-generation multifunctional heterostructures fabricated on wide bandgap 6H-SiC. The progress made through this research can be extended beyond the integration of tetragonal BTO on 6H-SiC to include a wide variety of tetragonal perovskite ferroelectrics, through the use of a high-quality, single crystalline MgO(111) template layer. The freedom associated with the effectiveness of the template layer can enable the static and dynamic tuning of next-generation multifunction heterostructure device with essentially endless multifunctional possibilities.
7.0 Recommendations

Throughout the course of the research discussed in this dissertation, there were certain aspects that require further attention. The following section will discuss recommendations towards the continued understanding of interface bonding mechanisms and functional coupling between the multilayers.

The first recommendation is geared towards the improvement of the hydrogen cleaning of the 6H-SiC. Although the custom built hydrogen flow furnace has proven to be an effective and valuable tool for 6H-SiC surface preparation, there remain some shortcomings. First, the lack of integrity and reliability of the Ta boat occasionally results in inadequate cleaning and wasted time. Further, the basic design of the equipment limits the size of the samples to approximately 0.5 cm × 0.5 cm. Although this sample size is sufficient for MBE growth performed in the Interface Engineering Laboratory at Northeastern University, they are often too small for collaborators to use in their systems, which typically require 1 cm × 1 cm samples. As a result, the uniformity and consistency of the surface preparation by hydrogen cleaning is compromised. In order to address the issues of sample size and maintaining reliable thermal contact, it is recommended that the heating component be modified. Rather than use resistive heating by applying current through a Ta boat, the existing furnace should be fitted with an induction heater. This will allow for consistent and uniform heating where the heating elements are less susceptible to corrosion. Further, the induction coils can be designed in an orientation to accommodate any size sample. Figure 7.1 below schematically illustrates the proposed induction coil design.
Figure 7.1: Schematic illustration of two possible induction coil configurations; a) vertical configuration for real time temperature measurement, but restricted H₂ flow, and b) horizontal configuration for unobstructed H₂ flow but restricted temperature measurement. The stand will be made of molybdenum, tantalum, tungsten, or pyrolytic carbon.

Induction heater design considerations were discussed at length with Blade & RF Technologies, LLC regarding the necessary components to meet the temperature and power requirements for successfully cleaning of larger (up to ~ 1 inch in diameter) 6H-SiC substrates. The following equipment was recommended:

Process Technologies Proposal #04-0808 (June 4, 2008)

**Item #1**- One (1) 3kW, water-cooled induction power supply. The power supply is 100% solid state with an output of 3kW at 135-400 kHz and rated for 100% duty cycle. The features are described as follows:

- Maximum Power…………………………..3kW
- Maximum Apparent Power………………..6.6kVA @230V input
- Maximum Power Factor…………………...0.50 @ 230V input
- Duty cycle………………………………….100%
- Maximum Voltage………………………….500Vrms
- Frequency…………………………………135-400kHz
• Minimum Response Time：0.1s³
• Maximum Allowed Off-Time：0.5s
• AC Line-to-line Voltage：208V – 240V ±10%, 50-60Hz.
• Line Current：3.6kVA
• Dimensions:  Length：20.5in  
  Width：11.7in  
  Height：12.7in  
  Weight：43.5 lbs
• Programmable interface with 12 separate heating profiles. Each profile can be programmed with 25 steps. Also included is a RS-485 connection for external monitoring and/or control of the power supply.

Price：$7,700.00
Note: a 5% discount will be offered for University status bringing the cost to $7,315.00

Item 2- Load coils are designed and manufactured to customer specifications as requested and quoted separately after the specifications are received and reviewed.

However, after further discussion, with the vendor, it was recommended that a 5 – 7 kW power supply (for the same price quoted) be considered as well. It was decided that once a purchase order had been placed, test would be conducted to determine the stage material an appropriate power supply.

A second recommendation is to focus time and energy on calibration of the RHEED system. By loading standards with well established and documented lattice spacings, it will be possible to quantitatively charactering the in-plane lattice spacings of the substrates and films. This can be of great importance when considering the effects of interface strain between adjacent functional oxide layers. Further, in the process of calibrating the RHEED system, time should be spent to modify the existing system to allow for real-time growth rate determination. Currently, the high energy electron beam (12 keV) is affected by stray magnetic fields. Although this deflection is minimal, the
slightest deviation in beam intensity can greatly affect the perceived intensity oscillations that are used to accurately determine layer-by-layer growth rates. In order to address this issue, it is recommended that a \( \mu \)-metal shield be inserted along the projected electron beam path. The \( \mu \)-metal shield is composed of a highly magnetically susceptible material that is designed to absorb stray magnetic fields. The addition of this shield will help generate a stable electron beam incident the sample surface.

The third recommendation is focused towards a better understanding of the interface bonding mechanisms between MgO/6\( H \)-SiC and BTO/MgO, and to demonstrate the concept of an oxygen bridge between the multilayers. This can be performed by high resolution TEM characterization of the interface. Although TEM is not capable of imaging oxygen atoms, their presence can be inferred from the surrounding lattices and atomic positioning. Further, electron energy loss spectroscopy (EELS) can be performed across the interfaces to potentially characterize the specific bonding within each oxide layer and the transition across the interface. As an initial probe into this investigation, TEM and EELS characterization of MgO/6\( H \)-SiC was performed through collaboration with Dr. David Muller and Dr. Lena Fitting Kourkoutis at Cornell University. Figure 7.2 illustrates the potential use for TEM and EELS for characterization of the oxygen bonding states at the MgO/6\( H \)-SiC, BTO/MgO, and BaM/BTO interfaces. EELS spectra of O-K (figure 7.2 (b)) and Mg-K (figure 7.2 (c)) are illustrated for an MgO film deposited on 6\( H \)-SiC. The spectra were collected along the inserted red line. Further, EELS spectra of O-K for STO with different oxygen vacancies (\( \delta \)) (figure 7.2 (d)) [156] is also illustrated to demonstrate the potential of EELS for determination of different
oxygen states. This could be of particular interest for determining the presence of an oxygen bridge.

![TEM and EELS characterization](image)

**Figure 7.2:** TEM and EELS characterization can be used to help determine the interface bonding states of the multilayers and the formation of an oxygen bridge. a) TEM of MgO/6H-SiC. The red line represents the EELS analysis location. b) EELS spectra O-K in MgO. c) EELS spectra of Kg-K in MgO. d) EELS spectra of O-K in STO at different oxygen vacancies ($\delta$) [156]. The distinction between O-K spectra may be a useful tool for determination and characterization of an oxygen bridge formation.

In addition to using TEM to characterize the interfaces between the multilayers, it can be a useful tool for characterizing the grain structure of the oxide layers. In particular, when the MgO films were heated to 650 °C, there was an observed 3-D to 2-D transition
in the RHEED patterns. Limitation of AFM prevented quantitative or even qualitative characterization of improved surface smoothing after heating. TEM characterization can aid in determining the how heating the sample affects the crystal structure and surface roughness. It is recommended that several samples be sent for high resolution TEM. These samples should include, but are not limited to; 1) 2 nm MgO grown at 140 °C (standard MgO), 2) 2 nm MgO grown at 140 °C then heated to 650 °C, 3) 2 nm MgO grown at 650 °C, 4) 10 nm MgO grown at 140 °C, 5) 10 nm MgO grown at 140 °C then heated to 650 °C, and 6) 10 nm MgO grown at 650 °C. These six samples should aid in determining the effects of temperature on the crystal structure for both thin (2 nm) and thick (10 nm) MgO films.

Another recommendation for future work is demonstrate the coupling of the functional properties between the ferrimagnetic BaM and ferroelectric BTO. This can be performed in a couple of ways. The first would be to measure the magnetization of the BaM as the BaM/BTO/MgO/6H-SiC heterostructure is ramped over a range of temperatures from -100 °C to 130 °C. Over this temperature range, the BTO will undergo phase changes from rhombohedral-orthorhombic (~ -90 °C), orthorhombic-tetragonal (~ 0 °C), and tetragonal-cubic (~ 120 °C). When the BTO undergoes a phase change, the crystal lattice will distort. If the BaM and BTO are effectively coupled, the distortion of the BTO lattice should induce a strain on the BaM at the interface, which would further affects the magnetization of the BaM. This would demonstrate the successful coupling through a magnetoelastic effect. Similarly, in order to demonstrate magnetoelastic coupling, it is recommended that the magnetization of the BaM be measures as an electric field is applied across the entire heterostructure. The applied field would result in the
polarization of the BTO film. If the BaM and BTO are effectively coupled, then the polarization of the BTO would impact the magnetization of the BaM. However, the magnetoelectric coupling between the BaM and BTO is also a result of magnetoelastic coupling. This is because the ferroelectric BTO is also piezoelectric. Under the applied field, the piezo response of the dipole moment and atomic displacement will induce strain at the BaM/BTO interface and further affect the magnetization of the BaM. This effect is different than the previous recommendation for demonstrating magnetoelastic coupling in the sense that the interface strain will be induced by an applied electric field rather than a phase change.

A final recommendation will be to evaluate the trade-offs between the hexagonal heteroepitaxy versus cubic epitaxy. The major benefits hexagonal epitaxy include; 1) the use of two promising wide bandgap semiconductors (GaN and SiC), which have superior semiconducting properties over traditional Si semiconductors and can be operating at high frequencies, and 2) the use of hexagonal ferrites (BaM), which have high uniaxial magnetic anisotropy. However, hexagonal heteroepitaxy limits the properties of the ferroelectric layer due to the poor ferroelectric properties that are inherent to the pseudo-hexagonal structure of the (111) orientation. In order to evaluate the trade-offs between hexagonal heteroepitaxy and cubic epitaxy, it will be necessary to consider all of the following properties; 1) operating conditions of the device (frequency, power, temperature – SiC or Si), 2) importance of ferroelectric/piezoelectric potential (BTO(001) or BTO(111)), 3) importance of magnetization (BaM, or spinel ferrites like cobalt ferrite or nickel ferrite), and 4) range of dynamic tuning. These properties will be device specific and require careful consideration. However, in order for the realization of next-generation
multifunctional devices, it will be necessary to integrate the multifunctional heterostructure on a wide bandgap semiconductor (hexagonal GaN or SiC) and tune the multilayers to have a wide range of dynamic tunability.
### 8.0 Glossary

#### Characterization Techniques
- AES – Auger electron spectroscopy
- AFM – atomic force microscopy
- ARXPS – angle resolved x-ray photoelectron spectroscopy
- C-V hysteresis – capacitance-voltage hysteresis
- EDS – energy dispersive x-ray spectroscopy; also known as EDAX and EDX
- EELS – electron energy loss spectroscopy
- EFM – electric force microscopy
- GADDS – general area diffraction detection system
- I-V hysteresis – current-voltage hysteresis
- MFM – magnetic force microscopy
- OED – optical emission detector; used to convert photons to a measureable voltage
- P-E hysteresis – polarization-electric field hysteresis
- RHEED – reflection high energy electron diffraction
- SEM – scanning electron microscopy
- TEM – transmission electron microscopy
- USPM – universal scanning probe microscopy
- VSM – vibrating sample microscopy
- XPS – x-ray photoelectron diffraction
- XRD – x-ray diffraction

#### Deposition Equipment
- CVD – chemical vapor deposition; deposition technique
- MBE – molecular beam epitaxy; deposition technique
- MOCVD – metalorganic chemical vapor deposition; deposition technique
- MOMBE – metalorganic molecular beam epitaxy; deposition technique
- PLD – pulsed laser deposition; deposition technique
- Sol-gel – deposition technique
- Sputtering – deposition technique
- UHV – ultra high vacuum

#### Device Applications
- CMOS – complementary metal oxide semiconductor
- FEFET – ferroelectric field effect transistor
- FET – field effect transistor
- MEMS – microelectromechanical systems
- MMIC – monolithic microwave integrated circuit
- MOSFET – metal oxide semiconductor field effect transistor
- NMOS – n-type metal oxide semiconductor
- NVRAM – non-volatile random access memory
- PMOS – p-type metal oxide semiconductor
- RAM – random access memory
**Materials**

3C-SiC – cubic silicon carbide; an indirect wide bandgap semiconductor
4H-SiC – hexagonal silicon carbide; an indirect wide bandgap semiconductor
6H-SiC – hexagonal silicon carbide; an indirect wide bandgap semiconductor
Al2O3 – aluminum oxide (sapphire); a potential next-generation gate oxide
BaM – barium hexaferrite (BaFe12O19); a hexagonal ferrimagnetic
BFO – bismuth ferrite (BiFeO3); a perovskite multiferroic
BTO – barium titanate (BaTiO3); a tetragonal, perovskite ferroelectric and piezoelectric
BST – barium strontium titanate (Ba1-xSrxTiO3); a tetragonal, perovskite ferroelectric and piezoelectric
GaAs – gallium arsenide; a direct bandgap semiconductor
GaN – gallium nitride (hexagonal, wurtzite); a direct wide bandgap semiconductor
KTO – potassium titanate (KTiO3); a perovskite oxide
LAO – lanthanum aluminate (LaAlO3); a perovskite oxide
LSCO – lanthanum strontium cobaltate (La1-xSrxCoO3); a perovskite oxide
MgO – magnesium oxide; a dielectric insulating oxide with rocksalt structure
NFO – nickel ferrite; a ferrimagnetic
PTO – lead titanate (PbTiO3); a tetragonal, perovskite ferroelectric and piezoelectric
PZT – lead zirconate titanate (PbZr1-xTixO3); a tetragonal, perovskite ferroelectric and piezoelectric
Si – silicon; an indirect bandgap semiconductor that is the benchmark for integrated circuit technology
SiO2 – silicon dioxide; a dielectric insulating oxide that is the benchmark dielectric for integrated circuit technology
STO – strontium titanate (SrTiO3); a cubic, perovskite, paraelectric and piezoelectric

**Miscellaneous Abbreviations**

BFOM – Baliga’s figure of merit
FWHM – full width at half maximum
JFOM – Johnson’s figure of merit
RMS – root mean square

**General Terminology**

Amorphous – a material with no atomic order or crystal structure
Antiferroelectric – a material with an equal number of dipole moments that align antiparallel to adjacent dipole moments, resulting in a net polarization of zero
Antiferromagnetic – a magnetic material with an equal number of magnetic moments that align antiparallel to adjacent magnetic moments, resulting in a net magnetization of zero
Attenuation – the loss electron intensity as they travels through a medium
Band bending – the difference in energy bands (conduction and valence) that occurs a junction of two dissimilar materials
Bandgap – minimum energy difference between the conduction band and valence band
Breakdown voltage – the voltage or applied field where leakage occurs
Chevrons – a diffraction phenomenon that is characteristic of faceted features
Coercive field – the strength of an applied field (magnetic or electric) that must be applied to remove all remnant magnetization or remnant polarization
Conduction band – range of electron energies sufficient to make electrons conduct under an applied field
Conduction band minimum – the minimum energy for which electrons are free to conduct under an applied electric field
Conductor – a material with no bandgap that can conduct electrons under an applied field; typically metals
Curie temperature – the temperature at which ferroelectric or ferromagnetic properties are lost, resulting in paraelectric or paramagnetic properties, respectively
Dielectric – synonymous with insulators, allow reduced amounts of current to flow through them and are typically used for alternating electric field applications
Doping – the intentional addition of impurities into an other wise pure material
Effusion cell – a piece of equipment also known as a Knudsen cell used in MBE to thermally sublimate a pure material for film growth
Epitaxy – the continued growth of a single crystal
Escape depth – (3l) defined as three times the inelastic mean free path
Ewald sphere – an imaginary sphere in reciprocal space that is used the physics of diffraction
Ex-situ – in a different local environment (for this dissertation, ex-situ is used to define anything outside of the UHV environment)
Fermi level – the energy level of the highest occupied state that lies between the conduction band and valence band
Ferrielectric – a degenerate antiferroelectric material that exhibits minimal ferroelectric properties
Ferrimagnetic – a magnetic material with an unequal number of magnetic moments that align antiparallel to adjacent magnetic moments, resulting in a net magnetization greater than zero
Ferroelectric – a material that exhibits a spontaneous and permanent dipole moment
Ferromagnetic – a magnetic material that exhibits a spontaneous and permanent magnetic moment
Fluence – used to define the total number of atoms (or molecules) that impinge on an area (#/cm2)
Flux – used to define the rate at which a number of atoms (or molecules) that impinge on an area (#/cm2 sec)
Frank-Van der Merwe – a basic model to describe a 2-D layer-by-layer growth mode
Heteroepitaxy – the continued growth of a single crystal of a dissimilar material
Heterostructure – structure consisting of two or more layers of dissimilar materials
Homoeopitaxy – the continued growth of a single crystal of the same material
Huttig temperature – defined as 1/3 of the melting point temperature and corresponds to the temperature where surface mobility is sufficient enough to undergo agglomeration
Inelastic mean free path – (IMFP, l) used to describe the distance an electron (or atom) can travel through a medium before losing energy
In-situ – in the original local environment (for this dissertation, in-situ is used to define the UHV environment)
Insulator – a material that has a large bandgap (5 – 10 eV) and poor electron transport properties
Kikuchi lines – a diffraction phenomenon that is characteristic of diffraction across an atomically flat surface
Lattice – relates to the atomic spacings that make up the unit cell of a crystal
Laue zone – distinct regions of the Ewald sphere that correspond to the lattice spacing of a crystal
Leakage current – a sudden decrease in resistivity, resulting in an abrupt increase in current flow
Magnetoelastic – a term used to describe the direct coupling between the magnetic properties of one material and the mechanical properties (stress, strain) of an adjacent material
Magnetolectric – a term used to describe the direct coupling between the magnetic properties of one material and the electric properties of an adjacent material
Mismatch – the difference in properties (thermal expansion coefficient, lattice spacing) that forms at the interface of adjacent materials
Monolayer – defined as the complete coverage of a surface by one unit cell thickness
Multiferroic – material whose intrinsic functionality exhibits two or more of the ferro-properties
n-type – when a material (typically a semiconductor) is doped with an atom that donates an extra electron, resulting in the Fermi level shifting towards the conduction band
Optical pyrometer – a piece of equipment used to measure temperature based on the optical detection of emitted wavelengths from a material’s surface
Oxygen bridge – a hypothesized concept used to describe the heteroepitaxy of multilayers of oxides through the sharing of oxygen at the interface
Oxygen plasma ion filter – oppositely charged plates located at the end of the oxygen plasma discharge tube designed to remove charge oxygen species form the remote oxygen source
Paraelectric – a material that will polarize under an applied field but cannot maintain a permanent dipole moment
Paramagnetic – a material that exhibits magnetism only in the presence of a magnetic field but cannot maintain a permanent magnetic moment
Perovskite – an oxide material with a chemical composition of ABO3 and is generally a cubic or tetragonal structure
Piezoelectric – a material that undergoes mechanical deformation under an applied field
Polycrystalline – a material that consists of mixture of single crystal domains
Polytype – variations in crystal structure for the same chemical compound or material (3C-SiC, 4H-SiC, 6H-SiC)
p-type – when a material (typically a semiconductor) is doped with an atom that donates an extra hole, resulting in the Fermi level shifting towards the valence band
Reciprocal space – used in physics to transpose real space into an imaginary lattice used in diffraction theory
Remnant magnetization – a permanent net magnetic moment that remains after a magnetic field has been removed
Remnant polarization – a permanent net dipole moment that remains after an electric field has been removed
Rocksalt structure – a cubic structure, typically binary (NaCl, MgO), where each atom of species A is equally spaced from six adjacent atoms of species B
Saturated magnetization – the maximum allowed alignment of magnetic moments due to a sufficiently high applied magnetic field
Saturated polarization – the maximum allowed alignment of dipole moments due to a sufficiently high applied electric field
Semiconductor – a material that has an electrical conductivity and transport properties in between conductors and insulators
Silicate adlayer – the formation of a surface layer different from the bulk of the materials that consists of silicon and oxygen
Single crystalline – an ideal material that has long range atomic order
Sticking efficiency (incorporation efficiency) – the percentage of atoms or molecules that contribute to film growth relative to the total number that impinge the surface.
Stranski-Krastanov – a basic model to describe a 2-D growth mode followed by a 3-D growth mode transition
Uniaxial anisotropy – refers to non-homogeneity of a specific property in only one crystal direction
Valence band – highest range of electron energies where electrons are normally present
Valence band maximum – the maximum allowable energy within the valence band
Volmer-Weber – a basic model to describe a 3-D island growth mode
Wide bandgap semiconductor – a semiconductor that has a bandgap greater than ~2 eV

Equation Variables

Greek
$\Delta E = \text{energy difference (eV)}$
$\varepsilon_0 = \text{emissivity of free space (1)}$
$\phi = \text{atomic flux (#/cm}^2/\text{sec)}$
$\gamma_{fs} = \text{chemical interaction between film and substrate}$
$\gamma_{fv} = \text{chemical interaction between film and vapor}$
$\gamma_{sv} = \text{chemical interaction between substrate and vapor}$
$\kappa = \text{dielectric constant (dimensionless)}$
$\sigma = \text{electrical conductivity (S/m)}$

English
$\alpha_i = \text{lattice spacing of material } i \text{ (Å)}$
$BE = \text{binding energy (eV)}$
$C = \text{capacitance (}\mu\text{F/cm}^2\text{)}$
$C_{ef} = \text{coercive field (kV/cm)}$
$E = \text{electric field (kV/cm)}$
$E_{CB} = \text{conduction band energy (eV)}$
$E_{VB} = \text{valence band energy (eV)}$
$f(v) = \text{velocity function}$
$k_B = \text{Boltzmann’s constant (} \sim 1.30 \times 10^{-23} \text{ J/K)}$
$KE = \text{kinetic energy (eV or J)}$
$M = \text{molecular weight (g/mol)}$
$m =$ mass of one atom (g or kg)
$P =$ polarization (µC/cm$^2$)
$P_{\text{max}} =$ maximum polarization (µC/cm$^2$)
$P_r =$ remnant polarization (µC/cm$^2$); also written as $P_{\text{rem}}$
$P_s =$ saturated polarization (µC/cm$^2$); also written as $P_{\text{sat}}$
$P =$ pressure (Torr)
$Q =$ measured switch charge (F)
$T =$ temperature ($^\circ$C or K)
$t =$ time (sec)
$v =$ velocity (m/sec)
9.0 References


[3] W. Wu, K. H. Wong, C. L. Mak, C. L. Choy, and Y. H. Zhang, "Epitaxial Pb(Zr_{0.52}Ti_{0.48})O_3/La_{0.35}Nd_{0.35}Sr_{0.3}MnO_3 heterostructures for fabrication of ferroelectric field-effect transistor," *Journal of Applied Physics*, vol. 88, pp. 2068-2071, 2000.


[59] H. S. Craft, R. Collazo, M. D. Losego, S. Mita, Z. Sitar, and J.-P. Maria, "Band offsets and growth mode of molecular beam epitaxy grown MgO(111) on


[70] W. A. Doolittle, A. G. Carver, and W. Henderson, "Molecular beam epitaxy of complex metal-oxides: Where have we come, where are we going, and how are we going to get there?," *Journal of Vacuum Science Technology B*, vol. 23, pp. 1272-1276, 2005.


[143] "http://www.las.inpe.br/~cesar/Infrared/rheed.htm."


Appendix
A: Chemical Spectroscopy

Chemical analysis was routinely performed on various substrates and films. The two types of spectroscopy used were x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Although both techniques are useful tools for analysis thin films, each has their own specific advantages.

A.1 Auger electron spectroscopy

Auger electron spectroscopy (AES) is an analysis technique that is typically used for chemical analysis where surface sensitivity and high spatial resolution are required. Unlike other common spectroscopy, including XPS and EDAX, AES does not focus on the primary excitation transitions. Rather, it is a technique that detects and characterizes electrons that are generated through a atomic relaxation process referred to as the Auger process.

A.1.1 Auger process

The emission of an Auger electron occurs through a series of events. Initially, a core level electron is ejected from an atom by an external energy source. Typically in AES, this is done with an electron beam with an incident kinetic energy between 2 – 5 keV. However, this process can also occur through excitation resulting from an incident photon. When the core level electron is ejected, the atom is temporarily in an excited state. Thermodynamics forces the atoms to relax to a lower energy state. This can occur through a number of different processes. In the case of AES, the relaxation process is
through the emission of an Auger electron. In order to relax to a lower energy state, an electron from a higher shell drops to the core level to replace the electron that was initially ejected. Finally, an Auger electron is emitted in order to balance the orbital and maintain an energetically stable atom. This process is schematically illustrated in figure A.1, which demonstrates a KLL Auger transition. The KLL nomenclature represents the orbitals where the initial excitation occurred (K), the orbital responsible for the subsequent relaxation (L₁), and the orbital where the Auger electron was generated (L₂3).

Figure A.1: Schematic representation of the Auger electron emission process.

As illustrated in the schematic Auger relaxation process, it should be apparent that the kinetic energy of the emitted Auger electron is independent of the incident energy. All that is required for the Auger process to occur is the ejection of a core level electron. Therefore, the energy balance incorporating the Auger process can be written as:

\[
E_{AE}^{KE} \approx E_K^{BE} - E_{L1}^{BE} - E_{L23}^{BE}
\]  
Eqn. A.1

\[
E_{AE}^{KE} \approx (E_K^{BE} - E_{L1}^{BE}) - E_{L23}^{BE}
\]  
Eqn. A.2

\[
E_{AE}^{KE} \approx (E_K^{BE} - E_{L23}^{BE}) - E_{L1}^{BE}
\]  
Eqn. A.3

\[
E_{AE}^{KE} \approx E_K^{BE} - (E_{L1}^{BE} + E_{L23}^{BE})
\]  
Eqn. A.4

The kinetic energy of the Auger electron is dependent on the specific binding energies of electron shell involved in the process. In reality, it is not possible to identify the exact origin of the Auger electron. This is illustrated in the previous equations as
well. Therefore, the general notation KLL is used to describe the discussed transition, where no distinction is made between the L₁ and L₂₃ orbitals.

The specific kinetic energy of an Auger electron is a result of the binding energies of the three levels involved in the overall Auger relaxation process. Therefore, the kinetic energy of the Auger electron can be sensitive to bonding state and the atom’s local environment. However, since each of the three levels can be affected differently, it is difficult to narrow down the specific cause of any observed chemical shift.

A.1.2 AES for chemical analysis

Once the Auger electrons are generated, typically from a high energy electron beam, they need to be collected and analyzed. This was performed using a single pass cylindrical mirror analyzer (CMA) with an integrated electron beam. The samples were placed under vacuum and aligned perpendicular to the incident electron beam and analyzer, approximately 1 cm from the electron aperture. During excitation, the Auger electrons leave the surface in a parabolic distribution. The Auger electrons then enter through a collector where they are focused by a series of deflection grids. The Auger electrons are finally intensified through the use of an electron multiplier, which is designed to increase the signal to noise ratio, and displayed in an energy spectra. Figure A.2 schematically illustrates the collection and analysis of Auger electrons.
As the Auger electrons pass through the optics of the CMA, an AES spectra is output, which displays the intensity, or counts, for each kinetic energy. For qualitative characterization of the compounds, a series of steps need to be taken to determine the relative amount of each element within the sampling volume. This requires the use of sensitivity factors, which are designed to account for differences in the probability of Auger electron emission for different elements. Each element has a specific probability, based on ionization potentials, for the emission of an Auger electron. The higher the probability, the more Auger electron will be emitted. The intensity of each electron can be generalized by the following equation.

\[ I = F \cdot n \]

**Figure A.2:** Representation of AES system including the single pass CMA, data collection, and collected AES spectrum.
\[ I_i = N_i (\beta_i \Phi_i \Psi_i \lambda_i) (AI_pRT \cos \theta) \]  

Eqn. A.5

Where:

- \( I_i \) = measured intensity
- \( N_i \) = number of atoms excited
- \( \beta_i \) = backscattered electrons
- \( \Phi_i \) = ionization cross-section
- \( \Psi_i \) = transition probability
- \( \lambda_i \) = escape depth
- \( A \) = analyzed area
- \( I_p \) = incident beam current
- \( R \) = roughness factor
- \( T \) = instrument transmission factor
- \( \theta \) = angle of incident beam from normal

Note that in this equation, the right hand side of the equation can be simplified into three parts. The first term is the unknown variable of interest, the second set of terms is material dependent, and the third set of terms is geometry dependent. In order to normalize the intensity, it is necessary to relate the measured intensity to a known reference. This is performed through the following normalization step.

\[
\frac{I_i}{I_{ref}} = \frac{N_i}{N_{ref}} \left( \frac{\beta_i \Phi_i \Psi_i \lambda_i}{\beta_{ref} \Phi_{ref} \Psi_{ref} \lambda_{ref}} \right) \left( \frac{AI_pRT \cos \theta}{AI_{p_{ref}}RT \cos \theta_{ref}} \right) 
\]

Eqn. A.6

\[
\frac{I_i}{I_{ref}} = \frac{N_i}{N_{ref}} \left( \frac{\beta_i \Phi_i \Psi_i \lambda_i}{\beta_{ref} \Phi_{ref} \Psi_{ref} \lambda_{ref}} \right) 
\]

Eqn. A.7

\[
\frac{I_i}{I_{ref}} = \frac{N_i}{N_{ref}} \frac{S_i}{S_{ref}} 
\]

Eqn. A.8

From this normalization sequence, the variables associated with system geometry are canceled out, leaving on the material dependent variables. These variables can be condensed down into a single variable called the sensitivity factor \( (S_i) \). For compounds with more than one element, an additional step is required to determine the relative atomic concentration \( (x_i) \).
From the previous equation, a relative atomic composition of a material can be determined. Quantitative characterization of the material to determine the number of atoms of each element within the sampling volume is significantly more difficult and requires well defined sensitivity factors that need to be obtained from a variety of different standards. This was not performed during the extent of the research for all materials discussed, and therefore AES was used as surface sensitive characterization technique for determining relative atomic concentrations and inferring local bonding states.

When the sample is excited by the electron beam, there is a continuous generation of secondary electrons in addition to the emission of Auger electron. The AES electron detector is not capable of discriminating between the different types of electron excitement. Therefore, the background distribution of electrons increases almost linearly with energy. This is illustrated in the representative AES spectra in figure A.2. The characteristic Auger electrons are more easily distinguished and characterized by differentiating the energy distribution spectra. This results in a flat background for the secondary electrons and distinct peaks for the Auger transitions. Characterization and relative compositional analysis can be more easily performed by comparing the peak to valley height for each element. However, it should be noted that the sensitivity factors used to characterize a non-differentiated spectra may be different that those used to characterize the differentiated spectra. A comparison of a differentiated and non-differentiated survey scan is illustrated in figure A.3. The Auger transitions become more
pronounced in the differentiated scan, which enables the subtleties of the spectra to be more easily characterized.

**Figure A.3**: Comparison of non-differentiated (bottom) and differentiated (top) AES spectra for 6H-SiC. The differentiate spectrum is typically used for chemical analysis and more easily identifies Auger transitions.

### A.1.4 AES surface sensitivity

AES is a surface sensitive technique used for qualitative or quantitative chemical characterization of a material. Because the emitted Auger electrons are independent of incident energy, they have a relatively low kinetic energy compared to the excited core level electrons. The kinetic energy range for SiC, is between 0 and 550 eV, where Si LMM is around 88 eV, C KLL is around 272 eV, and O KLL is around 510 eV. The low kinetic energy of the Auger electrons results in a shorter inelastic mean free path ($\lambda$, IMFP). The mean free path of an electron is related to the distance an electron of a specific energy can travel through a specific medium without any energy loss. The IMFP
for an electron with a kinetic energy of 272 eV (C KLL) through SiC is around 9 Å. Typically, the sampling depth is defined as $3\lambda$ (27 Å) and is the depth from which 95% of the analyzed electrons are generated. When characterizing a material that is on the order of tens to hundreds of nanometers in thickness, 27 Å can be considered surface sensitive. In addition, the spatial resolution of AES can theoretically be as small as an electron. In reality, the electron beam has a size distribution. For all AES characterization discussed, the spot size of the electron beam had a diameter around 5 µm.

**A.2 X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) is another useful characterization technique for determining elemental compositions and bonding states. Unlike AES, XPS uses characteristic x-rays to excite the sample and detects the emitted photoelectrons. These photoelectrons are primary excitations whose energy is greatly influenced by the specific bonding environment from where it was generated. Figure A.4 illustrates the photoemission process.

![Figure A.4: Schematic representation of photoelectron emission.](image)

**Figure A.4:** Schematic representation of photoelectron emission.
Because the photoelectron is a primary excitation, its kinetic energy is dependent on the incident energy of the photon and its specific binding energy. The kinetic energy is represented by the following equation.

\[ KE = h\nu - BE - \phi \]  
Eqn. A.10

\[ BE = h\nu - KE - \phi \]  
Eqn. A.11

As represented in the previous equations, the kinetic energy of a photoelectron is equal to the incident photon energy \((h\nu)\), minus the binding energy of the electron, minus the work function of the system \((\phi)\). The work function is defined as the minimum amount of energy (eV) required to move an electron from the Fermi level into vacuum. Typically this value is around several eV.

A.2.1 XPS for chemical analysis

Typically, there are two x-ray sources that are used for photoelectron emission. These are Al K\(\alpha\) (1486.6 eV) and Mg K\(\alpha\) (1253.6 eV). For the XPS system used for characterization discussed in this thesis, the x-rays were incident the sample at 54° off normal to the sample. Once the photoelectrons have been excited, they are analyzed by a hemispherical analyzer. The photoelectrons first pass through an aperture plate, which was set at an allowance diameter of 1.1 mm for all characterization discussed. The photoelectrons are then focused through a series of retardation lenses before entering into the hemispherical analyzer. The hemispherical analyzer consists of several copper hemispheres of progressively larger size. By applying a voltage bias between the inner and outer hemispheres, only electrons of a specific energy will pass through the detector. Electrons with too high an energy will impact the outer hemisphere, while electrons with
too low an energy will fall into the inner hemisphere. By sweeping the bias voltage between the hemispheres, it is possible to sweep across a wide energy range, thus generating the XPS spectra. It is important to note that the collection of photoelectrons is done with respect to the kinetic energy of the electrons. Once the electrons have been generated, the detector cannot discriminate between photoelectrons, secondary electrons, or Auger electrons. Therefore, if a core level electron from carbon (C 1s) is generated by an Al Kα x-ray (1486.6 eV), it will a kinetic energy that is 233 eV higher than if it were generated by a Mg Kα x-ray (1253.6 eV). Although the detector is tuned to analyze the kinetic energy of the electrons, the software is programmed to automatically subtract the incident x-ray energy (input by the operator) and work function (determined from calibration). The resulting spectra are then displayed in terms of binding energy. Figure A.5 schematically illustrates the excitation, collection, and analysis for XPS.
It is also important to note that although XPS is typically a characterization technique for analyzing core level photoelectrons, the excitation process also generates Auger electrons. Since the detector cannot distinguish between the origins of the electrons, most XPS spectra also include characteristic Auger transition peaks. Deciphering between photoelectron peaks and Auger peaks is possible through the use of multiple x-ray sources. Since the kinetic energy of the Auger electrons is independent of incident energy, but photoelectrons are dependent, by plotting the spectra with respect to binding energy will result in an apparent shift of 233 eV for the Auger transitions. During analysis, it is important to be aware of the positions of all Auger transitions in order to
prevent overlapping between the unwanted Auger peaks and the desired photoelectron peaks. Figure A.6 illustrates the 233 eV shift for Auger transitions.

**Figure A.6**: Representation of XPS spectra collected on the same samples using the two different anodes. Red corresponds to Mg Kα and blue corresponds to Al Kα x-ray excitation. Photoelectron peaks remain at the appropriate binding energy, while the Auger transitions experience an apparent shift of 233 eV.

Similar to AES, qualitative and quantitative analysis can be performed using XPS. The height and area of each peaks is characteristic of a specific number of electrons that were generated within the sampling volume. By comparing the peak areas associated with different elements, it is possible to obtain a relative atomic composition. This process is similar to that described previous for AES.
\[ I_i = N_i(\sigma_i, \lambda_i, \theta_i)(yfAT) \]

Eqn. A.12

Where:
- \( I_i \) = measured intensity
- \( N_i \) = number of atoms excited
- \( \sigma_i \) = photoelectric cross-section
- \( \lambda_i \) = inelastic mean free path
- \( \theta_i \) = orbital symmetry factor
- \( y \) = detector efficiency
- \( f \) = x-ray flux
- \( A \) = analysis area
- \( T \) = analyzer transmission efficiency

The measured intensity of the photoelectrons is again dependent on three variables; the number of atoms that were excited, a materials dependent parameter, and a system dependent parameter. Through the same process mentioned previously in the AES, the system dependent parameter will be canceled out during qualitative analysis of the relative atomic concentrations. The end result will be identical to the atomic composition \((x_i)\) equation listed previously. However, the sensitivity factors for AES and XPS will not be the same, but rather dependent on the technique used.

Since the photoelectrons are generated through primary excitation of the material, the specific kinetic energy (and binding energy) of the photoelectrons are much more sensitive to the local binding environment from where they originated. Therefore, XPS is a much more useful technique for determining specific bonding states of various atoms. Depending on the material system, there can be a chemical shift on the order of several eV.
A.2.2 XPS surface sensitivity

Similar to AES, XPS can be considered a surface sensitive characterization technique. However since the excitation of photoelectrons is dependent on the incident energy of the x-ray, the sampling depth of XPS is relatively deeper than that of AES. As a sampling depth reference to AES, the C 1s photoelectron generated within SiC has a binding energy around 283.8 eV. The corresponding kinetic energy is either 1202.8 eV (Al Kα radiation) or 969.8 eV (Mg Kα radiation). From these kinetic energies, the resulting IMFP values are 26.1 Å and 22.1 Å for Al Kα radiation and Mg Kα radiation, respectively. As discussed previously regarding the surface sensitivity of AES, the sampling depth is defined as $3\lambda$, which results in sampling depths of 78.3 Å and 66.3 Å. These values are significantly larger than the representative sampling depth of C KLL for AES, but are still considered surface sensitive when considering film thicknesses can be tens to hundreds of nanometers in thickness. In addition to having a larger sampling depth, the spatial resolution of XPS is significantly larger. In AES, the spatial resolution is determined by the deflection of the electron beam. However, with XPS the spatial resolution is determined by the detector aperture, which is typically on the order of millimeters.
B: Reflection High Energy Electron Diffraction

Reflection high energy electron diffraction is an in-situ analysis technique that takes advantage of the benefits offered by ultra high vacuum. Similar to low energy electron diffraction, both RHEED and LEED use the concept of reciprocal space and the Ewald sphere, which will be covered later. LEED involves a low energy electron incident beam perpendicular to the film surface. This geometric configuration prohibits the use of LEED as a real time analysis technique. However, because of the geometry of RHEED, it can be used as a real time analysis technique. Therefore, RHEED can be used to determine the growth rate of the thin films as well as the crystallinity, and orientation.

B.1 Geometric configuration for RHEED

As mentioned previously, RHEED can be used as a real time analysis technique. This is because it is based on the scattering effect of a high energy electron beam that is incident the film at a glancing angle no greater than 2°. Where LEED uses an electron beam less than 1 keV, RHEED uses an electron beam anywhere between 5 and 100 keV. However, RHEED is still a surface sensitive analysis technique because the glancing angle of the incident beam has a penetration depth on the order of a few monolayers.
As illustrated in figure B.1, the electron beam generated by the electron gun has an incident angle around $2^\circ$. The beam is then diffracted and imaged on the phosphor screen. The resulting image can be used to determine the surface characteristics of the film. The inset illustrates two types of diffraction, three-dimensional crystalline (top) and flat surface (bottom). Since most surfaces are not perfectly flat, the diffraction pattern is a result of both 3-D crystal diffraction and surface diffraction. Through analysis of the resulting pattern, it is possible to infer the structure and morphology of the surface.

Although RHEED is a very popular analysis technique for determining certain characteristics of the film surface, the complexity of diffraction patterns has prevented any complete formal theory. There are however, many simplified approaches that are sufficient for the determination of certain characteristics, such as unit cell dimensions and crystal orientation.

**B.2 Reciprocal space and lattice vectors**

From the basics of RHEED theory, it is possible to predict a diffraction pattern based on crystal structure and orientation. Likewise, from the diffraction pattern, it is
possible to determine the crystal structure and orientation. The method by which electrons are diffracted is highly based on the reciprocal lattice of the film lattice and is explained by Bragg’s law. Therefore, it is important to understand the transition from real space to reciprocal space. A detailed example of this can be seen in section C.2.

In real space, a simple unit cell (cubic, tetragonal) is expressed by its three characteristic corner atom $a_1$, $a_2$, and $a_3$, which are conventionally expressed as $a$, $b$, and $c$ respectively. In reciprocal space, the respective translation can be expressed by the following [B2].

$$b_1 = 2\pi \frac{a_2 \times a_3}{V} \quad b_2 = 2\pi \frac{a_3 \times a_1}{V} \quad b_3 = 2\pi \frac{a_1 \times a_2}{V}$$  \hspace{1cm} \text{Eqn. B.1}

Where $V$ is the volume of the primitive unit cell in real space and $b_i$ is the equivalent reciprocal lattice of $a_i$.

For simplicity, consider a simple tetragonal unit cell with lattice vectors $a$, $b$, and $c$. These lattice parameters of the unit cell are expressed as $a$, $b$, and $c$, where $a = b < c$. The reciprocal lattice vectors are similarly symbolized as $a^*$, $b^*$, and $c^*$.

\[\text{Figure B.2: Schematic illustration of the lattice vector transition from real space (a) to reciprocal space (b) [B2].}\]
In real space, the lattice vectors can be expressed as; $a_1 = ax; a_2 = ay; a_3 = cz$.

Using equation 1, it is now possible to determine the reciprocal vectors [B2], which can be expressed as;

$$
\begin{align*}
    b_1 &= \frac{2\pi}{a^2c} ax = \frac{2\pi}{a} x \\
    b_2 &= \frac{2\pi}{a^2c} ay = \frac{2\pi}{a} y \\
    b_3 &= \frac{2\pi}{a^2c} az = \frac{2\pi}{c} z
\end{align*}
\quad \text{Eqn. B.2}
$$

This results in, $b_3 < b_1 = b_2$. The complexity of reciprocal space increases substantially as the unit cells become more complex.

**B.3 Diffraction characteristics and the Ewald sphere**

Another major concept in the basic theory of RHEED is concept of the Ewald sphere. The Ewald sphere is an imaginary sphere characteristic of the incident electron beam and the reciprocal lattice vectors. In real space the incident electron beam has a direction ($n$), wavelength ($\lambda$), and wave vector ($k$). This wave vector is characteristic of both direction and wavelength by $k = \frac{2\pi n}{\lambda}$. When the incident beam is diffracted, it is scattered with similar characteristics; $k' = \frac{2\pi n'}{\lambda}$.

![Figure B.3](image)

**Figure B.3:** Schematic illustration of diffraction vectors [B3].
Considering vector geometry and figure B.3, a diffraction intensity will reach a maximum when \( R \cos \theta + R \cos \theta' = R \cdot n - R \cdot n' = m \lambda \), where \( m \) is an integral number of the wavelength. Applying the Laue condition with the diffraction vectors and figure B.3, \( R \cdot (k - k') = m2\pi \). This occurs when the change in wave vector \( (k - k') \) is equal to the reciprocal lattice vector described in the previous section. This can be simplified by a graphical representation of the Ewald sphere.

![Figure B.4: Schematic illustration of the construction of the Ewald sphere [B3].](image)

The diameters of the Ewald sphere is determined by \( (k - k') \), which is representative of the incident electron beam and diffraction maxima from the reciprocal lattice vectors. Diffraction maxima only occur during constructive interference.

**B.4 Combinatorial analysis involving reciprocal lattice vectors and Ewald sphere**

By combining the reciprocal lattice vectors with the Ewald sphere diagram, it is possible to see how the diffraction patterns are generated. For simplicity, take a simple cubic structure. The reciprocal lattice results in a mesh type grid with equal spacing.
For a perfectly flat surface, the resulting series of \((k - k')\) possibilities would be infinite, resulting in a rod of intensity maxima. However, real surfaces are seldom perfectly flat. The effects of which will be discussed later in section 2.5. The reciprocal mesh can be overlaid on top of the Ewald sphere to illustrate the rod position with respect to reciprocal space.

Figure B.5: Schematic illustration of possible \(k - k'\) changes in the wave vectors \([B3]\); a) top view of reciprocal mesh, b) side view of reciprocal mesh.

Figure B.6: Schematic representation from the top showing the rod placement within the Ewald sphere for a simple cubic structure \([B3]\).
The rod placement follows an ordered arrangement as a result of the ordered spacing of atoms within the simple cubic structure. The numbers in parenthesis are used to label the rods with two Miller indices \((hk)\), where \(k\) represents the zone, and \(h\) represents which side of the axis the rod falls with respect to the incident beam. It is important to remember that the Ewald sphere is actually a sphere and not a circle, as it has been represented by thus far. As a result, the rods intersect the Ewald sphere forming an arc known as a Laue ring. It is where the rods intersect the Ewald sphere that the diffraction patterns are observed on the phosphor screen.

![Figure B.7: Three dimensional model of the rods intersecting the Ewald sphere; a) view from the top, b) view from the front (origin), and c) view with 45° rotation.](image)

In figure B.7, the green rods represent \((h1)\), yellow represent \((h2)\), and so on. For figure C.7 (b) and (c) it is easy to see the Laue ring that is formed by the intersection of
zone 1 with the Ewald sphere. The visible diffraction image is limited to only the top half of the sphere due to the bottom being blocked by the sample.

It should be clear that the complexity of RHEED analysis increases substantially with more complex unit cells. Although the lattice vectors and reciprocal lattice vectors are more difficult to calculate, the basic theory is the same. Prediction of diffraction patterns are generally accomplished through the use of computer modeling because of the complexity of reciprocal space mapping.

**B.5 Interpretation of RHEED patterns**

As mentioned earlier, it is possible to predict the diffraction pattern given certain characteristics of a known film. It is also possible to determine the crystal structure and orientation by doing the opposite. To do so, it is necessary to know how to interpret the RHEED patterns. Since most surfaces are not perfectly flat, the resulting intensity maxima are not always distinct spots. It is therefore necessary to relate the size and shape of the spots to surface features.

*Figure B.8:* Schematic illustration of diffraction resulting from different surface features [B4]; a) ideal, single crystalline, flat surface, b) polycrystalline surface, c) single crystalline with 3-D island features, and d) single crystalline with 2-D features.
In the previous figure, the ideal surface results in distinct spots located on the Laue rings. Polycrystalline films result in no distinct spots but it is still possible to see the Laue rings. 3-D growth patterns result in distinct spots that have a distinct pattern, but do not coincide with the Laue rings. Finally, 2-D growth results in distinct spots with vertical elongation that do coincide with the Laue rings. The vertical elongation is characteristic of surface features that are nearly flat. For (c), further interpretation can be inferred from the shape of the spots. Circular spots are representative of tall and wide crystals, horizontally elongated spots of tall and narrow crystals, and vertically elongated of short and wide crystals [B1].

After obtaining the diffraction patterns, it is possible to infer the crystallinity and orientation of the film surface. As just mentioned, the shape and location of the spots is representative of crystal structure. Direct measurement of the spacing can be used to determine orientation. Just as it is possible to predict the spacing in the diffraction pattern based on lattice parameters and crystal structure, it is possible to do the opposite.

**B.6 Monitoring film growth using RHEED**

RHEED can be used further to determine the growth rate and growth mode of thin films. Since RHEED is a real time analysis technique, it is possible to obtain diffraction patterns during growth. As the thin film grows, the intensity of the RHEED pattern will fluctuate with surface coverage.
In addition to monitoring the growth rate through intensity oscillation, it is also possible to determine the growth mode. During 2-D growth, the intensity oscillations will have a definite repeating pattern. From this repeating pattern, the growth rate can be determined. However, during 3-D growth, there is no definite repeating pattern. This is because the surface features grow in random clusters, forming islands.

### B.7 Real space to reciprocal space transition

Adapted from [B7]

**Two dimensional surface transition from real space to reciprocal space**

Real space lattice vectors: $a_{surf}$ and $b_{surf}$

Reciprocal lattice vectors: $a_{surf}^*$ and $b_{surf}^*$

Direct relationship between real space lattice vectors and reciprocal lattice vectors:

\[
\begin{align*}
a_{surf}^* \cdot a_{surf} &= 2\pi & \text{Eqn. B.2} \\
b_{surf}^* \cdot b_{surf} &= 2\pi & \text{Eqn. B.3} \\
a_{surf}^* \cdot b_{surf} &= 0 & \text{Eqn. B.4} \\
b_{surf}^* \cdot a_{surf} &= 0 & \text{Eqn. B.5}
\end{align*}
\]
Where \( \cdot \) represents the dot product of the vectors, therefore;

\[
\begin{align*}
\mathbf{a}_{\text{surf}}^* \perp \mathbf{b}_{\text{surf}} & \quad \text{Eqn. B.6} \\
\mathbf{b}_{\text{surf}}^* \perp \mathbf{a}_{\text{surf}} & \quad \text{Eqn. B.7}
\end{align*}
\]

and;

\[
\begin{align*}
|\mathbf{a}_{\text{surf}}^*| = \frac{2\pi}{|\mathbf{a}_{\text{surf}}| \sin(\alpha)} & \quad \text{Eqn. B.8} \\
|\mathbf{b}_{\text{surf}}^*| = \frac{2\pi}{|\mathbf{b}_{\text{surf}}| \sin(\alpha)} & \quad \text{Eqn. B.9}
\end{align*}
\]

Where \( \alpha \) is the angle between \( \mathbf{a}_{\text{surf}} \) and \( \mathbf{b}_{\text{surf}} \)

**Show that the area of the reciprocal lattice unit cell is the inverse of the area of the real space unit cell.**

\[
\mathbf{G}_{hk} = h\mathbf{a}^* + k\mathbf{b}^* 
\]

Eqn. B.10

Where \( h \) and \( k \) are Miller indices

The basic vectors of the superstructure can be written as;

\[
\begin{align*}
\mathbf{a}_{\text{surf}}^* &= m_{11} \mathbf{a}^* + m_{12} \mathbf{b}^* & \quad \text{Eqn. B.11} \\
\mathbf{b}_{\text{surf}}^* &= m_{21} \mathbf{a}^* + m_{22} \mathbf{b}^* & \quad \text{Eqn. B.12}
\end{align*}
\]

\[
\begin{bmatrix}
\mathbf{a}_{\text{surf}}^* \\
\mathbf{b}_{\text{surf}}^*
\end{bmatrix} = \mathbf{M}^* \begin{bmatrix}
\mathbf{a}^* \\
\mathbf{b}^*
\end{bmatrix} 
\]

Eqn. B.13

Where the relationship between \( \mathbf{M} \) and \( \mathbf{M}^* \) is;

\[
\mathbf{M}^* = (\mathbf{M}^{-1})^T 
\]

Eqn. B.14

The relationship between the elements of \( \mathbf{M} \) and \( \mathbf{M}^{-1} \) are;

\[
\begin{align*}
m_{ij} &= \frac{m_{ij}^*}{\det \mathbf{M}^*} & \quad \text{Eqn. B.15} \\
m_{ij} &= -\frac{m_{ji}^*}{\det \mathbf{M}^*} & \quad \text{Eqn. B.16}
\end{align*}
\]

The area, \( A \), for real space is given by;
The area, $A^*$, for reciprocal space is given by;

$$A^* = |a_{surf}^* \times b_{surf}^*| = |a_{surf}^*| |b_{surf}^*| \sin \alpha = 4\pi^2/A$$  Eqn. B.18

**Sketch of real space lattice vectors and reciprocal lattice vectors**

for a fcc(100)(1×1)

![Sketch of real space lattice vectors and reciprocal lattice vectors for fcc(100)(1×1)](image)

**Figure B.10**: Schematic representation of the lattice transition between real space and reciprocal space for a fcc(100)(1×1).

The lattice vectors $a^*$ and $b^*$ are parallel with the real space lattice vectors and will have lengths given by $2\pi(|a| \sin (90))^{-1}$ and $2\pi(|b| \sin (90))^{-1}$.

for a fcc(100)(2×2)

![Sketch of real space lattice vectors and reciprocal lattice vectors for fcc(100)(2×2)](image)

**Figure B.11**: Schematic representation of the lattice transition between real space and reciprocal space for a fcc(100)(2×2).
The lattice vectors $a^*$ and $b^*$ are parallel with the real space lattice vectors and will have lengths given by $|a_{surf}^*| = 2\pi(|a_{surf}| \sin 90) = |b_{surf}^*| = \frac{1}{2}(2\pi)$.

for a fcc(111)(1×1) and fcc(111)(2×1)

![Diagram](image)

**Figure B.12:** Schematic representation of the lattice transition between real space and reciprocal space; (a) and (b) fcc(111)(1×1), (c) and (d) fcc(111)(2×1).

### B.8 RHEED summary

Reflection high energy electron diffraction is a very useful analysis technique for determining surface characteristics of thin films. RHEED diffraction patterns can be used to infer crystal structure and orientation, as well as monitor growth rate and growth mode. Through basic RHEED theory, it is possible to predict RHEED patterns using reciprocal lattice vectors and the Ewald sphere. Inversely, it is possible to determine lattice spacing.
and crystal structure based on the diffraction pattern spacing. Finally, intensity oscillations, spot shape, and spot location can be used to infer growth rate and growth mode. In addition to the fore mentioned analysis, RHEED can be used for many other types of characterization, such as crystal reconstruction during annealing or cool down. RHEED is certainly a very useful technique for thin film analysis in UHV.

**B.9 References for Appendix B: Reflection High Energy Electron Diffraction**


C: General experimental procedure

For all oxide film growth, the same basic procedure was followed. The basic steps consisted of substrate preparation, analysis of the starting substrate surface, film deposition, and analysis of the film.

C.1 Substrate preparation

6H-SiC was purchased from a variety of different vendors, including Cree, Dow Corning, Bandgap Technologies, II-VI, and Intrinsic Semiconductor. Although preliminary and exploratory studies were performed using various samples from the different vendors, all representative films in this thesis were grown on n-type (nitrogen dopant $9 \times 10^{14} - 1 \times 10^{19} \text{ cm}^{-3}$), on-axis ($\pm 0.5^\circ$) 6H-SiC samples purchased from CREE (research grade: W6NRD0X-000). Each sample was cut with a diamond tip scribe to ~0.5 cm $\times$ 0.5 cm in size.

All samples were initially degreased in a series of heated solvents in order to remove residual carbon contamination. The samples were handled using stainless steel tweezers that had been routinely cleaned in order to prevent any undesired contamination. The standard degrease procedure consisted of: 1) 5 minutes in trichloroethylene at 80 °C, 2) 5 minutes in trichloroethylene at 80 °C, 3) 2 minutes in acetone at 80 °C, 4) 5 minutes in methanol at 80 °C, 5) 5 minutes in methanol at 80 °C, and 6) blow dry with ultra high purity argon. In between each of the solvent steps, the sample was spray rinsed with the subsequent solvent in order to prevent the previous solvent from drying on the surface.
Each sample was then loaded into the custom built hydrogen flow furnace by placing them on the tantalum strip. The loading window was the secured down with clamps. Once tightened, high purity argon was flowed into the furnace at 5 slpm for 10 minutes in order to purge the system of oxygen from the atmosphere. High purity hydrogen was then flowed into the system through a second flow meter at flow rates ranging from 1 slpm up to 40 slpm. The gas composition and flow rates were studied and optimized to 11.4 slpm of only hydrogen, resulting in what will be referred to as the “standard hydrogen cleaning”. Once the hydrogen flow rate was established, the exhaust gas was carefully ignited in order to burn off hydrogen. The integrated cooling water was then turned on and set to a sufficient flow rate (not measured) in order to keep the furnace walls at a relatively cool temperature.

The temperature was then increased by supplying current from the DC power supply through the Ta strip. The temperature was measured by a two-color optical pyrometer and was positioned directly above the SiC at a distance of ~9.5 inches. At this distance, the divergence from the pyrometer was negligible, resulting in a circular analysis area roughly 2 mm in diameter. However, due to the transparency of the SiC, it is safe to assume that the actual temperature reading is not representative of the SiC surface, but rather the temperature of the underlying Ta strip. The current was increased at 5 A every 30 seconds, which correlates to ~200 °C/min. Once the desired temperature was reached, the temperature was held constant for the duration of the cleaning. The sample was then cooled at 2.5 A every 30 seconds (~100 °C/min). Although the heating and cooling rates, as well as the ultimate temperature and time were varied, the “standard hydrogen cleaning” was run between 1600 – 1700 °C for 30 minutes. Due to the high
temperature and reactivity of the hydrogen gas, during cooling, the Ta strip would break. This most often occurred when the cooling current was around 25 A, with the temperature well below the two-color detection limit of 600 °C. As a result, the sample would fall to the bottom of the furnace. It was therefore necessary to minimize contamination if the sample flipped over when it fell. To address this, fresh Al foil was placed on the bottom of the furnace at the start of every cleaning.

Once the Ta strip broke, the power supply, cooling water, and gas flow rate were turned off. Argon was then flowed into the furnace at 5 slpm in order to keep an inert head pressure when the furnace was opened. The sample was immediately removed, mounted onto a molybdenum puck with silver paste, loaded into the UHV loadlock, and put under vacuum. Although the amount of time from opening the furnace to the sample being under vacuum varied based on experience the typical length of time was around 60 seconds.

**C.2 Film deposition**

Film deposition was performed in the growth chamber with the use of the remote rf-atom source and the different effusion cells. The molybdenum puck was transferred onto the heater and moved into position, approximately 8 inches from the sources. Each individual source was then turned on and brought up to the desired operating condition. For Mg and Ba, the sources were programmed to ramp to the desired crucible temperature through a PID control Eurotherm. The cells were heated at a rate of 20 °C/min. Typical operating temperatures for Mg were between 300 – 400 °C, while typical operating temperatures for Ba were between 500 – 560 °C. Although Ba has a higher
vapor pressure than Mg, it was necessary to increase the Ba flux in order to obtain sufficiently fast enough growth rates for depositing films that were hundreds of nanometers thick. The Ti source was turned on by manually setting the desired current through the Ti-ball. Due to the fact that the Ti-ball was not originally designed as an accurate effusion source, the current increments were in intervals of 0.5 A. Typical operating currents for the Ti source were between 42 – 49 A.

The oxygen plasma source required much more care and attention due to the delicacy of the Al₂O₃ discharge tube and aperture plate. The power was initially increased to 100 W. Oxygen was then introduced though a high-precision, sapphire seal leak valve. Although no flow meter was used to quantitatively measure the oxygen throughput, a basis was established by monitoring the ion gauge pressure reading. Slowly increasing the oxygen flow would eventually lead to the ignition of the low plasma. This typically occurred at an ion gauge pressure reading around 5.0×10⁻⁶ Torr. Once the low plasma was lit, the power was increased at a rate of 50 W every 5 minutes up to 200 W. At 200 W, the oxygen flow was further increased to ignite the high plasma. This typically occurred at an ion gauge pressure reading around 1.0×10⁻⁵ Torr and was indicated by a drastic increase in the OED reading (0.5 mV → 100 mV) and reflected power. The reflected power was immediately dropped to zero by manually tuning two internally coupled capacitors. The oxygen flow was then adjusted in order to establish the desired ion gauge pressure reading, which was maintained for all oxide growths at 5.0×10⁻⁶ Torr. The power was then adjusted (as low as 90 W and up to 600 W) to obtain the desired OED reading. For most growths, the OED reading was maintained at 35 mV, with the
exception of systematic growth studies that investigated the impact of oxygen species on the growth mechanisms by increasing the plasma power to generate more atomic oxygen.

The substrate temperature was established by supplying DC power through the tantalum wires that were woven into the ceramic heater stack. The current was supplied through by another PID control Eurotherm. The current limit was set at 13.5 A in order to prolong the operating life time of the heater stack. At 13.5 A, the backside temperature of the puck, as measured by the type C thermocouple, was between 800 – 900 °C. More accurate temperature measurements of the substrate surface were collected real-time during each film growth. Typical front face temperature was on the order of 50 – 100 °C cooler than the thermocouple reading. The heating and cooling rate of the substrate was preprogrammed prior to the start of the growth. Typical heating rates were between 50 – 75 °C/min. Typical cooling rates were much slower (as low as 5 °C/min) depending on the material and film thickness. For example, SiC, MgO, and BTO have significantly different thermal expansion coefficients. In order to prevent thermally induced cracks from forming, thicker films were cooled slower than thin films.

C.3 Film characterization

Analysis of the starting surfaces and films were performed in-situ and ex-situ. In this case, the local in-situ environment is defined as UHV. Therefore, AES and XPS will be considered in-situ characterization techniques while RHEED is both an in-situ and real time characterization technique because RHEED can be performed before, during, and after film growth. Ex-situ characterization consists of all techniques performed after the
sample has been removed from the UHV environment. These techniques include SEM, AFM, and XRD.

RHEED was performed on all substrates and films before, during, and after growth. The accelerating voltage was typically held constant at 12.5 keV with a filament emission current of 1.6 mA. RHEED is a surface sensitive technique that can be used to accurately characterize in plane lattice spacings, crystal structure, crystal orientation, growth modes, and growth rates. Further, the RHEED patterns can be used to infer less quantifiable properties like film texture.

XPS was most often performed using the Al Kα x-ray source (1486.6 eV). However, depending on the materials being analyzed, it was necessary to use the Mg Kα x-ray source (1253.6 eV) in order to shift the Auger transitions away from the photoelectron transitions. Regardless of the incident x-ray, data collection was performed using the same detector settings. The aperture to the hemispherical analyzer was set at a diameter of 1.1 mm, which permitted sufficiently high signal to noise within the spectra when used in conjunction with the following data collection settings. For all survey scans (large energy range, typically BE = 1100 – 0 eV) the settings were set to 1 eV/step and 50 msec/step at a pass energy of 89.45 eV. For elemental scans (small energy range typically ±10 eV around the photoelectron peak of interest) the settings were set to 0.05 eV/step and 50 msec/step at a pass energy of 35.75 eV.

Once all in-situ analysis was complete, the samples were removed from the UHV system. Ex-situ characterization was performed by AFM, SEM, and XRD. AFM characterization was performed in non-contact (tapping) mode at various drive amplitudes and setpoint voltages. Depending on the size and quantity of the surface
features, smaller drive amplitudes and higher setpoint voltages were necessary for smoother films. For most films and substrates, a series of scans were collected at different locations. The maximum scans size was $40 \, \mu m \times 40 \, \mu m$, as limited by the piezotube scanner head. Most scans were collected at a scan rate of 1 Hz and a line resolution of $1024 \times 1024$. SEM characterization was performed at an accelerating voltage of 2 keV and a working distance of 3 – 12 mm. XRD characterization was performed over a $\theta$-$2\theta$ range of $5^\circ – 180^\circ$. 
**D: Crystal lattice**

Crystallographic orientations and directions are essential for understanding and interpreting the structure and epitaxy of different materials. All crystalline materials have a distinct repeating unit cell that make up the overall crystal structure of the film. Each unit cell is defined by its structure (cubic, tetragonal, hexagonal, etc.) and its lattice parameters. The simplest repeating unit is referred to as the Bravais lattice. The crystal structures discussed in this thesis consisted of hexagonal (6H-SiC), cubic (MgO), and tetragonal (BTO).

**D.1 Bravais lattice**

The nomenclature for designation of the Bravais lattice is independent of the lattice parameters of the specific material. Rather, it is solely dependent on the crystal structure. Typically, the Bravais lattice is defined by three coordinates (a, b, c) similar to the lattice parameters of a crystal. As an example, consider a perfect cube. The coordinates of the cube can be displayed with respect to a Cartesian coordinate system (x, y, z). In the case of a perfect cube, a = b = c, and all angles are equal to 90°. The locations where the unit cell intercept the x, y, z coordinate system is represented by a, b, and c, respectively. Regardless of the actual lattice spacing of the crystal, a, b, and c, are equal to 1 for each unit cell. Figure D.1 illustrates the Bravais lattice for a cube with respect to the Cartesian coordinate system.
Every crystal structure consists of various crystal planes that make up the surfaces of the crystal. For the example illustrated previously in figure D.1, there are six symmetric crystal planes. However, for more complex structures, such as hexagonal structures, there are eight crystal planes, which consist of six symmetric side planes and two symmetric end planes. Further details regarding the hexagonal crystal structure will be discussed later. Lattice planes are defined by the use of parenthesis \((hkl)\), where \(h\), \(k\), and \(l\) are used to define the coordination of the plane by \(h = 1/a\), \(k = 1/b\), and \(l = 1/c\). Therefore, if a plane intercepts (bright yellow in figure D.2) the x-axis at a, but no other axis, the corresponding coordinates of the plane would be \((a, \infty, \infty)\). Since \(a = 1\), the crystal plane is defined as \((1, \infty, \infty)\) or \((100)\). Similarly, if the plane intercepts the y-axis at b (bright green) or the z-axis at c (bright red), then the corresponding planes are \((010)\) and \((001)\), respectively. The same technique can be extended to more complex planes that
intercept multiple axis. For example, the (101) plane (bright blue) intercepts the x-axis and z-axis at a and c, respectively. The (111) plane (orange) intercepts all three axis at a, b, and c.

Figure D.2: Representations of crystallographic planes within a simple cubic crystal structure; a) (100), b) (010), c) (001), d) (101), and e) (111). The coordinates are based on the Cartesian coordinate system oriented as in figure D.1.

For a symmetric structure, similar to the cubic schematic illustrated in figure D.2, the (001), (010), and (100) planes are essentially identical. These planes can be further classified as a family of planes, which is designated by the \( \{hkl\} \) nomenclature. Therefore, \( \{100\} \) can be used to include all (001), (010), and (100) planes. This can be extended further to include all fractional crystal planes including (002), (020), and (200). Note that the 2 is not representative of a second unit cell, but rather half of the original unit cell due to the 1/a coordination.

The same technique used to describe a simple cubic structure can be extended to describe more complex structures like hexagonal structure. Although the coordinates of a hexagonal crystal structure can be reduced into x, y, and z coordinates, it is often more
common to describe the structure with a fourth coordinate. A comparison of the two possible coordinate systems is illustrated in figure D.3.

Figure D.3: Schematic representation of a hexagonal crystal structure, which can be described by three (left) or four (right) coordinates.

Through this thesis, any discussion regarding hexagonal crystal structures was represented using the four component coordinate system. Regardless of the coordinate system, designation of crystal planes is identical. Illustrated in figure D.4, are representations of three common crystal planes, (0001) – bright green, (10\(\bar{1}\)0) – bright red, and (11\(\bar{2}\)0) – bright blue. Note that the designation of a negative is due to the negative intercept of the plane on the specific axis.
Figure D.4: Representation of crystallographic planes of a hexagonal structure; a) (0001), b) (10\(\bar{1}\)0), and c) (11\(\bar{2}\)0)

In addition to the three planes illustrated in the previous figure, if the hexagonal crystal is symmetric, (6H-SiC) then there are in fact six symmetric red planes and six symmetric blue planes. Due to their symmetry, the planes can once again be grouped into a family of plane, represented by \{10\(\bar{1}\)0\} and \{11\(\bar{2}\)0\}.

**D.3 Crystal directions**

Determination of a crystal direction can be simplified greatly by first understanding the technique used to distinguish crystal planes. Once a crystal plane has been determined, the crystal direction is defined as the direction perpendicular to that plane and is designated by \([hkl]\) or \([hklm]\), where the [...] is normal to the surface of the (...) plane.
Figure D.5: Schematic representation of two sets ([red] and [blue]) of six symmetric crystallographic directions for a hexagonal structure and the two corresponding direction families (<red> and <blue>).

Similar to the {...} notation to describe a family of planes, the <…> notation can be used to describe a family of directions. With symmetric crystal structures, many planes and directions are essentially identical. Therefore, without knowing the specific plane or direction, the general {...} and <…> notation should be used. Crystal planes and directions are especially useful when describing the orientation of films (XRD, RHEED) in order to characterize the growth direction and overall crystallographic orientation, which can greatly affect the functional properties of the materials.
E: Thickness Calculations

Throughout the discussion section, numerous film thicknesses were presented. This appendix will more thoroughly explain the thickness calculations. All thickness calculations were derived from XPS substrate signal attenuation and integrated into the NIST database 82: Electron EAL. EAL is an abbreviation for effective attenuation length. The basic principles behind the calculations are as follows. For a bare substrate, there is an unattenuated photoelectron signal that is initially collected through XPS. As a film is deposited on the substrate, the quantity of the photoelectron generated from the substrate that reach the film/vacuum interface without energy loss decreases. This decrease in intensity is referred to as attenuation. The thicker the overlayer, the greater the photoelectron attenuation. Complete attenuation will eventually occur when the film is too thick to allow any signal originating from the substrate. By knowing specific properties (density, valence level, etc.) of the film overlayer, as well as the system geometry and electron energies, it is possible to estimate film thickness based on the degree of substrate signal attenuation. These calculations do assume an ideal, perfectly smooth, 2-D film and minimal surface loss features. These thickness calculations have an inherent error between 10-20% due to transport approximations, surface roughness, surface excitations, and surface refraction.

Two thickness calculations are employed in the NIST database 82; the equation of Gries and the TPP-2M equation of Tanuma, Powell, and Penn. Both equations are designed to estimate the inelastic mean free path (\(\lambda\), IMFP) of electrons with a specific kinetic energy. The sampling depth, which is the most relevant variable for the thickness calculations is defined at \(3\lambda\), and makes up the depth from which 95% of the generated
photoelectrons reach the vacuum interface without any loss. The equation of Gries is defined as:

\[
\lambda = 10k_1 \left( \frac{V_a}{Z^*} \right) \left( \frac{E}{\log E - k_2} \right)
\]

\[
V_a = \frac{M}{\rho} = \left( \frac{pM_A + qM_B + \ldots + rM_C}{\rho(p + q + \ldots + r)} \right)
\]

\[
Z^* = \left( \frac{pZ_A^{\frac{1}{2}} + qZ_B^{\frac{1}{2}} + \ldots + rZ_C^{\frac{1}{2}}}{p + q + \ldots + r} \right)
\]

- \( k_1 = \text{input parameter} \)
- \( k_2 = \text{input parameter} \)
- \( \rho = \text{density} \)
- \( M = \text{molecular weight} \)
- \( Z = \text{atomic number} \)
- \( E = \text{electron energy (eV)} \)

The TPP-2M equation is defined as:

\[
\lambda = \frac{E}{E_p^2} \left( \beta \ln(\gamma E) - \frac{C}{E} + \frac{D}{E^2} \right)
\]

\[
\beta = -0.10 + \frac{0.944}{(E_p^2 + E_g^2)^{0.5}} + 0.069 \rho^{0.1}
\]

\[
\gamma = 0.191 \rho^{-0.5}
\]

- \( C = 1.97 - 0.91U \)
- \( D = 53.4 - 20.8U \)
- \( U = \frac{N_e\rho}{M} = \frac{E_p^2}{829.4} \)
- \( E_p = \text{plasmon energy} \)
- \( E_g = \text{bandgap energy} \)

By inputting the necessary parameters into the database, it was possible to extract an equation for the relationship between signal attenuation and film thickness. The specific equations that are used to estimate this relationship involve complex emission distribution functions and scattering theory. These equations can be referred to in the

For the majority of film thicknesses reported, the thicknesses were estimated based on the attenuation of the Si 2p photoelectron peak. As an example, the thickness of a MgO film can be estimated by the equation:

$$MgO_{\text{thickness as-deposited}} = -27.636 \ln \left( \frac{Si_{\text{SiC as-deposited}}}{Si_{\text{SiC pre growth}}} \right) + 0.2011$$

In this equation, the thickness of MgO in angstroms is related to the attenuation of the Si 2p attenuation. The attenuation is equal to the intensity of the peak after film growth divided by the intensity before film growth. From this equation, and similar equations for the attenuation of Mg 2p through BTO and Si 2p through BTO, all film thicknesses were estimated within a 10-20% error. TEM characterization of a MgO film confirmed that the estimated film thickness by this method was within the inherent error range and around 10%.

In addition to estimating film thickness for as-deposited film, section 5.2.5 in the Results and Discussion section discusses the formation of a SiOₓ layer during various exposure treatments at elevated temperatures. Due to the intricacy of the SiOₓ interface formation and lack of reference attenuations, the thickness calculations became significantly more complex. Listed below is a detailed description of the process to estimate the MgO and SiOₓ layer thicknesses.
1) The thicknesses (Å) of the as-deposited films were calculated based on the NIST database by the equation:

\[
MgO_{\text{thickness \ as-deposited}} = -27.636 \ln \left( \frac{Si_{\text{SiC \ as-deposited}}}{Si_{\text{SiC \ pre \ growth}}} \right) + 0.2011
\]

2) From this thickness, a relationship between Mg 2p area and thickness was determined. This is possible because the area is directly related to the total number of atoms responsible for emitting photoelectron within the sampling volume. Therefore, for every area, \(a\), we have thickness, \(t\) (Å).

3) This relationship is then used to calculate the thickness of MgO after treatment. Assuming the MgO remains on the surface (verified by RHEED), the new area, \(a'\), can be related to the new thickness, \(t'\) (Å), designated by \(y\) above.
4) Since \( y \) is now known, \( Y\% \) can be calculated by the equation above. This is the component of substrate attenuation that is due to the MgO film only. This value is now fixed and is no longer a variable in the equation. If there was no SiO\(_x\), then the silicon would be attenuated \( Y\% \). However, the silicon is attenuated to \( X\% \), where \( X\% < Y\% \). The extra attenuation is due to the SiO\(_x\). (Note: attenuation is not linear so it is not safe to assume \( Y\% + Z\% = X\% \))

5) The overall attenuation of silicon originating from bulk SiC (Si\(_{SiC}\) ...) is known by taking the ratio of the Si 2\( p \) area after treatment and the area from the clean substrate (\( X\% \)).

6) From the NIST database, a relationship was developed between SiO\(_x\) thickness (\( z \)) and silicon attenuation (originating from SiC) (\( Z\% \)).

7) The overall attenuation of silicon is attenuated by \( y \) (\( \text{Å} \)) of MgO (known) and \( z \) (\( \text{Å} \)) SiO\(_x\). The only unknown is now \( z \), which was manually varied in the above equations to get different values for \( Z\% \).

8) Now there is a known (fixed) overall silicon attenuation of \( X\% \), a known (fixed) silicon attenuation of \( Y\% \) through MgO, and a variable (unknown) silicon attenuation through SiO\(_x\). This means that the overall attenuation consists of both the \( Y\% \) and \( Z\% \) components by the relationship \( X\% = Y\% \times Z\% \). Meaning that the original silicon signal is attenuated to \( Z\% \) initially, resulting in \( A \times Z\% = A' \). The attenuated signal \( A' \) is then attenuated \( Y\% \), resulting in \( A' \times Y\% = A'' \). Giving the overall equation of \( A'' = A \times Z\% \times Y\% \). Since \( A''/A = X\% \), we get \( X\% = Z\% \times Y\% \)

9) This can now be iterated by adjusting \( z \) to get the appropriate \( X\% \)

Appendix: 47
Although accurate thickness quantification is very difficult by this method, the associated error is consistent for each sample, which allows for qualitative comparison between the different exposure conditions. Thus arguments are made based on a relative comparison in order to support the qualitative analysis of undesirable interface degradation between the MgO and 6H-SiC.