Understanding thin film formation through Molecular Beam epitaxy studies of atomic-level interactions in order to link deposition process conditions to device performance in 2 materials: MgO and Cs₃Sb

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ABSTRACT

The understanding and control of initial states of film formation acquired by building correlations between deposition parameters (e.g. substrate temperature, relative fluxes) and film metrics (e.g. chemistry, structure, quantum efficiency) can open up new possibilities in the development of engineered thin film materials that can meet the evolving and necessary performance requirements of next-generation two-dimensional electronic materials. Robust correlations between deposition parameters and film metrics are also necessary to engineer scalable manufacturing processes that produce consistent material quality results. The work of this dissertation builds the case for dynamic, real time characterization of film formation and explores next-generation X-ray light source materials needed to achieve this probing of bond formation.

Studies of the chemistry and structure evolution of the MgO films grown on SiC suggest that the starting substrate surface chemistry and structure is critical to effective integration, and the etching mechanism using hydrogen seems to be key in controlling the starting surface. We have investigated the effect of two different cleaning mechanisms on the chemistry and structure of 6H-SiC (0001). The hydrogen furnace cleaning at 1600 °C of 6H-SiC (0001) substrates surfaces proved to produce a smooth, uniformly stepped surface and a $\sqrt{3}\times\sqrt{3}\ R30^\circ$ surface reconstruction, with less than 10 at% residual oxygen contamination. Whereas, the atomic hydrogen cleaning of 6H-SiC (0001) substrates was observed to produce a (1×1) surface structure with less than 7 at% residual oxygen contamination at relatively low temperature of 700 °C. In addition the structure and initial layers of crystalline MgO (111) films deposited on SiC (0001) by MBE are greatly affected by the resulting chemistry of the MgO films. The MgO deposited by MBE on SiC prepared
by the hydrogen furnace was found to have both two dimensional and three dimensional features even at thickness of around 2nm. Although the MgO template is seen to be effective and necessary to promote the pseudo-hexagonal, heteroepitaxy of BTO(111), The chemistry and structure of high quality BTO films are highly dependent on that of the under-layer MgO films. Therefore, it is necessary to understand atomic level mechanisms involved in the nucleation and growth of thin films on solid surfaces, in order to develop consistent processing strategies capable of producing high-quality MgO thin film in a reproducible way. However, the challenge of reproducing desired film properties is generally highly impeded by the limitations of static characterization techniques that are available and used in the MgO film study. Dynamically observing how bonds are formed in real-time at surfaces and interfaces is needed in order to have a more consistent process for enable films through a variety of techniques.

The challenges and limitations of using static characterization techniques to develop a consistent process for enable high quality MgO and BTO films led to the study of Cs$_3$Sb systems for next-generation X-ray light sources capable of probing atomic bonding in a dynamic way. Through the use of MBE techniques, a new growth method capable of growing atomically smooth Cs$_3$Sb thin films was explored. The co-deposition of Cs$_3$Sb yielded stoichiometric thin films with high quantum efficiency (20% at 405 nm, 8% at 532 nm) which is one step toward the overarching goal of developing nano-engineered materials that favor electron transport in the direction normal to the surface, while maintaining high quantum efficiency and minimizing the energy spread of the electrons. Detailed investigations performed suggested that the successful growth of photoactive Cs$_3$Sb thin
films is highly dependent on a careful balance between the initial stoichiometric flux ratio, substrate temperature and growth rate.

Although, many other important properties (surface roughness, intrinsic emittance, response time) were not investigated in this study, the successful demonstration of the co-deposition of high quantum efficiency Cs$_3$Sb thin films is an important contribution toward exploring novel mechanisms capable of improving desired fundamental material properties. The full implementation of next-generation X-ray light sources remains a goal which goes beyond the current status of this study: toward showing atom-to-atom detail of the time evolution of electronic charge in bonds. This can be beneficial for all applications, including MBE where viable and reproducible processes for commercially manufacturing 2-D materials are still being developed.
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CHAPTER 1: Understanding the impact of growth parameters on the successful integration of MgO on SiC and BTO on MgO/SiC


1.0 INTRODUCTION

Barium titanate (BaTiO$_3$) is a popular ferroelectric semiconductor oxide used in the electronics industry. Because of its spontaneous polarization it has been used in technological applications such as data storage, transducers and capacitors. Recently its thermoelectric properties have attracted attention [1]. The generalized hypothesis driving this research is that since properties of oxide materials can be controlled by manipulating chemistry, nano-scale structure, understanding the nucleation and growth mechanisms of single crystal BTO films is the first step toward successfully engineering thin film heterostructures on wide bandgap semiconductors that are capable of yielding desired thermoelectric performance. Because of its capability for atomic level control, molecular beam epitaxy (MBE) is a perfect tool to effectively understand the nucleation and growth mechanisms necessary to control chemistry and structure. The research focus is on understanding atomic level mechanisms involved in the nucleation and growth of oxide thin films on solid surfaces in order to enable development of processing strategies that integrate high quality films on SiC and ultimately provide guidelines on how to engineer thin films with desired properties. Therefore, the strategy of this work was to use MBE to grow BTO thin films on the wide bandgap semiconductor SiC using a desirable interface layer, in order to understand the growth mechanism and interface layer impacts on those growth mechanisms.

This work explored: 1) the role of different starting surfaces on the resulting film quality by developing repeatable, well characterized SiC starting surfaces using two different cleaning methods, 2) the understanding of the initial bonding state at the SiC-MgO interface in order engineering an effective template based on chemical O-bonding
and lattice constant, 3) the impact of various fluxes and surfaces on film quality to understand initial growth mechanisms of BTO/MgO/SiC.
2.0 BACKGROUND

Many materials and processing challenges must be overcome to effectively study the integration of BaTiO₃ films with 6H-SiC, including interface mixing both at the substrate and in between functional layers, stoichiometry control to achieve desired functional film properties, and structure control to engineer films. In order to overcome these challenges, it is necessary to incorporate known characteristics of the oxides (e.g: oxygen-to-oxygen atom spacing) with mechanisms of thin film growth in order to understand what influences and impacts those mechanisms.

2.1 Functional oxides: Barium Titanate (BTO)

The properties of functional oxides are sensitive to changes in their environment, which makes them ideal candidates for dynamic devices such as sensors and smart controllers. Example environmental changes include temperature, mechanical stress, electric field, or magnetic field. In order to take advantage of the functionality of these oxides and tune their properties and advance their performance for next-generation devices, optimization of their growth onto a wide bandgap semiconductor is necessary.

2.1.1 Barium Titanate structure, BaTiO₃ (BTO)

Barium titanate (BTO) adopts the perovskite (ABO₃) structure with Barium ions, large in size (~158 pm) occupying the corner sites, titanium ions small in size (~60 pm) located at the centers of the cube (the oxygen octahedral) and the oxygen anions are on the face-centers. The lattice type is cubic with \( a = 4.009 \) Å. A more comprehensive schematic of the crystal structure of BTO is given in Figure 1.
Figure 1: Crystal structure of BTO. Green atom is barium and blue-red octahedral are TiO$_6$[2]

The BaTiO$_3$ simple cubic perovskite also undergoes three phase transitions with temperature as shown in Figure 2. A change in the geometry around the metal ions caused by a change in structure and phase can cause distortions consequently affecting the splitting energy around the metal ions and potentially its thermoelectric properties.

Figure 2: Phase transitions in bulk BaTiO$_3$ and direction of the polarization vector P [3]

The Ba$^{2+}$ ions (blue balls) are located at the corners of the unit cell, the O$^{2-}$ ions (red balls) are at the centers of the six planes of the unit cell, and Ti$^{4+}$ ion (green ball) is in the center of the unit cell. The paraelectric-to-ferroelectric transition occurs at $T_C$ around 403 K and its perovskite structure changes from the cubic paraelectric phase to a
ferroelectric tetragonal phase [3]. Each transition is accompanied by its own atomic displacement, structure and microscopic strain. A permanent ionic dipole moment in ferroelectric phases results from the displacement of the $O^{2-}$ and $Ti^{4+}$ ions from their symmetrical positions. The strong dependence of the properties of metal oxides on atomic structure mean a high degree of control over the stoichiometry as well as the structure of the films is required to achieve the desired phase. This makes MBE a perfect tool to both study and deposit these materials.

Controlling the oxidation state of the metals in BTO is important because different metal oxidation state will generate different chemistry, structure, bond length which are seen in literature to impact film properties [4]. In addition to the chemistry, the underlying substrate can largely affect thin-film BTO’s properties because the substrate surface plays a role in how the film in grown therefore. When growing epitaxial films the crystallographic properties of the substrate, especially the crystal symmetry and lattice constant are major influences on epitaxial film quality. With MBE, we can discover how to tune the metals oxidation state during film growth and link structural and chemical changes to process parameters.

2.2 Wide band-gap (WBG) semiconductor substrate: 6H-SiC(0001)

The increasing spectrum of important functionalities required for developing and optimizing materials to our modern requirements of high-temperature operation, device density, and energy efficiency, requires substrates that go beyond the capability of silicon. Wide bandgap (WBG) semiconductor materials are defined as materials with a band gap greater than the 2.2 eV of silicon [5]. 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, making the power electronic modules using these materials significantly more powerful and energy efficient than those made from conventional semiconductor materials. The physical and electrical properties of SiC 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, as seen in Table 1. For this reason, the study of BTO thin film growth mechanisms is coupled to its integration on wide band-gap semiconductors specifically 6H-SiC.

Silicon carbide (SiC) is a wide bandgap semiconductor which has over two hundred different polytypes (same chemical formula, different crystalline structure). Different polytypes of SiC are actually composed of different stacking sequences of the Si–C bilayers. Therefore, the nomenclature number indicates the number of atomic stacks per unit cell, and the letter indicates the crystal structure. For example, “6H” refers to hexagon polytypes with 6 stacking layers. Therefore, 6H-SiC has six stacked tetrahedrons per unit cell, which are arranged in a hexagonal (H) structure. The most popular polytypes of SiC are 6H-SiC, 4H-SiC, and 3C-SiC. As laid out in Table 1, the three common SiC polytypes have different electrical properties from each other.

<table>
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<tr>
<th>Table 1: Comparison of the electrical properties of major SiC Polytypes with Silicon and GaN [6].</th>
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<tr>
<td>Property</td>
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<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>Bandgap</td>
</tr>
<tr>
<td>Electric Breakdown Field (KVcm⁻¹)</td>
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<tr>
<td>Thermal conductivity (W/cm-K)</td>
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Although 6H-SiC, 4H-SiC, and 3C-SiC and GaN all exhibit properties as WBG semiconductors, The high bandgap energy, low intrinsic carrier concentration and high thermal conductivity of 6H-SiC cause WBG-based devices to tolerate much higher operating temperatures in a smaller size than the equivalent silicon-based device, enabling previously impossible applications. The high breakdown field and high thermal conductivity of 6H-SiC coupled with high operational junction temperatures theoretically permit extremely high-power densities and efficiencies to be realized in SiC devices.

2.3 Epitaxy and Atomic mismatch

Epitaxy is defined as the extension of the crystal structure from a crystalline substrate [7]. There are two types of epitaxy: homoepitaxy and heteroepitaxy. Homoeptaxy refers to epitaxial film growth where the film and substrate are the same material with the same crystal structure and orientation. An example of this is the epitaxial growth of MgO on an MgO substrate, denoted (MgO/MgO). Heteroepitaxy refers to film growth where the film is a different material than the substrate yet retains the atomic structure alignment with the substrate. An example of heteroepitaxy is the growth of BTO on a SiC substrate, denoted (BTO/SiC), which is the primary focus in this proposal. 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 structural properties, resulting in a mismatch.
between the film and substrate. However, convention defines heteroepitaxy as the direct integration of a single crystalline film on a single crystalline substrate [8].

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

\[
\text{Lattice mismatch} : \frac{a_{i+1} - a_i}{a_{i+1}} \times 100 \quad (1)
\]

Where \(a_{i+1}\) is the bulk lattice parameter of the subsequent film and \(a_i\) is the bulk lattice parameter of the substrate.

These lattice parameters refer to the unstrained lattice parameters of the substrate or the film and are defined as the length of one unit cell of the crystalline material. During film growth, the lattice 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 crystal structure of a surface is usually different as that of the bulk material because the loss of periodicity in the vertical direction leaves energetic broken bonds. A “critical thickness” where the surface structure differs from the bulk occurs when the atoms with uncompensated energetic bonds seek to lower their energy by reorganizing. As a result of loss of periodicity of underneath layer/substrate, a disturbed interface layer is generated known as selvedge. The selvedge layer is a reconstruction of the top four atomic layers of the substrate. There is a change in the electron density and electron state in the selvedge layer, which can cause a difference in the electron properties between the selvedge layer and the bulk semiconductor substrate [16], as well as a difference in atomic spacing.
creating a potentially different “lattice constant” on the surface than the bulk crystal structure would suggest. 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 [9]. These strains can propagate causing various defects in the films. If the lattice mismatch between the film and substrate is too large, the resulting film is often polycrystalline or even amorphous.

Lattice mismatch can also be compensated by unit cell arrangement. Equation (25) only relates lattice constants to a lattice mismatch parameter, assuming a 1:1 unit cell line up. However, it is possible to have other configurations that reduce lattice mismatch, when the net lattice spacing between a serious of atoms is similar. As illustrated in the Figure 3, four unit cells of cubic film line up with three unit cells of a cubic substrate. For example, MgO film, with a lattice constant of 4.213 Å, has a 34.1% mismatch with GaAs substrate, with a lattice constant of 5.65 Å. This large lattice mismatch can be resolved when 4 MgO atoms line up with 3 GaAs atom at the interface, which results in a mismatch of 0.58 % for the 4:3 pattern [10].

Figure 3: Cross-sectional HRTEM images of MgO films deposited on GaAs(001) at 100 °C, yellow and white circles indicated the 4:3 registry of the MgO and GaAs lattice respectively[9]
In addition, using an interlayer or template layer between the substrate and the thin film can improve the quality of the resulting film both by eliminating reactions between the semiconductor substrate and the thin film layer and by providing a more favorable lattice match on which the film can sit [11]. Templates are thin films of a few nanometers thick, which serve as a bridge between the substrate and film. The lattice parameter of a template material can often lie between that of substrate and film. An example of this is BaTiO$_3$ (BTO) on SiC (0001), using MgO (111) as a template layer. 6H-SiC (0001) has a bulk lattice spacing of 3.08 Å compared to the oxygen to oxygen lattice spacing of BTO(111), which is 2.83 Å. The oxygen to oxygen lattice spacing of MgO (111) is 2.98 Å, which when integrated as a heteroepitaxial template, can reduce lattice mismatch and help create an effective interface through controlled heteroepitaxy [12].

The use of a template layer may enable the growth of single crystal films, however, its use changes the interfacial properties. As a result, the performance of the ultimate device may be limited by the MgO interlayer. Consequently, there must be a tradeoff between effective integration of tetragonal metal oxides with the wide bandgap semiconductor (requiring a template layer) and film properties. Addressing this tradeoff is beyond the scope of this dissertation, but this needs to be considered when developing strategies for engineering interface to integrate single crystal films.

2.3.1 Thin film growth mechanism: Generalized Theories

There are three generalized way of describing thin film growth mechanisms: (1) Volmer–Weber (island growth), (2) Frank–Van der Merwe (layer-by-layer growth), and (3) Stranski–Krastanov growth (combined island and layer-by-layer growth). These growth mechanisms are illustrated in Figure 4. Volmer–Weber island growth (Figure
4(a) occurs when the smallest stable clusters nucleate on the substrate and grow three-dimensionally so that island features form. One simplistic explanation for this growth behavior is that the atoms or molecules being deposited are more strongly bonded to each other than to the substrate material. This is often the case when the film and substrate are extremely dissimilar materials. This growth mode is typically observed when metal and semiconductor (i.e., Group IV, III–V, etc.) films are grown on oxide substrates.

Frank–Van der Merwe (layer-by-layer growth) (Figure 4(b)), occurs when the extension of the smallest nucleus on the surface occurs preferentially in two dimensions resulting in the formation of planar sheets. In layer-by-layer growth the depositing atoms or molecules are more strongly bonded to the substrate than each other and each layer is progressively less strongly bonded than the previous layer. This effect extends through the growing film until the bulk bonding strength is reached called critical thickness. When the critical thickness is reached, the film will “relax” into its bulk structure which may or may not disrupt the epitaxy of the growing film.

The Stranksi–Krastanov mechanism (Figure 4(c)), is a combination of layer-by-layer and island growth. After forming one or more monolayers in a layer-by-layer fashion, continued layer-by-layer growth becomes energetically unfavorable and islands begin to form. This sort of growth has been observed in a number of metal–metal and metal–semiconductor systems.
Figure 4: Illustrations of the basic growth modes including (a) Volmer–Weber (island), (b) Frank–Van der Merwe (layer-by-layer), and (c) Stranski–Krastanov growth [6].

Nucleation and growth mechanism 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 [8]. In general, the growth mechanism 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 understand the nucleation and growth mechanism for epitaxial film interaction.

In general, the growth mechanisms can be controlled kinetically or thermodynamically. More specifically, 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. When a molecule or an atom hits a surface, it can jump off or become
adsorbed to the surface. The time that the adatom spends remaining on the surface is called the residence time. This adatom or molecule that stays on the surface can either physically adsorbs on the surface (physisorption), or chemically bonds to the surface (chemisorption). During the limited residence time, those adsorbed species can migrate along the surface, and then either find a favorable site bond to the surface or desorb back into the gas phase.

The probability that a gas molecule that hits a surface will stay permanently on the surface and involve in the film growth is called a sticking coefficient. Once the bond is formed with the substrate, film nucleation and growth mechanisms are controlled by the chemical interaction between these adatoms, the substrate atoms, and the vapor phase atoms. The atomistic nucleation process on the substrate surface during a vapor deposition is illustrated in Figure 5. The mechanical equilibrium among the horizontal components of the interfacial tensions between the constitutive phases yields Young’s equation:

\[ \gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta \quad \text{or} \quad \cos \theta = \frac{(\gamma_{sv} - \gamma_{fs})}{\gamma_{fv}} \]  

(2)

Where the \( \gamma \) is the interfacial energy, subscripts \( s, f, \) and \( v \) stand for substrate, film, and vapor respectively, and \( \theta \) is the contact or wetting angle.
Figure 5: Schematic of basic atomistic nucleation process during film growth [6].

This equation helps to better understand the three types of film growth. For island growth, \( \theta > 0 \) therefore \( \gamma_{sv} < \gamma_{fs} + \gamma_{fv} \). If \( \gamma_{fs} \) is neglected, this relation suggests that island growth occurs when the surface tension of the film exceeds that of the substrate that result in three-dimensional growth. Hence this is why metals tend to cluster or ball up on ceramic or semiconducting substrates.

On the other hand, in layer-by-layer growth, the film wets the substrate, hence \( \theta \approx 0 \) and therefore \( \gamma_{sv} \geq \gamma_{fs} + \gamma_{fv} \). In this growth mode, the atoms of the depositing film are preferentially bound to the substrate while not to each other. This growth is also called two-dimensional growth. Crystalline growth or epitaxial growth of high quality film requires this growth mode for flatness and uniformity of thickness. A special case of this condition is so-called homoepitaxy where the interface between substrate and film essentially vanishes and \( \gamma_{fs} = 0 \). For high quality layer-by-layer deposition one typically needs a film and substrate with only small differences in surface energy and in general materials with low surface energies will wet surfaces with higher surface energies. In the last case, for Stranski–Krastanov growth initially \( \gamma_{sv} \geq \gamma_{fs} + \gamma_{fv} \) is satisfied leading to layer-by-layer growth, but the buildup of strain energy from lattice mismatch of film and substrate can lead to a transition to island like growth (three-dimensional growth) typically after 5–6 monolayers. In the model of Figure 5, the process goes as follows:
energetic vapor atoms impinge on the solid surface of the substrate, then, they may desorb immediately or remain on the surface for a period of time. While on the surface, they can migrate across the surface until they meet a nucleus and attach to it, meet a reactive site on the surface and attach to it, or desorb. As the nuclei grow, they can coalesce with other nucleating regions to form larger regions of film. When this coalescence continues, exposure of previously covered substrate allows further nucleation and the increases in size of the coalescing regions allow more adatoms adding to their bulk.

2.3.2 Thin film growth mechanism: The Realistic Challenges

The film nucleation and growth mechanisms discussed previously are simplistic models that apply to an idealized system such as a metal-on-metal deposition. As film material deposits on the surface of the substrate, nucleation can occur in a number of ways at step edges or defects which have different energy profiles. The lack of detailed atomistic assumptions makes those mechanisms an attractive broad generality. However, when considering systems such as BTO grown on SiC, where impinging oxygen radical interacts with the growing surface in addition to reaction with available atoms, the growth mechanisms may become more intricate. Since different atoms have different sticking coefficients on the surface, the atomic densities of the elements on the surface will be different, and thus influence the nucleation and growth process.

The generalized models also do not take into account relative chemical reactivity of the atoms to the surface or to each other. The complexity of nucleation and growth mechanisms for vapor deposition of non-ideal materials in heteroepitaxial system cannot be fully modeled by the generalized theories. This is particularly true when growing
nano-scale films where the interface is a large proportion of the film volume and plays just as much of a role in the film properties as the film itself.

In addition, the substrate surfaces themselves are not inert to the nucleation and growth process. Surfaces are defined as a few atomic layers on the top of a solid and represent an atomically clear interfacial separation between condensed-phase and gas-phase atoms. Associated with these interfaces or surfaces are interfacial energies. Because the atoms at free surfaces have fewer bonds with surrounding atoms than that of bulk atoms, they tend to be less constrained and more energetic. The difference of the interatomic energy of atoms at these two locations is the cause of surface energy. The basic definitions of surface energy is related to the reversible work (dW) on a material when its surface area (A) is increased, or dW= γdA. The change in either A or γ can change the surface energy.

It is very important to understand the nature of substrate surface energy, because it determines the interactions between the gas-surface, the reactivity of the surface, and thus the subsequent film growth. Substrate surface reconstruction leads to a different crystal structure at the surface than that of the bulk material, consequently alters the surface free energy. Different kinds of reconstructions lead to different starting point for the growth process and different initial template for subsequent film growth. The reconstruction may also impact surface reactivity. In addition to surface reconstruction, anything that modifies the energy of the surface will affect the reactivity. Surface modifications relevant to this work that can affect gas-surface interactions are 1) atomic steps on the surface which have the potential to provide different reaction probabilities for an adsorbed species than an atomic plateau [13], and 2) the chemistry of the surface.
Thus, the generalized theories of nucleation and film formation are not adequate to explain or control the heteroepitaxial interface formation for complex oxides on WBG semiconductors. The purpose of this dissertation is to help better understand the true complexity of the mechanisms and enable future researches to develop robust and consistent manufacturing processes.

2.4 Thin film characterization

In this section different analytical instrumental techniques used to characterize our thin films are described with relevant principles of their operation. The characterization techniques involve in this study consist of in-situ (sample is not exposed to laboratory air) and ex-situ (outside of the vacuum chamber) techniques. In-situ reflection high energy electron diffraction (RHEED) is used to monitor the crystallinity and measure the surface atomic arrangement for single crystal surfaces and surface reconstruction. X-ray photoelectron spectroscopy (XPS) is used to measure atomic stoichiometry of the films and bonding states of the atoms. Atomic force microscopy (AFM) is used to measure surface morphology and transmission electron microscopy (TEM) is used to image atomic structure.

2.4.1 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is the most widely used surface analysis technique to determine the composition and bonding information of a sample surface. In this context, the surface is defined by the electron escape depth from the materials and is typically 10 nm or less below the top layer of atoms. The sample is irradiated with soft x-rays (1486.6eV) from an Al anode or (1253.6eV) from an Mg anode) causing electrons to be
emitted from the sample surface. The kinetic energy of the emitted electrons is then analyzed by the electron spectrometer. From the measured kinetic energy of the emitted electron, and the known incident x-ray energy, the electron’s binding energy is determined by the following energy balance[14]

\[ BE = h\nu - KE - \phi \]  \hspace{1cm} (3)

Where \( BE \) is the binding energy of the photoelectron, \( h\nu \) is the energy of the incident photon, \( KE \) is the kinetic energy of the photoelectron, and \( \phi \) is the work function of the spectrometer. The work function term \( \phi \) is an adjustable instrumental correction factor that accounts for the few eV of kinetic energy given up by the photoelectron as it becomes absorbed by the instrument's detector. It is a constant that only needs to be adjusted when calibrating the instrument to a specific UHV chamber arrangement. Since the binding energy of the photoelectron is characteristic to a specific atom and atomic orbital regardless of incident energy and instrumentation, it can be used to identify the elements present. As a result, the position and shape of the photoelectron spectra can be used to obtain the bonding states of specific elements.

For iron, the Fe2p core level spectrum is mostly used to differentiate the oxidation state of iron. The Fe 2p peak is always split into two due to spin–orbit coupling (Fe 2p_{1/2}, Fe 2p_{3/2}). Nevertheless, in the oxidized state an additional satellite peak appears in between the Fe 2p_{1/2} and Fe 2p_{3/2} components: for FeO (Fe^{2+}) this peak is situated 4.5 eV above the Fe 2p_{3/2} component, while in the case of Fe_{2}O_{3} (Fe^{3+}) the satellite occurs 8 eV above the Fe 2p_{3/2} component. The spectrum on the right in figure 6 contains reference peaks of the three possible combinations of Fe oxidation states. In the particular case of Fe_{3}O_{4}, the presence of Fe^{2+} and Fe^{3+} in a 1:1 ratio leads to the equal presence of both
satellites and thus an unresolved structure between the two spin–orbit components. The absence of a resolved satellite peak is therefore characteristic of the Fe$_3$O$_4$ layer.

![Fe 2p XPS spectrum of a Fe3O4 (3 nm) thin film with reference spectra of FeO, α-Fe2O3 and Fe3O4 single crystals [24]](image)

Figure 6: Fe 2p XPS spectrum of a Fe3O4 (3 nm) thin film with reference spectra of FeO, α-Fe2O3 and Fe3O4 single crystals [24]

XPS can be considered a surface sensitive characterization technique. The photons that hit the sample have limited penetrating power in a solid of the order of 1-10 micrometers, but the surface sensitivity arise from the emission and detection of the photoemitted electrons. The mean free path of an electron is a few nm, therefore XPS can analyze up to the top 10 nm of material. Our 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 (1253.6 eV) and Al (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 is performed using the integrated Shirley method, which is the preferred method for inorganic crystalline solids [14]. The analysis spot size for XPS is controlled by a manually set aperture and is typically set at a diameter of 1.1 mm. The analysis
volume is therefore defined as the cylinder of 1.1mm diameter and 10nm height. XPS data collection and processing is performed using RBD Instruments AugerScan software version 3.22.

The basis for quantification of XPS is that the photoelectron intensity, in other words, the area of the background subtracted photoelectron peak, of an element’s core level is proportional to the number of atoms within the analyzed sample volume. For a sample that is homogenous in the analysis volume, the number of photoelectrons per second in a specific spectral peak is given by:

$$I = n f \sigma \theta y \lambda A T$$  \hspace{1cm} (4)

Where \(n\) is the number of atoms of the elements per \(\text{cm}^3\) of sample, \(f\) the x-ray flux in photon/\(\text{cm}^2\)-sec, \(\sigma\) is the photoelectric cross section for the atomic orbital of interest in \(\text{cm}^2\), \(\theta\) is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, \(y\) is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, \(\lambda\) is the mean free path of the photoelectrons in the sample, \(A\) is the area of the sample from which photoelectrons are detected, and \(T\) is the detection efficiency for electrons emitted from the sample. From (4):

$$n = I / f \sigma \theta y \lambda A T$$  \hspace{1cm} (5)

The following relation shows the relative atomic concentrations of elements A and B assigning the denominator in eq (31) the symbol \(S\), defined as the atomic sensitivity factor.

$$\frac{n_A}{n_B} = \frac{I_A/S_A}{I_B/S_B}$$  \hspace{1cm} (6)
Note that the dependence on $f$ and $\theta$ is canceled out if the measurement is performed under identical conditions. All the parameters in the denominator of eqn 5 are constant except $\sigma$ and $\lambda$ who vary somewhat from material to material, Thus for any spectrometer, we may develop a set of relative values of $S$ for all of the elements. A generalized expression for determination of the atom fraction of any constitution in a sample, $C_x$ can be written as:

$$C_x = \frac{n_x}{\sum n_i} = \frac{I_x/S_x}{\sum I_i/S_i}$$

(7)

X-ray photoelectron spectroscopy is also used to determine the thickness of thin films using NIST database 82: Electron Effective Attenuation Length (EAL).

### 2.4.2 Reflection High Energy Electron Diffraction (RHEED)

Reflection High Energy Electron Diffraction (RHEED) is an in-situ electron diffraction technique for the determination of surface structure in a high vacuum environment. Here a high-energy electron beam (5-100 keV) is directed toward the sample at a grazing angle, less than $2^\circ$ of incident. As a result, the resulting diffraction pattern is characteristic of only the top few monolayers of the crystal making RHEED a surface sensitive technique. 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. RHEED is therefore a surface sensitive analysis technique.

RHEED can be used for interpreting and extracting various features of the crystal. For a perfectly 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 distinct spots.

Figure 7: RHEED characterization of the crystal structure of BTO films grown on MgO/6H-SiC with various Ba/Ti stoichiometric ratios[15]

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 determining the crystal structure and growth rate, other information can be extracted from the RHEED patterns. The presence of Kikuchi lines is 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. Through analysis of the resulting pattern, it is possible to infer the structure and morphology of the surface.
2.4.3 High Resolution Transmission electron microscopy with energy dispersive X-ray spectrometry (HRTEM with EDS)

High-resolution transmission electron microscopy (HRTEM) is useful for studying the local environment of materials since it combines structural and chemical characterization at the nanometer scale. HRTEM is particularly useful for interface characterization, verification of sample thickness, identification of structural defects and analysis of mechanical strain. For transmission electron microscopy imaging, the specimen has to be extremely thin (on the order of 0.1 to 10 nm) for the highly absorbable electrons to penetrate the solid and form an image. We will work with collaborators to both collect and arrange HRTEM data. The aim is 1) to image directly the thin film and to study their structural quality, 2) to image dislocations by their strain contrast, and 3) to study interactions of the thin film with defects, particularly dislocations.

The transmission electron microscope can be compared with a slide projector. In a slide projector light from a light source is made into a parallel beam by the condenser lens; this passes through the slide (object) and is then focused as an enlarged image onto the screen by the objective lens. In the electron microscope, the light source is replaced by an electron source, the glass lenses are replaced by magnetic lenses, and the projection screen is replaced by a fluorescent screen, which emits light when struck by electrons, or, more frequently in modern instruments, an electronic imaging device such as a CCD (charge-coupled device) camera. The whole trajectory from source to screen is under vacuum and the specimen (object) has to be very thin to allow the electrons to travel through it. Not all specimens can be made thin enough for the TEM [16]
EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. When the electron beam hits the sample, there is a high probability that an X-ray will be generated. The resulting X-ray escapes the sample and hits the detector which creates a charge pulse in the detector. This short-lived current is then converted into a voltage pulse with an amplitude reflecting the energy of the detected X-ray. Finally, this voltage pulse is converted to a digital signal and one more count is added to the corresponding energy channel. Once the measurement is completed, the accumulated counts produce a typical X-ray spectrum with the major peaks superimposed on the background. Characteristic X-rays result from electron transitions between inner orbits, which are normally full. The relative weights of the Characteristic X-ray lines in each family are consistent and this, along with their energies, allows related peaks in the X-ray spectrum to be recognized. By measuring the energies of the major X-ray peaks in each family, the corresponding element can be identified.

2.4.4 Atomic force microscopy

Atomic force microscopy (AFM) is used to analyze the surface morphology of substrates and films. In addition, compared to usual scanning electron microscopy, AFM is a powerful instrument that can provide direct spatial mapping of surface morphology with nanometer resolution, allowing quantitative investigation of surface topography and roughness[17]. Our AFM characterization is performed using an Ambios Technology 2SAAVO USPM. Typically, AFM characterization is 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 is set at 1024×1024 and collected at a scan frequency of 1 Hz. AFM characterization of the surfaces is limited to the 40 µm lateral
movement of the piezotube. Therefore, multiple AMF scans need to be collected across
the sample surface in order to ensure an accurate representation of a large sample surface.
3.0 CRITICAL LITERATURE REVIEW

The heteroepitaxy of similar oxides can often be used as a basis for understanding what processing variables will be important to controlling the desired outcome in the material system of interest. It is also known [refs from our lab] that using a simple 2-element oxide as a template or “bridge” layer can promote effective integration of complex oxides with semiconductors. This literature review focuses on MgO as a known template on SiC, and 3-element oxides similar to BTO.

3.1 MgO film growth

From recent studies of MgO film growth, literature shows that substrate crystal symmetry, growth time, Mg flux and oxygen species play a key role in oxide film quality [15][18][43]. Because MgO is a binary oxide, it is obvious that the presence of oxygen (and magnesium) is necessary for the formation of MgO. However different limiting growth mechanisms have been reported. Hoerman, et al.[19] reported that by maintaining a constant oxygen plasma background pressure of $10^{-5}$ Torr and constant precursor flux of $10^{-7}$ Torr, at a substrate temperature of 650 °C, the growth rate of the MgO was 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.

However, when growing MgO using atomic oxygen in excess and a substrate temperature of 140°C, magnesium (Mg) flux controlled the growth rate and film
composition [15]. The reaction was seen to be dependent on the availability of magnesium atoms on the surface of the substrate. In this study, all of the MgO films were roughly the same thickness (20 – 25 Å). Therefore an increase in Mg flux was directly related to an increase in MgO growth rate. It was found that by increasing the Mg flux from $2.5 \times 10^{13}$ atoms/cm$^2$ sec to $3.6 \times 10^{14}$ atoms/cm$^2$ sec, the effective growth rate was increased from $\sim 0.25$ Å/min to $\sim 1.35$ Å/min. The linear relationship between Mg flux and MgO growth rate indicates a magnesium absorption controlled mechanism. This was concluded to be 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.

Although the growth mechanism is dominated by the availability of magnesium at the surface, AFM characterization of MgO nucleated and grown under various oxygen environments revealed that the reactivity of the atomic oxygen might be important in the quality of the resulting MgO films [20]. From the discussion above, it is proposed that the crystal structure, chemistry and morphology thin films strongly depend on oxygen gas pressure, oxygen species and substrate temperature.

### 3.2 BTO film growth

BTO has been studied extensively for a variety of different applications such as storage capacitors for dynamic random access memory. Its thin film counterpart is now being studied extensively due to the fact that the physical properties of BTO in thin films can be tuned or modified due to well-controlled growth conditions, careful selection of substrates, strain effects, interfacial and coupling effects leading to control of crystal structure. This can be explored to further enable the control of the electronic structure, hence thermoelectric properties of strong correlated systems like BTO. BTO films have
been grown on a variety of substrates by methods such as PLD, sputtering and MBE and those previous experiments have shown that deposition parameters play an important role in tuning the properties of the films. Therefore a critically analysis of the progress in thin film BTO growth can incorporate the findings and understandings necessary for the successful integration of high quality-BTO thin films on semiconductors with precise control of stoichiometry, crystallinity and orientation necessary for the tuning of its properties.

3.2.1 Influence of growth parameters on BTO film growth

Thin film growth by physical vapor deposition is a nonequilibrium process based on a competition between kinetics and thermodynamic factors. The kinetics (growth rate, adatom migration rate) and thermodynamic equilibrium (growth temperature, phase stability) parameters strongly influence the thin film crystallinity and crystallographic orientation. The role of the substrate temperature in controlling structure and composition of the film is a primary one. For example, Nb-doped BaTiO$_3$ thin films were deposited SrTiO$_3$ substrates using pulsed laser deposition (PLD) [21]. The substrate temperature was controlled from 575$^\circ$C to 800$^\circ$C. In result, a higher density of defects in the films grown at 800$^\circ$C compared to the films grown at 575$^\circ$C resulting in a change of lattice symmetry from a tetragonal to a cubic structure with the increase of growth temperature. BaTiO$_3$ films ($\sim$18–20 nm) were grown on SrTiO$_3$/Si under $1 \times 10^{-7}$ Torr of oxygen at different temperatures ranging from 410$^\circ$C to 580$^\circ$C [22]. The RHEED patterns displayed in Figure 8 exhibit rings when the temperature exceeds 480$^\circ$C. This could denote a polycrystalline surface but all the samples, except the one grown at 580$^\circ$C, are found to be single crystalline by X-ray diffraction. Off-stoichiometry might be induced by the temperature, leading to the segregation of Ba on the surface.
Figure 8: a)-(f) RHEED patterns recorded along the [100] azimuth of BaTiO3 grown under an oxygen pressure of $1 \times 10^{-7}$ Torr at (a) 410 °C, (b) 440 °C, (c) 480 °C, (d) 500 °C, (e) 525 °C, (f) 580 °C. [20]

At a given substrate temperature, the literature shows that the O$_2$ partial pressure also plays an important role on thin film stoichiometry and structure. For example, Zhao et al. observed a dependence of the crystallographic orientation on the oxygen pressure in the range of $1.5 \times 10^{-6}$ to $10^{-1}$ Torr for films grown on SrTiO$_3$ by laser MBE [105]. Different deposition processes involving different mechanisms and energy range for the impinging species at the substrate surface show a similar trend with oxygen pressure: an increasing oxygen pressure leads to a change from $c$-axis to $a$-axis growth (although the pressure ranges are necessarily different depending on the techniques). Gonzalo et al. studied the composition, homogeneity and crystalline structure of BTO films grown on MgO substrates by pulsed-laser deposition and found that Ti/Ba
composition is depends on the oxygen pressure. The relative content of Ba is close to that of the ideal composition: $\text{BaTiO}_3$ ($C_{\text{Ba}} = C_{\text{Ti}} = 0.5$) for films grown either at low ($P \leq 10^{-2}$ mbar) or high ($P \geq 2 \times 10^{-1}$ mbar) oxygen pressures, whereas the films show a large Ba excess in the intermediate pressure range for films grown at $\approx 10^{-1}$ mbar. The oxygen pressure is therefore expected to impact the occurrence of oxygen vacancies, the cationic composition, the nature of the defects, and the resulting strain state which is going to impact film properties.

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 TiO$_2$ 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.\cite{23} reported epitaxial growth of alternating STO/PTO (SrTiO$_3$/PbTiO$_3$) 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$_2$. 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 \cite{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. 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.

3.2.2 Influence of surfaces and interfaces on BTO film growth

Lee et al.[24][25][26] used different single crystalline, cubic oxide substrates, including MgO, STO, and KTaO$_3$ (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. The authors reported that lattice strain was much more influential on crystal structure and orientation than thermal strain. 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 also worth noting that it was reported that the formation of preferential c-axis orientation of PTO is 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. This is an important property to consider when investigating effect strain-enhanced film properties.

Another study 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 9, 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 9: Comparison of stresses between PZT and MgO, STO, and KTO; (a) effective lattice strain, (b) lattice/thermal strain ratio, and (c) net elastic strain [26].

Figure 9 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, the effect illustrated in Figure 9 (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. 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 and supports the possibly of exploiting interface strain for tuning thin film properties.

3.3 Interface importance and strain-induced functionality

Epitaxial strain induced in a thin film due to lattice mismatch with a substrate serves as a versatile controlling parameter of physical and chemical properties, including the electronic structure, conductivity, and crystallographic symmetry. Not only can it fine-tune the properties, but it can also sometimes stabilize novel behaviors, which cannot be found in bulk counterparts. Epitaxial strain is usually associated with a change in in-plane lattice constant accommodated through structural distortions such as changing the internal bond lengths or changing the angle or pattern of rotations and tilts of the oxygen octahedral (Figure 10).

![Figure 10: Schematic of possible mechanisms for epitaxial strain accommodation in perovskite.](image)
For example thin film LaCoO$_3$ (LCO) has been reported to exhibit a long-range ferromagnetic ordering below (80 K), whereas bulk LCO shows a nonmagnetic ground state. In fact, in epitaxial thin films, the mechanical stress due to the lattice mismatch between the film and substrate increases with the film thickness until the critical thickness is reached where the film relaxes.

To understand the microscopic origin of the ferromagnetism and the effect of strain, high quality epitaxial LCO thin films were grown on various substrates to impose different strain states. Woo Seok et al.[27] confirmed that high quality epitaxial thin films were grown with atomically sharp interfaces and surfaces. The films also exhibited systematic strain dependent distinct dark stripes. For the LCO film grown under slight compressive strain, only a few in-plane stripes were rarely observed (Figure 11a). As tensile strain was applied, on the other hand, LCO started to show stripes running perpendicularly to the surface (Figure 11b). As the degree of tensile strain increased, more such stripes appeared, eventually forming a fairly regular superstructure.
They observed the strain dependent microscopic lattice modulation in LCO epitaxial thin films, which yielded a novel spin state ordering. Now, in order to assess the nature of the lattice modulation-induced stripe patterns, interatomic distances from the STEM image shown in Figure 11 were mapped out. The intensity profiles for the red and green lines drawn in Figure 12a and the interatomic spacing between the neighboring La atoms are shown in Figure 12b and c, respectively. While region I (green) showed more or less equal spacing between the La atoms, region II (red) showed a clear spatial modulation, which resulted in vertical dark stripes in the image.

Figure 12: Image simulation of structural nanodomains. (a) Experimental, cross-sectional Z-contrast STEM image for the LCO film on STO (b) Intensity profile (c) In-plane atomic distances between La atoms extracted (d) Simulated, cross-sectional STEM image for a LCO film on STO (e) Cross-sectional and (f) top views for the artificially constructed LCO film structure. Yellow and orange lines in the top-view image indicate the opposite monoclinic distortion for the neighboring domains. [27]
It is known that an increase of the overall Co–O bond length in an octahedral coordination of only 0.1 Å can change the spin state from low to high spin [28]. In the present case, the Co–O bond length in the tetragonally distorted octahedra increased by as much as 0.5 Å due to the local lattice distortion (Fig.15c), which could result in an electronic structure closer to that of a square planar coordination of Co$^{3+}$. Such an unusual coordination would give rise to a distinctively different orbital occupation and spin state and hence different properties and effect [27].

Back et al. also reported the effect of tensile stress on the thermoelectric power and electrical resistivity of La$_2$NiO$_{4+\delta}$ thin film [29]. They demonstrated that the thermoelectric power in the films can be manipulated by epitaxial stress, independently of the electrical resistivity. This effect can be understood by considering the role of tensile stress on the polaron size and its contribution to the entropy per added carrier. In order to discuss a possible relationship between epitaxial strain and transport properties, two series of films of different thicknesses were grown either at 10 mTorr or 200 mTorr of oxygen. Their results show that the thermopower decreases with increased oxygen content, which is consistent with hole doping. At both oxygen concentrations, the thermopower is largest in the thinnest (most highly stressed films) and then decreases in the thicker films as their lattice parameters relax toward the bulk value. This effect of stress is actually very large, the thermopower of the thinner samples increased by more than 100% with respect to the thicker ones. This demonstrates that the thermoelectric power of La$_2$NiO$_{4+\delta}$ films is sensitive to both oxygen content and lattice strain.

These studies highlight the collective phenomena in a transition metal oxide, who’s magnetic and electronic properties are globally modified by a local structural change induced by epitaxial strain. This effect is not only crucial for the growth of BTO
but can become equally important for the growth of MgO. Since the MgO films are intended to primarily serve as an interfacial layer for subsequent epitaxial growth of metal oxide functional films, any structural strain induced in the MgO film during the growth process is pivotal to its operational quality.

3.3.1 Influence of oxygen vacancies on metal oxide chemistry

In addition to changes in internal bond lengths due to strain another possible important parameter forced by coherent epitaxy is a change in the defect profile. Oxygen vacancy is a common native point defect that can control a number of distinct properties of oxides. Aschauer et al. [30] used the perovskite CaMnO$_3$ to analyze the strain dependence of the oxygen vacancy formation reaction. When an oxygen vacancy is introduced high-spin Mn$^{3+}$ (0.645 Å) is most likely to be compensating on Mn$^{4+}$ (0.53Å) sites, it is clear that the reaction should be accompanied by a considerable volume expansion, which indeed is supported by experiments [31]. Since volume increases (decreases) with tensile (compressive) strain, the oxygen vacancy formation energy is expected to be sensitive to strain. In addition to this volume effect, strain may also affect the oxygen vacancy formation energy through its effect on the electronic energy levels. The electrons from the loss of O$_2$ which reduce Mn$^{4+}$ to Mn$^{3+}$ occupy the eg orbitals, the energies of which are strongly affected by the coordination geometry of the surrounding ions. Figure 13 shows the modeled oxygen ordering.
As expected from the known unit cell volume expansion caused by oxygen vacancies, we find that tensile strain lowers the formation energy for oxygen vacancies in CaMnO$_3$. The formation energy decreases considerably by 0.4eV corresponding to 20% of the bulk value for formation of the in-plane vacancy at 4% strain. Based on the studies cited oxygen vacancies and epitaxial strain may affect BTO and MgO film growth.

### 3.3.2 Sources of oxygen vacancies in oxide materials

One of the major sources of oxygen vacancies occurs during the formation of the crystalline film. For example Chen *et al.*[32] reported a strong influence of oxygen pressure on the ferroelectric properties of BTO films grown on SrTiO$_3$ (001) substrates by pulsed laser deposition. Guo *et al.*[33] studied the local structure around the Fe atoms in iron oxides films by XAFS$^1$. Fe$^{3+}$ ions are located in an octahedral environment in the hexagonal corundum structure of Fe$_2$O$_3$ while one-third of the iron ions are located on

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$^1$ X-Ray Absorption and Fluorescence
tetrahedral sites and two-third are located on octahedral sites (one-half being Fe$^{2+}$ and the other half Fe$^{3+}$) in the cubic inverse spinel structure of Fe$_3$O$_4$. Thus, based on their results, they believe that Fe oxidation state varies from FeO (Fe$^{2+}$) and Fe$_3$O$_4$ (Fe$^{2+}$/Fe$^{3+}$) (1×10$^{-5}$ Pa) to Fe$_3$O$_4$ (Fe$^{2+}$/Fe$^{3+}$) (1×10$^{-3}$ Pa) and then Fe$_2$O$_3$ (Fe$^{3+}$) (1×10$^{-2}$, 1×10$^{-1}$ Pa) with an increase of the oxygen gas pressure during the growth, which is consistent with the observed XRD data. The results confirmed by the magnetic hysteresis loop, where the saturation magnetic moment of the thin film grown at the oxygen gas pressure of 1×10$^{-3}$ Pa is 492 ± 10 emu/cm$^3$, that with increasing or decreasing gas pressure, the magnetic moment of the films dramatically decreases due to the properties of Fe$_2$O$_3$ and FeO phases in the films.

Oxygen pressure has been shown to have a significant influence on the structure and properties of BaTiO$_3$ films. Zhao et al. [34] observed a dependence of the crystallographic orientation on the oxygen pressure in the range of 1.5×10$^{-6}$ to 10$^{-1}$ Torr for films grown on SrTiO$_3$ by laser MBE. Zhu et al. [33] observed a change in the type of predominant defects in laser-MBE grown BaTiO$_3$ on SrTiO$_3$ by varying the oxygen pressure in the range of 1.5×10$^{-7}$ to 1.5×10$^{-4}$ Torr. Rutkowski et al. observed a dependence with P(O$_2$) of (Ba,Sr)TiO$_3$ film composition grown by MBE on SrTiO$_3$ [35].

On the other hand a perovskite oxide can transform into a brownmillerite structure with decreasing oxygen partial pressure; this process can occur reversibly even at low temperature [36][37][38]. In their study Kim et al. (La$_{0.5}$Sr$_{0.5}$)CoO$_{3-δ}$ (LSCO) thin films grown on NdGaO$_3$ (NGO) formed a brownmillerite like structure. This brownmillerite structure exhibited oxygen vacancy ordering along the (100) pseudo- cubic direction, where every other CoO$_2$ plane becomes oxygen- depleted CoO$_{2-x}$, whereas the other half of the planes stays stoichiometric. For x = 1, all Co cations in the oxygen-depleted planes
are tetrahedrally coordinated, whereas Co cations in the stoichiometric planes are octahedrally coordinated [37]. The change in the geometry around the metal ion caused by the depletion of oxygen can consequently affect its spin state.

From the above studies it is proposed that the crystal structure, chemistry of oxide thin films strongly depend on oxygen gas pressure during the growth. By utilizing the benefits of UHV, which include substrate surface preservation and low contamination rates, it is hypothesized that through precise control of the O$_2$ pressure by MBE, it will be possible to fully understand the effect of O$_2$, so that a process for desired interface can be engineered.
4.0 EXPERIMENTAL APPROACH

The ultra-high vacuum environment (UHV surface, chemical, and structural characterization) allows the atomic-level controlled environment necessary to study these influences. By utilizing the benefits of UHV and MBE, it was possible to understand how subtle differences in surfaces impact the nucleation and growth mechanisms of oxide films in order to successfully integrate single crystalline, epitaxial Barium titanate (BaTiO$_3$) on 6H-SiC with controlled orientation and stoichiometry. The role and interactions of species flux and processing parameters on the nucleation and growth mechanism of the oxide film was studied. This goal was accomplished through careful substrate surface preparation, flux and temperature studies and the correlation of stoichiometry and structure of the thin films. The first section will describe the experimental procedure employed in the growth and characterization of BaTiO$_3$ in order to successfully integrate single crystalline, epitaxial BaTiO$_3$ on 6H-SiC with controlled orientation and stoichiometry. The overall goal was broken down into smaller, more specific objectives that could be addressed individually and simultaneously. These objectives include 1) 6H-SiC substrate surface preparation, 2) heteroepitaxial integration of a high-quality, single crystalline MgO template layer, 3) understanding the heteroepitaxial integration of high-quality BTO. This implies that a detailed description of the thin film growth methods for each objective will be provided.

4.1 Hydrogen surface preparation/cleaning

Among those parameters influencing crystal structure, crystal quality and orientation of thin film, is the crystallographic properties of the substrate, especially the
crystal symmetry and the in-plane lattice constant. Since the goal is to understand the parameters affecting an effective integration with 6H-SiC which introduces a ~46% in-plane lattice mismatch with the film in compression, the quality of the epitaxial oxide film is predicted to highly depend on the starting 6H-SiC surface properties. Since, one of the most important requirements for integration of functional oxides on semiconductor is the formation of a smooth and abrupt interface between the oxide and the substrate, developing controllable strategies for reliable and effective surface cleaning is needed to produce consistent starting surfaces. The SiC substrate (6H-SiC) was cleaned by both ex-situ and in-situ methods. The ex-situ method include degrease, chemical cleaning, and hydrogen cleaning using H₂ gas in an hydrogen flow furnace, based on the procedure developed by Dr. Cai’s Ph.D study [39]. The in-situ method involved the use of an hydrogen atomic beam source to etch the surface of the substrate. Successful surface preparation requires the removal of unwanted surface contaminants, removal of scratches (tens to hundreds of nanometers deep), and the production of a smooth, uniform, reproducible surface. For the ex-situ cleaning approach, the 6H-SiC substrate is first degreased and then cleaned in a custom-built hydrogen furnace. A detailed description of the hydrogen cleaning procedure will be provided in Appendix B.

In order to obtain the desired chemistry quality and reproducibility of the starting surface, various processing variables were adjusted. These variables are cleaning temperature, time of H₂ exposure, and H₂/Ar gas composition are studied and optimized. Two other parameters were seen to affect the surface chemistry of the Si-face of the Silicon carbide: the contact between the SiC substrate and the heating element (the Ta boat made of tantalum foil), and the cooling rate. Heating of the 6H-SiC substrate was
carried out in the custom-built hydrogen furnace mentioned early which is powered by a Sorenson DCR 20-115B. The current was controlled manually and was limited to 100 Amps. The heating rate of the Ta boat was set at ~5A for every 30 second which was further limited by the deformation of the Ta boat. It was observed that when the heating rate was too fast, the Ta boat would deform resulting in poor thermal contact with the substrate and therefore non-uniform heating. This non-uniform heating can create a gradient in etching profile which directly affects the dynamics at the surface. The cleaning temperature was varied between 1400°C and 1600°C, and the Ta Boat formation process was later automated in order to have a more consistency and precision in Ta boat dimensions. The cooling rates varied from greater than 1000°C /min (uncontrolled) to 200°C /min.

4.2 Thin film preparation and growth: Molecular Beam Epitaxy

The MBE system available in the Interface Engineering Laboratory at Northeastern University and used for all oxide film growth and characterization in this study consists of two interconnected custom-built UHV chambers shown in Figure 14 with base pressure typically around 1.0×10⁻⁹ Torr.
Prior to any analysis and experiment, all samples are loaded through a small load lock chamber that is connected to the analysis chamber and separated by a UHV-compatible gate valve. The load lock chamber is independently pumped by a mini turbo pump (Turbovac 50). Once a sufficiently low pressure is measured by Leybold Ionivac hot cathode gauge (approximately 2×10^{-7} Torr), the samples are transferred in to the analysis chamber by using a magnetic arm. The analysis chamber is pumped by a Varian 500181B ion pump, which maintains a background pressure of ~2×10^{-9} Torr. It is also equipped with AES and XPS and connected to an adjoining UHV growth chamber, separated by a manually manipulated gate valve that allows transferring samples between chambers without breaking vacuum. Samples are transferred to the growth chamber (which maintains a background pressure of ~2.0×10^{-9} torr measured by an ion gauge) using another similar magnetic linear transfer arm. From the transfer arm, the sample is then transferred onto a substrate heater, which can be moved in and out (Z movement) as well as rotate azimuthally.

The growth chamber pumped by a Leybold Turbovac 600 C Turbo Pump is fitted with a custom built heater, a dual source low temperature effusion cell (for Ba and Mg), a high temperature effusion cell (Fe), a remote oxygen plasma source, a modified varian Ti-Ball (for Ti) and a RHEED system. For MgO and BTO 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. The (PBN) ceramic crucible containing the reactant is surrounded by a heating filament. This filament radiatively heats the crucible, which in turn conducts heat to the source material. As the filament increases the source temperature, the source particles evaporate out of the crucible towards the substrate. The flux of the material exiting this crucible can be controlled by the heat applied through the filament. The atomic (Ba, Ti, Mg, Fe) fluxes are calculated based on the thermocouple temperature reading and vapor pressure calculations based on equation 35

$$\phi = \frac{3.51 \times 10^{22} PA}{\pi L^2 \sqrt{MT}}$$

(8)

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 ($^\circ$C)

Based on this equation increasing the temperature of the appropriate cell (thermocouple resolution of 1$^\circ$C), increases the flux of that metal the opposite is also true. By having the ability to maintain a stable cell temperature to within 1$^\circ$C, it is possible to tune the individual fluxes to obtain desired film chemistry. Typical fluxes range 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. The effusion cell temperatures are maintained at temperatures several hundred degrees Celsius below the melting point. If
the material melts, when the material is cooled again, the ceramic crucible will crack. Due to the low vapor of titanium, a Ti-ball sublimator is used. However, precised 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.

The oxygen is supplied through the use of an Oxford Applied Research remote oxygen rf-atom source model HD25. The plasma is generated within an Al₂O₃ discharge tube and exited through an Al₂O₃ aperture plate with 276 holes that are 0.2 mm in diameter. The source is fitted with ion filter bias plates that are located at the end of the discharge tube and consisting of two parallel plates aligned parallel to the flow of oxygen. One plate is connected to ground, while the second is connected to a voltage source. When the plates are energized, by supplying a voltage bias between the two plates, any charged species (O*, O₂*, etc) would be deflected and removed from the neutral species. Typically, only neutral species with lower kinetic energy were involved in film growth. The ratio of O/O₂ is a function of how much energy is put to split the O₂ therefore it is a function of power and by varying the rf power, it was possible to vary the relative amount of O₂ that was cracked into different atomic oxygen. Thus, any flux relationship is with the active O and the metal. The oxygen environment is a combination of oxygen species, the flux is represented on the basis of individual atoms. Since, the chamber pressure reading is characteristic of molecular oxygen, the flux calculation will be performed on the basis of O₂ molecules and then multiplied by two. The oxygen flux will be calculated from the following equation:

\[
\phi_O = 2\phi_{O_2} = 2\left(\frac{3.513 \times 10^{22} P}{\sqrt{MT}}\right)
\]  

(9)
Where:

\[ \phi = \text{atomic flux (#/cm}^2\text{sec)} \]
\[ P = \text{chamber pressure (Torr)} \]
\[ M = \text{molecular weight (g/mol)} \]
\[ T = \text{temperature (K)} \]

4.3 **Heteroepitaxy of template layer**

Owing to the very good lattice match between the pseudo-hexagonal structure of MgO(111) and the hexagonal (0001) structure of SiC and between the rocksalt structure of cubic MgO and the tetragonal structure of perovskite oxides, MgO provides an ideal template for the heteroepitaxy of subsequent oxide film on 6H-SiC. For this study, the MgO templates were deposited on 6H-SiC using a low-temperature effusion cell filled with magnesium shavings (99.98%, Alpha Aesar) at a substrate temperature of 140°C in a constant oxygen plasma (100 W) environment with an oxygen pressure of 5.0 ± 0.2 \( \times 10^{-6} \) Torr (excess oxygen). Typical operating temperatures for Mg source were between 326°C-350°C. Ultimately, the MgO thin films must be single crystalline, smooth, and must have an abrupt, thermodynamically stable interface with the 6H-SiC substrate.

4.4 **BTO Thin film preparation on SiC by MBE**

One of the key factors contributing to the success of the growth of BTO via MBE is the establishment of a growth window defining the range of growth condition to achieve stoichiometric BTO. The growth of three element materials by MBE is complex because tiny flux deviations and/or fluctuations during growth result in the growth of non-stoichiometric films incorporating a high density of point defects and/or segregation of secondary phases therefore the first step was to understand the relative fluxes necessary in order to achieve single crystal, stoichiometric BTO (111).
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, the BTO film must be single crystalline and smooth and form an abrupt and effective interface with the underlying layer. Therefore, it is necessary to engineer a process capable of integrating high-quality, ferroelectric BTO on the MgO/6H-SiC.
5.0 RESULTS AND DISCUSSION

5.1 Silicon carbide (6H-SiC) substrate cleaning

The n-type 6H-SiC used were supplied by Cree Inc. and the surface of the as-received 6H-SiC surfaces consisted of residual oxygen and carbon contamination and deep (tens to hundreds of nanometers) scratches which will result in defective subsequent films. Hydrogen (H$_2$) cleaning at about 1600°C is seen to remove oxygen and carbon contaminations as seen in Figure 15 where the XPS characterization the surface before and after H$_2$ cleaning is shown. XPS survey scans revealed the presence of silicon, oxygen and carbon on the surface but also a significant decrease in residual oxygen (down to ~9 at%). In addition, tight scans of the C1s photoelectrons of the Si-terminated orientation (Figure 15 (c)) indicated the removal of C-O bonding. Further, there is a slight increase in the asymmetry of the Si2p photoelectrons (Figure 15 (b)) towards a higher binding energy which is associated with the presence of Si-O bonds.
Figure 15: XPS characterization spectra of 6H-SiC surface. (a) Survey scans, (b) Tight (elemental) scans of Si 2p showing the difference in bonding states of degreased and H2 cleaned surfaces. (c) Tight scans of C 1s spectra of degreased and H2 cleaned surfaces.

The effect of H2 cleaning on the morphology, roughness and structure of the starting surface was examined with atomic force microscope (AFM) operating in wave mode (noncontact/tapping) and with RHEED. AFM images of the as-received 6H-SiC (0001) substrate in Figure 16 (a), shows mechanical scratches randomly distributed on the surface of depth of several nanometers and width to 150 nm, which arose in the polishing process.
After H$_2$ cleaning for 18 min, no evidence of the scratches was found and Figure 16 (c) shows the etched surface with a highly smooth surface (rms roughness of 0.43 nm over a 1$\mu$m$^2$ area) and regular arrays of atomically flat terraces. Correspondingly, RHEED characterization (Si-terminated) before and after hydrogen cleaning along the <11 20> direction (one of the two directions responsible for the repeating patterns) which corresponds to the directions normal to the {11 20} plane of the 6H-SiC unit cell lattice is shown in Figure 16 (b) and (d). The surface structure prior to hydrogen cleaning showed a diffuse hexagonal (1×1) pattern which 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. A transition from the diffuse hexagonal (1×1) pattern to a $\sqrt{3}×\sqrt{3}$R30$^\circ$ surface reconstruction is also observed after H$_2$ cleaning. This surface reconstruction was determined by the formation of two fractional rings L$_{1/3}$ and L$_{2/3}$ in between the integral Laue rings L$_0$ and L$_1$. The addition of these diffraction
characteristics is associated with a reconstruction that is a result of the silicate adlayer formed during hydrogen cleaning.

However, the O composition of the H₂ cleaned SiC is seen to have a significant impact on the formation of the two fractional Laue rings, \(L_{1/3}\) and \(L_{2/3}\). Figure 17 compares the RHEED patterns of three H₂ cleaned 6H-SiC samples with different resulting atomic oxygen composition. An increase in oxygen composition from left to right where (a) has 9 at% oxygen on the surface and the other two samples displayed in (b) and (c) have 10 and 12 at% oxygen respectively as determined by XPS after H₂ cleaning. RHEED patterns of SiC with 9 at% oxygen shows the expected intermediate Laue rings \(L_{1/3}\) and \(L_{2/3}\)

![Image of RHEED patterns showing increasing oxygen at%](image)

**Figure 17:** Three surfaces with different chemistry and structure resulted under the same cleaning conditions.

However the Laue rings from the \(\sqrt{3}\times\sqrt{3}R30^\circ\) surface reconstruction become unclear and faint with increase %O composition which can be indicative of partial reconstruction, less crystal ordering and a rougher SiC surface caused by the excess oxygen. While oxygen is necessary for the formation of the silicate adlayer, excess
oxygen can be detrimental to the film/substrate interface preventing the formation of high quality films. Therefore the O composition of the starting SiC surface should be controlled and kept at 9% or lower for subsequent film growth.

It is worth noting that all three samples were cleaned using the same apparent operating procedures and cleaning parameters. However they resulted in three different % O compositions. This is thought to be due to uncontrolled variability in temperature on the surface during the cleaning process. Since temperature is one of the primary factors in both the etching process and the removal rate of the substrate surface components, the resulting SiC surface will be impacted by temperature fluctuations. The fluctuation in temperature can be caused by poor contact with the heating element (Ta boat) which would result in uneven and/or reduced thermal transfer and a lower surface temperature.

In the H\textsubscript{2} cleaning set up, the cleaning temperature is controlled by increasing the current supplied from a DC power supply through the Ta strip (Detailed explanation of the set up is discussed in appendix B). Consequently, output current values to reach the same temperature also showed fluctuations and seemed to be a function of the width of the Ta Boat. For the same output current, a narrower boat would result in a higher temperature due to the reduced cross-sectional area for current flow causing increased resistance. However, the narrower the Ta boat and the higher the temperature, the more deformation of the boat would occur which in turn caused uneven contact with the rigid and flat SiC substrate. Therefore, in order to have precise control over the temperature, the heating and cooling rates were fixed to rates that maintained the integrity of the Ta boat, resulting in sufficient contact between the Ta and the substrate, and the formation of the boat was done using an automated mold as opposed to doing it by hand in order to
have the same boat size. However, no significant improvement in repeatability was seen in resulting surface oxygen content.

Shown in Table 2 are the free energies of dissociation of SiC, the formation of silane, and other suggested reactions used to describe the decomposition of silicon carbide in the presence of molecular hydrogen [40].

**Table 2: Free energies of formation/reaction for potential reactions during the hydrogen etching of 6H-SiC (0001) surfaces.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1400 °C</td>
</tr>
<tr>
<td>SiC=Si+C</td>
<td>14.6</td>
</tr>
<tr>
<td>H₂(g) = 2H</td>
<td>60.4</td>
</tr>
<tr>
<td>Si = Si(g)</td>
<td>48.8</td>
</tr>
<tr>
<td>2C + H₃ = C₃H₅</td>
<td>32.1</td>
</tr>
<tr>
<td>0.5Si + H₂ = 0.5CH₄</td>
<td>11.3</td>
</tr>
<tr>
<td>0.5Si + H₂ = 0.5SiH₄</td>
<td>22.5</td>
</tr>
<tr>
<td>1/2SiC + H₂ = 1/2Si + 1/2CH₄</td>
<td>18.5</td>
</tr>
<tr>
<td>2SiC + H₂ = 2Si + C₃H₅</td>
<td>61.2</td>
</tr>
<tr>
<td>1/4SiC + H₂ = 1/4SiH₄ + 1/4CH₄</td>
<td>20.5</td>
</tr>
<tr>
<td>2/5SiC + H₂ = 2/5SiH₄ + 1/5C₂H₅</td>
<td>30.3</td>
</tr>
<tr>
<td>C + H = 1/2C₂H₅</td>
<td>-14.2</td>
</tr>
<tr>
<td>1/4C + H = 1/4CH₄</td>
<td>-24.6</td>
</tr>
<tr>
<td>1/4Si + H = 1/4SiH₄</td>
<td>-18.9</td>
</tr>
<tr>
<td>1/4SiC + H = 1/4Si + 1/4CH₄</td>
<td>-20.9</td>
</tr>
<tr>
<td>SiC + H = Si + 1/2C₂H₅</td>
<td>0.4</td>
</tr>
<tr>
<td>1/5SiC + H = 1/5SiH₄ + 1/10C₂H₅</td>
<td>-15.0</td>
</tr>
<tr>
<td>1/8SiC + H = 1/8SiH₄ + 1/8CH₄</td>
<td>-19.9</td>
</tr>
</tbody>
</table>

All of the reactions using one mole of molecular hydrogen show a positive value for the free energy of reaction, which suggest that none of these reactions would occur spontaneously at these temperatures. However, in the presence of atomic hydrogen the free energies of formation and of reaction where SiH₄ and/or the hydrocarbons are
products become negative. Therefore we can hypothesize that the following key mechanisms play a role in the surface reconstruction of 6H-SiC.

1. \( H_2 \rightarrow 2H \)  
2. \( H + SiC (O,C) \rightarrow SiC (C) + (Si)Hx↑ + H_2O↑ + SiOx \)  
3. \( H + SiC (C) \rightarrow (Si)Hx↑ + CH_y↑ \)

First, the \( H_2 \) molecules are cracked at the hot surface into reactive atomic hydrogen. Studies by Siebert et al. [41] suggested that the SiC (0001) surface may be terminated by atomic hydrogen in a \( C_3Si–H \) configuration that formed as a result of the decomposition of molecular hydrogen on this surface at temperatures as low as a 1000 °C. The etching at 1600 °C may also be accomplished by a preferential reaction of the atomic hydrogen with the silicon forming volatile silane (SiH₄) molecules. The carbon atoms from the decomposition of Si-C will be hydrogenated and released as CH₄ gas. Although Table 2 shows that reactions in atomic hydrogen environment at the operating temperature range seem to be spontaneous, those reaction kinetics can be slower or altered at the lower temperature range due to a decrease in concentration of atomic hydrogen. Therefore poor thermal contact between the Ta Boat and the substrate resulting in uneven heating will affect the rate of reaction and the type of reactions happening at the surface. This can result in higher surface roughness and slow removal of contaminants.

It was also found that as the %O composition on the cleaned SiC surface increases, the MgO film thickness decreases. This suggests that the oxygen content of the surface impacts the initial wetting of the Mg and O on 6H-SiC thus changing the sticking coefficient of the species. Therefore, a reliable and successful cleaning procedure must be developed in order to produce consistent and well-characterized starting surfaces. Attaining defect- and contamination free SiC surfaces, is essential to the quality of
subsequent film. In order to avoid the issues of sample size and maintaining reliable thermal contact, UHV hydrogen atom thermal gas cracker was explored. The idea is that the hydrogen cracker source generates atomic H without the need of H2 to crack on a sufficiently heated substrate. Dr. Eberl MBE-Komponenten GmbH hydrogen cracker uses a tungsten filament at about 1500°C to crack hydrogen gas with an estimated H2 cracking efficiency of 60%. The etching process and surface reactions are thus being activated with the hydrogen atom energy.

Dr. Golshan has explored the cleaning and characterization of Ge (100) substrate using atomic hydrogen in her Ph.D study [42]. In her work, variables such as cleaning temperature, time of H exposure, have been studied to better understand the hydrogen cleaning process. Results showed the ability of atomic H to react with surface oxides, leading to an increase by approximately 4-fold in the bulk Ge 3d (30 eV) component, and a reduction in the GeO contamination component (33 eV). Using those results and conclusions it was possible to extract commonalities in the processing conditions and mechanisms responsible for the repeatable removal of contaminations and develop a more reliable SiC substrate cleaning process. 6H-SiC substrates were degreased with organic solvents and the introduced into UHV (ultra-high vacuum) chamber where they were exposed to hydrogen atoms at substrate temperature of 800 ºC.

Exposure of the surface to atomic hydrogen resulted in the removal of oxygen down to 7% oxygen, which is lower than the value of at% oxygen (9% Oxygen) achieved via the use of the ex-situ hydrogen (H2) flow furnace. The XPS scans of the atomic hydrogen-cleaned 6H-SiC surfaces reveal the chemical bonding states of silicon (Si 2p spectrum) as shown in Figure 18 (c) illustrating the removal of Si-O bond from the surface after atomic hydrogen (H) cleaning. In addition, as seen in Figure 18 (d, f), the C-
O bond signal decreased in magnitude, and almost disappear after cleaning. These results suggest that the remaining oxygen on the surface is bonded to carbon rather than to silicon. These results when compared to the XPS scans of the H₂ cleaned surface (reconstructed surface), Figure 18 (a), where the Si 2p spectrum shows a clear Si-O signal at ~102 eV, can also be interpreted as an absence of a silicate adlayer reconstruction (SiₓOᵧ). Additionally, RHEED data do not show the anticipated reconstructed √3×√3R30º structure as the intermediate Laue rings are not observed (Figure 18(h)) which can be a significant indication of the absence of surface reconstruction.

Figure 18: XPS spectra of 6H-SiC surface. Si 2p and C 1s after H₂ cleaning (a, b), after atomic H cleaning (c, d) and degreased before any cleaning (e, f). Insets provide the corresponding RHEED patterns (g,h,i) showing the difference in reconstructed pattern for cleaned SiC.
The atomic hydrogen source reduced amounts of oxides on the surface at a comparatively low temperature. When looking at Table 2, it can be seen that the free energy to form silane via reaction of Si with atomic H is increasingly negative as the temperature is decreased. We can speculate that at lower temperatures, the silane reaction becomes dominant which in turn suppresses the formation of Si$_x$O$_y$.

Although the atomic hydrogen treatment may help with reproducibility issues, these results show that the treatment of 6H-SiC surfaces using an atomic hydrogen (H) beam source and using a hydrogen (H$_2$) flow furnace will produce surfaces with different chemistries as well as different structures. Further investigation is required to better understand the reactions between hydrogen, carbon, silicon and oxygen on the surface. If the cleaning process resulting in a $\sqrt{3}\times\sqrt{3}R30^\circ$ surface reconstruction (namely using H$_2$ at 1600 °C) is indeed initiated by the dissociation mechanism of molecular hydrogen to atomic hydrogen on the Si-terminated SiC surface, then perhaps looking at atomic H cleaning using a slower etching rate (fluence variation), a lower H/H$_2$ ratio and/or introduce small amounts of oxygen might provide more insights into understanding the mechanism of the hydrogen cleaning process.

5.2 Heteroepitaxy of the template layer

Effective heteroepitaxial integration of BaTiO$_3$ on wide bandgap semiconductor SiC requires an approach that will overcome the large lattice mismatch challenges of integrating a cubic structure on a hexagonal substrate as well as potential unwanted chemical reactions in order to create an abrupt interface. MgO was shown to be an ideal candidate as an engineered template for the integration of metal oxides on SiC and to bridge the gap in lattice mismatch because it can promote alignment by taking advantage
of the similarities in oxygen sub-network between the two layers. This translates to a potential O-to-O chemical alignment of the oxygen in the SiC silicate adlayer, the oxygen in the MgO template and the oxygen of the function oxide. An example of this is given in Figure 19, which illustrates BTO on 6H-SiC, where MgO (111) can act as a template. The $\sqrt{3} \times \sqrt{3} R30^\circ$ reconstruction of 6H-SiC has lattice parameters of $a=3.08$ Å and $c=15.11$ Å, while BTO (111) has an in-plane lattice spacing of 2.82 Å. The lattice parameters of cubic MgO (001) is $a=4.21$ Å and the lattice spacing in the MgO pseudo hexagonal structure (111) plane is 5.96 Å. Therefore, the lattice mismatch between template and film is reduced to 4.4%.

![Diagram of lattice matching of O sub-network for BTO on MgO (111) and 6H-SiC](image)

**Figure 19**: Schematic illustration of lattice matching of the O sub-network for BaTiO3 on MgO (111) and 6H-SiC.

Previous studies in our lab have shown that a thin (2.5 nm) MgO layer was both effective and necessary for the heteroepitaxial integration of BTO on 6H-SiC [refs]. Crystalline MgO (111) films were grown by MBE at a temperature of 140°C (as measured from the heater thermocouple) on the silicon face of a H2 cleaned 6H-SiC. The oxygen plasma was held constant at 100 W and a chamber pressure of $5 \times 10^{-6}$ Torr. The Mg:O flux ratio was ~1:20 and produced single crystalline MgO films.
The following work lays out the factors that affect the quality of the MgO template layer. Figure 20 shows results of the growth of MgO on H₂ cleaned 6H-SiC of different O% composition using constant growth parameters (substrate temperature, Mg, O flux). As it was discussed earlier, RHEED images of SiC with oxygen composition higher than 10 at% do not show the anticipated reconstructed √3×√3R30º structure and the intermediate Laue rings are faint. The RHEED images presented below show two MgO films grown on two H₂ cleaned 6H-SiC starting surfaces with different oxygen compositions, Figure 20 (a) 9 at% oxygen and Figure 20(b) 12% oxygen.

![RHEED patterns of 6H-SiC and MgO films](image)

**Figure 20:** RHEED patterns of (a) and (c) H₂ cleaned 6H-SiC with 9 at% and 12 at% oxygen, respectively. (b) and (d) MgO films grown on (a) and (c) respectively.

When the O% composition was below the level seen to promote surface reconstruction (< 10%), the RHEED patterns is somewhat streaky suggesting the growth of MgO thin films exhibiting single crystalline structure with two-dimensional 2D growth features and some 3D characteristics. On the other hand, when the Oxygen at% is
above 10% the RHEED patterns suggest that the film follows a 3-D growth mechanism. Previous studies on the growth of MgO showed a transition from 2D to 3D occurs when the film thickness exceeds 5 nm. The initial few layers of MgO indicated an apparent layer-by-layer wetting of the surface prior to the formation of the 3-D columnar grains [43]. This suggested that, the initial growth mechanism might in fact follow a 2-D layered growth mode and this was attributed to the initial nucleation reaction of atomic oxygen with the silicate adlayer where atomic oxygen acts to activate the surface by encouraging the Si-O-Si bonds in the silicate adlayer to break and further allowing the formation of a Si-O-Mg oxygen bridge. If the observed 2 D streaky-like features observed in RHEED images is a true representation of a smoother surface, achieving a 2-D single crystalline MgO film is important for the use of MgO as a template layer for functional oxide integration, where it is important to establish an abrupt interface. In order to investigate the initial wetting pattern, RHEED was used to monitor the growth of MgO films. Figure 21 shows real-time monitoring of the MgO RHEED pattern revealing no evidence of a smooth 2-D layer during initial stages of film growth. The RHEED pattern of the initial few layers of MgO indicate an apparent the 3-D growth as indicated by the distinct spots within the zeroth Laue zone.
Figure 21: Real-time monitoring of the MgO RHEED pattern during film growth on a) an H₂ cleaned SiC surface with 12% oxygen composition. b)-f) represents the progression of RHEED patterns during MgO film growth.

These results suggest that the initial layers of MgO films might be highly affected by the crystal quality of the substrate surface. At 12% oxygen, the excess O on the cleaned SiC surface may form other bonds (Si-Oₓ or C-Oₓ) than just the silicate adlayer (Si₃O₅)[15], and thus cause a partially reconstructed and rough SiC surface. This is indicated by the fainter reconstruction rings, and likely affects how the incoming atomic oxygen interacts with the substrate surface. Since all the MgO films were deposited on 6H-SiC at roughly constant growth conditions (substrate temperature, Mg, O flux), the increase in the starting substrate surface oxygen composition can be directly related to MgO film growth rate. As illustrated in Figure 22, decreasing the starting surface oxygen composition from 12 to 7 O at%, caused the growth rate increase from ~1 A/min to ~3.13 A/min.
Figure 22: Correlation between substrate starting % O composition and resulting MgO film grown under the same conditions.

Although 2-D features are dominant in the MgO film grown for these studies, it is apparent that the resulting MgO film obtained Figure 23 (b) has a different structure when compared with the one obtain in previous successful MgO growth, Figure 23 (d).
Figure 23: RHEED patterns of (a) H2 cleaned 6H-SiC with 9 at% and (b) corresponding MgO film grown reported by Dr Goodrich T., (c) H2 cleaned 6H-SiC with 9 at% and (d) corresponding MgO film grown reported in this study

The RHEED pattern of the film shown in figure 23 (b) is streakier than the RHEED patterns of (d) indicating a smoother MgO surface. This suggests that the crystal structure and orientation of the MgO films may be highly dependent not only on the crystal quality of the substrate but also on the integrity of the crystalline structure of the substrate during film nucleation and the initial stages of growth. Therefore it is necessary to understand the physical mechanisms involved in the nucleation and growth of the thin films. This becomes more important for complex oxides that often have multiple structures for a given stoichiometry, therefore small changes in stoichiometry within the unit cell can affect the structure and resulting properties.

5.3 Heteroepitaxy of BaTiO₃ on SiC by MBE

One of the key factors contributing to the success of the growth of BTO via MBE is the establishment of a growth window defining the range of growth condition to achieve stoichiometric BTO. The growth of 3-element materials by MBE is complex, therefore the first step is to understand the relative fluxes necessary in order to achieve single crystal, stoichiometric BTO (111). For all initial BTO films designed to narrow down the stoichiometry window, the growth parameters used were identical to those in the previous work by Dr. Goodrich Ph.D [15].
5.3.1 Establishing the operating conditions for BTO growth window

The very first step in establishing the operating window in the Ba-Ti-O system, is to understand relative fluxes necessary to grow BaTiO$_3$ with proper chemistry and structure. A detailed calibration of the Ti-ball flux with respect to current setting estimated the Ti flux at the highest current setting (44.5) to be $4.46 \times 10^{12}$ /cm$^2$ sec which is less (by a factor of 2) than the Ti flux at that same setting reported in previous studies. Therefore, for BTO film growth designed to narrow down the stoichiometric window, the oxygen pressure was set at $5 \times 10^{-6}$ torr correlating to an equivalent molecular oxygen flux of $3.6 \times 10^{15}$ /cm$^2$.sec, the Ti-ball was set at the highest current of 44.5 A ($4.46 \times 10^{12}$ /cm$^2$.sec) and the Ba flux was adjusted in order to obtain a Ba:Ti ratio of 1:1. The oxygen plasma power (controlling the O$_2$: O ratio) and the substrate temperature were held constant at 100 W and 650 °C, respectively. Figure 24 shows the RHEED pattern of the crystal structure of BTO films grown on MgO/6H-SiC with various Ba/Ti ratios, as determined by XPS. The Ba/Ti flux ratio is defined as the calculated ratio of the incoming species on the surface growth front and the Ba/Ti is defined as the atomic ratio from the resulting film (i.e ratio of incorporated species).
Column (c) represents the RHEED pattern of the resulting BTO films showing the impact of changing the Ba/Ti flux ratio on both the crystallinity and the stoichiometry. As the Ba/Ti flux ratio increases the Ba/Ti ratio also increases and the resulting crystal structure of the film goes from single crystal with 3D features (Ba/Ti = 0.3 and 0.6) to polycrystalline (Ba/Ti = 0.8) to amorphous (Ba/Ti = 1.98). However, crystallinity in the films is observed without the correct Ba/Ti ratio expected for a stoichiometric BTO film. XPS characterization of the BTO film with Ba/Ti = 0.3 is shown in Figure 25.
Figure 25: XPS tight scans of Ti 2p$^3$, Ba3d$^5$ and C1s for BTO grown on MgO/6H-SiC resulting in Ba/Ti ratio of 0.3

The XPS tight scan of the Ti2p3 region and the Ba3d5 region show peaks at the binding energy ~458.5 eV and 779.65 eV. The above results indicate the presence of Ti$^{4+}$ and Ba$^{2+}$ respectively, confirming the fact that Ti and Ba oxidized to form TiO$_2$ (tetragonal) and BaO (rock-salt) and are in the correct oxidation state. However, traces of unwanted C-O/C-C are also present in the film as indicated by the XPS tight scan of the C1s region. Similar traces of unwanted C-O bonds are also seen in the XPS scans of the MgO template suggesting that the chemistry of the MgO underlayer highly impacts the chemistry of the BTO subsequent film where interface mixing may cause carbon diffusion.
6.0 CONCLUSION

The goal of this work was to use molecular beam epitaxy (MBE) to understand the nucleation and growth mechanisms that control the integration of single crystal BTO films on SiC using an insulating layer (MgO) that takes advantage of the oxygen sub-network to align crystal structure. The research shows that substrate surface quality can impact chemistry and structure of next-layer film deposition, which in turn will significantly affect the properties of resulting films.

The starting substrate surface proved critical to the effective integration of stoichiometric BTO on 6H-SiC. Temperature stability seemed to be key in controlling the final oxygen composition during hydrogen etching of the starting surface. The hydrogen furnace cleaning at 1600 °C of 6H-SiC (0001) substrates surfaces produced a smooth, uniformly stepped surface and a $\sqrt{3}\times\sqrt{3}$R30° surface reconstruction with less than 10 at% residual oxygen contamination. However, the process was found to be unreliable due to uncontrollable constraints. The more reliable process using atomic hydrogen for cleaning 6H-SiC (0001) substrates produces a starting surface with less than 7 at% residual oxygen contamination at relatively low temperature of 700 °C. This process also produces a reconstruction different from the anticipated $\sqrt{3}\times\sqrt{3}$R30° surface reconstruction needed for the MgO/BTO oxide growth. The high quality, single crystalline MgO (111) deposited on SiC (0001) prepared by the hydrogen furnace, was found to have a mixture of two-dimensional and three-dimensional features with traces of unwanted contamination that is seen to propagate through the BTO films preventing the high-quality integration of BTO on SiC.
The challenge of understanding the causes of inconsistence in the desired film properties is generally impeded by the limitations of the static characterization techniques (XPS) that were available and used in this study. Dynamically observing how bonds are formed at surfaces and interfaces is needed in order to understand how to enable a more consistent.

Alkali antimonide is a class of materials that has the potential to create light sources capable of probing the dynamics of the atomic scale which can be beneficial to all applications from understanding and treating disease to growing novel materials. Research on Cs$_3$Sb thin film growth through collaborations with Dr. Mark Hoffbauer and the ACERT team at the Los Alamos National Laboratory is presented in the next chapter.
8.0 REFERENCES


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CHAPTER 2: The influence of growth parameters on the performance of Cs$_3$Sb thin film photocathodes
9.0 INTRODUCTION

A longstanding objective of the light-generation and imaging community is to produce high-energy x-rays to observe the dynamic world of molecules and atoms. Such a specific light source is needed because x-rays have wavelengths (related to their energy) comparable to interatomic distances, which makes them suitable for the study of atoms and bonds. X-ray imaging for material characterization is already a powerful technique. However, next-generation coherent x-rays sources are needed [1][2] to transition from static pictures of atomic arrangements to the concept of time-dependent dynamical behavior of atoms to provide film-like sequences of chemical processes.

A key element of modern accelerator-based X-ray instruments is the cathode, a material that can be made to emit electrons by applying energy in the form of photons via the photoemission process. The emitted electrons are then accelerated using radio-frequency electromagnetic fields [3][4]. The next-generation x-ray sources require high brightness electrons that are emitted from the cathode with both identical energy and identical direction (related to electron momentum). For this emission process to be effective, high-quality cathode materials with high quantum efficiencies (~50%) are needed. Traditional approaches for increasing quantum efficiencies (QE) have failed because advances in one of the materials properties that increase QE has resulted in a degradation in the intrinsic emittance of the photocathode that degrades the accelerator performance. Among various photocathode materials, alkali antimonides, such as K₃Sb, Cs₃Sb, and K₂CsSb, have great promise in the application of future light sources because of their high QE, fast response time, and low thermal emittance [16][17]. Previous studies have shown that traditional deposition methods used to grow alkali antimonide
photocathode films have intrinsic drawbacks that render the process to not be reproducible and thus not reliable for achieving high QE materials [5]. Hence, exploring novel growth methods to synthesize Cesium antimonide (Cs₃Sb) photocathodes with the desired properties is in great demand. The materials science focus of this research was to use Molecular Beam Epitaxy (MBE) to gain understanding of a reproducible process for growing Cs-Sb photocathodes by directly correlating photoemission metrics (spectral response, quantum efficiency (QE), intrinsic emittance, and response time) with specific surface and bulk materials characteristics (thin-film stoichiometry, surface and bulk crystallinity, and surface morphology).
10.0 BACKGROUND

The ultimate problem that needs to be addressed in the photocathode community is the inversely coupled relationships between QE, emittance, and lifetime of cathodes. Ideally, one would like to decouple the competing physical processes that traditionally govern these metrics and independently control and tune them. In order to do so, it is important to understand the fundamental processes that govern photocathode performance. Therefore, a brief background will be provided on photocathode metrics that are relevant to this study that includes: quantum efficiency, thermal emittance, time response, and cathode lifetime. As mentioned in the previous section the challenge is to make cathode materials capable of producing a beam of electron that is bright, with minimal energy and momentum spread. High beam brightness is needed because a very large fraction of X-ray photons will pass through a typical sample without scattering, meaning that only a small percent of the X-ray photons actually contribute towards the imaging task. Therefore, a very bright x-ray source is needed to probe materials at the length scales of interest.

Beam brightness is defined as the ratio of the current (number of electron emitted) and the beam emittance, where emittance is the product of the beam size and the angular spread. High performance electron beams relevant to all next-generation light source devices require high brightness, which is achieved by creating beams with very low emittance and high peak current density (10-100A/cm²) with short (~1ps) beam pulses.
Small thermal emittance allows the beam to be tightly focused, while high peak current enables coherent (synchronized) photon emission in a device. Beam brightness depends strongly on quantum efficiency (QE) of the cathode, defined as the ratio of emitted electrons to incident photons.

10.1 Quantum efficiency

The mechanism behind a photocathode is based on the photoemission process. The photoemission process involves three steps: excitation of an electron by a photon absorption, transport of that electron to the surface, and electron emission from the surface over the energy barrier. In Figure 26, the three-step emission mechanism is illustrated.

Figure 26: Schematic representation of the Three-step model of photoemission from a metal [15]

The photoemission can be seen as a three steps process, as explained by the Spicer’s model [15]:

1. Absorption of a photon with a consequent excitation of an electron
• This process is affected by the incident photon energy (usually from a laser) and the material properties governing absorption such as the band gap.

2. Motion of the electron towards the surface of the solid

• This process is affected by processes whereby the electron loses energy through electron-electron or electron-phonon scattering.

3. The escape of the electron into the vacuum, if the final electron energy is high enough to overcome the surface barrier.

• This process is affected by the work function \( \phi \), which is the minimum energy needed to remove an electron from a solid to a point outside the solid surface often referred to as the vacuum level.

The overall Quantum Efficiency (QE) of a photocathode is defined as:

\[
QE = \frac{\text{number of emitted electrons}}{\text{number of incident photons}}
\]

In practical units QE can be expressed as:

\[
QE[\%] = \frac{124 \cdot Q[nC]}{\lambda[\text{nm}] \cdot E[\mu J]}
\]

where \( Q \) is the bunch charge, \( \lambda \) is the incident laser photon wavelength and \( E \) is the laser incident energy on the photocathode.

QE calculations include the optical characteristics of the cathode (absorption reflectance, transmittance, penetration depth), the electron transport characteristics of the cathode (scattering mechanisms, mean free path/relaxation time), and the surface energy barrier characteristics of the cathode (for metals, work function; for semiconductors, electron affinity and band structure. QE as stated also assumes that the emission is not
space-charge limited in other words, photocurrent is linear with optical intensity in every respect. It is important to note that QE is a number ratio of electrons to photons and as such is unitless; it is not the related ratio of electric current density to optical irradiance, a ratio of Coulombs to Joules. QE relates to the electric current density and the optical irradiance via the optical wavelength and Planck's constant, the speed of light, and the electron. QE can be determined experimentally by measuring the incident laser power and the resulting emission current, assuming the laser spot size is smaller than the cathode and the temporal response of the cathode is instantaneous, such that the time response of the emitted electron pulse closely follows that of the incident laser.

10.2 Thermal emittance

Emittance of an electron beam (or any charged particle beam), at its simplest, incorporates the ideas of beam size and angular spread. It is the measurement of the spread in energy of the electron beam. In theory, if a beam is produced in which all electrons travelled along the same vector, indefinitely, this would be a zero emittance beam. Low emittance beams of electrons are essentially small diameter, well collimated beams, and are desirable due to good preservation of the electron beam quality during propagation through the accelerator components in a Free Electron Laser (FEL), including the interactions along the undulator structure. Preserving low electron beam emittance in a FEL, increases the ability to perturb the electron beam using magnetic and electric fields such that it produces a monochromatic and exceptionally bright X-Ray beam, both of which are of great importance for next-generation X-Ray light sources.
11.0 LITERATURE REVIEW

Several studies have been done to optimize the growth of alkali antimonide in order to prepare thin films with the required properties. In most cases however, thin films exhibit high thermal emittance and low quantum efficiency. The surface roughness, morphology, and off-stoichiometry compositions in the thin films, none of which have been controlled to date, are the probable causes of the compromised properties observed in alkali antimonide thin films. The existence of a distortion in the electric field near the cathode surface due to surface roughness can be considered to be the dominant source of an increase in the intrinsic emittance impacting the quantum efficiency [7]. Moreover studies of quantum efficiency (QE) degradation of the alkali-antimonides have found that the dominant effect in the degradation process is due to surface poisoning through reactions with residual reactive gases containing oxygen that change the film stoichiometry [8] Therefore understanding the growth mode and growth mechanism in detail, with the aim of being able to precisely control surface roughness and stoichiometry is of the utmost importance in the development of high performance alkali antimonide photocathodes.

11.1 Alkali antimonide thin film growth
Alkali antimonide films (K$_2$CsSb, Cs$_3$Sb) have been grown on a variety of substrates by different methods such as pulsed laser deposition (PLD), sputtering and MBE. Much progress has been made in obtaining improved quantum efficiency (QE). However, most of the recipes followed for growing alkali antimonide materials are largely obtained by a trial and error process focused on trying to maximize the quantum efficiency without any understanding of the chemical and structural changes that take place on the surface during growth. Such changes can be very sensitive to the growth conditions and are the dominant cause of the surface roughness [8] It is essential to understand the correlation between processing conditions (processing temperature), film characteristics (stoichiometry, crystal structure, morphology) and cathode metrics (spectral response, quantum efficiency, intrinsic emittance, and response time) in order to develop reliable growth procedures that maximizes the performance of Cs$_3$Sb photocathodes.

11.1.1 Influence of growth techniques on Alkali antimonide film growth

In recent years, the growth mechanism of sequentially grown K$_2$CsSb photocathodes has been studied by synchrotron X-ray techniques. It has been revealed that surface roughness drastically increases during photocathode growth. A study by Schubert et al. [9] looked at the sequential growth of K$_2$CsSb photocathodes using core-level x-ray photoelectron spectroscopy (XPS) to reveal the chemical composition and oxidation state of the components after each growth step and also using an UHV-atomic force microscope (UHV-AFM) for roughness determination and surface morphology. The rms roughness of a full photocathode with a quantum efficiency of 1.1% was determined to be about 25 nm over 100 nm spatial period. Based on the field and
roughness dependence of the emittance, it was found that above 3 MV/m the roughness is the dominant effect on the emittance. Therefore, at 20 MV/m accelerating field, which is where the akali photocathodes are expected to perform for high-brightness applications [10], the emittance of a 25 nm rms photocathode would be about 1 μm/mm which is more than twice the needed 0.4 μm/mm rms thermal emittance value.

Another study by the same group [11] looked at X-ray reflectivity (XRR) of photocathodes grown using three different methods: sequential deposition, co-evaporation of K and Cs and sputter deposition. For sequential evaporation experiments, a first layer of 3nm Sb was deposited on a Si substrate, followed by K deposition until the photocurrent maximized. Cs was then deposited to maximize the photocurrent of the final film. For the co-evaporation experiments, a first layer of 1.5nm Sb, according to reading from a QCM, was deposited on a MgO substrate, K and Cs were then co-evaporated onto the Sb layer until the photocurrent reached a maximum. Sputter deposition was carried out on MgO substrates in 3 layers for a total thickness of 30 nm using a K₂CsSb target.

XRR analysis on the final photocathode grown sequentially revealed that the roughness of the 469 Å thick film was 32 Å with a measured quantum efficiency at the 532 nm wavelength of 4.9%. For the film grown using a co-evaporation technique, the first Sb layer shows a thickness of 36.7 Å and 5.2 Å roughness. After evaporating K and Cs, the thickness increases to 159.3 Å and the roughness rises to 9.22 Å. As the growth continues, the surface roughness of this photocathode roughly stays at around 10 Å, while the thickness increases to 489 Å. The final photocathode with a thickness of 725 Å and 24.9 Å roughness, had a final QE of 4.5 % at a wavelength of 532nm. The surface roughness for the sample grown via sputtering was about 6.87 Å after 3 layers of
sputtering and the thickness is fitted to be 512 Å. The spectral response measurement however for the sputtered cathode shows the quantum efficiency to be approximately 1% at 532 nm wavelength. As seen in Figure 27 the surface roughness can be improved by using a modified growth recipe, such as alkali co-deposition onto a thin Sb layer. However, while sputtering significantly improves the surface roughness, it leads to poor quantum efficiency potentially due to poor control of stoichiometry during growth.

Figure 27: Comparison of surface roughness vs. thickness between photocathodes grown by sequential evaporation, co-evaporation and sputter deposition. [11]

These results show that co-deposition yields smoother surfaces than those obtained by sequential deposition but the reasons behind them are still obscure. Therefore, it is important to understand these changes in terms of kinetics in order to develop reliable and reproducible growth procedures.

11.1.2 Influence of Substrate temperature on Alkali antimonide film growth

Suzanne et.al [5] reported on film characteristics during the various stages of the deposition of K₂CsSb photocathodes at different substrate temperatures. Samples were grown on p-doped Si(100) substrates through thermal evaporation in ultrahigh vacuum
Following the standard growth technique, the photocathode material was grown in a sequential manner. First, 15 nm of Sb was thermally evaporated from PtSb beads with a rate of 0.2Å/s. Then 70–90 nm of K was deposited giving a maximum photoyield (QE) of 0.05%–0.1%. Following this, 90–120 nm of Cs was deposited until a photoyield maximum is reached. Two samples at two different substrate temperatures were studied. The substrate of the first sample was kept at room temperature (RT) and the second sample was studied at a substrate temperature of 100 ºC. For the sample at RT, XRD measurements of the first layer (Sb layer) show a single peak at d = 3.757Å corresponding to the (003) orientation of Sb is observed showing that the antimony grows in a crystalline form with (003) as the preferred orientation at room temperature. For the sample at the elevated substrate temperature of 100 ºC, as in the room temperature case, a single peak at d = 3.757Å corresponding to the (003) orientation of Sb is also observed. However, the elevated substrate temperature in this case causes the Sb to crystallize much faster.

Figure 28(b) (e) shows XRD measurements of the K layer deposition on the Sb layer in 10 nm interval steps. Compared to the room temperature case, the reaction of Sb and K at 100 ºC is much more complex. Initially, in both cases (RT and 100 ºC), during the deposition of the first 20 nm of K, the Sb structure is dissolved forming a K-Sb amorphous mixture beyond 20 nm K layer thickness as evidenced by the disappearance of the Sb(003) peak. However, at the substrate temperature of 100 ºC several intermediate phases of KₓSbᵧ are formed at 50–60 nm of K layer thickness which are not seen in the sample grown at RT. These phases disappear at 70 nm of K layer thickness to form the cubic phase of K₃Sb, with the diffraction peaks of the (200) and (111) plane detectable.
By 80 nm of K layer thickness, the hexagonal phase begins to form, h(002) peak, and by 90 nm it becomes the dominant phase. On the other hand when depositing K on the Sb layer at room temperature, there are no intermediate phases of $K_xSb_y$ formed at 50–60 nm, the K-Sb amorphous mixture persisted until it crystallized to form two stable phases the hexagonal (h(002) peak) and the cubic (c(111) peak) phases of $K_3Sb$.

The effect of temperature is also seen during the Cs deposition step where during the deposition at room temperature Cs reacted with the cubic phase of $K_3Sb$ to form the cubic phase of $K_2CsSb$ as indicated by the disappearance of the c(111) peak of $K_3Sb$ and the appearance of the c(002) peak of $K_2CsSb$ with increasing Cs layer thickness. However the XRD measurement shows a slight decrease of the h(002) peak representative of the hexagonal phase of $K_3Sb$ remaining mostly unreacted even after 120 nm of Cs deposition. When $T_s= 100 ^\circ$C, Cs reacts very quickly with the cubic phase of $K_3Sb$ to form $K_2CsSb$ at only 10 nm of Cs layer thickness. The hexagonal $K_3Sb$ starts to convert much later, after approximately 70 nm of Cs is deposited. However after 120 nm of Cs deposition, most of the hexagonal $K_3Sb$ structure is converted and the sample is mainly $K_2CsSb$. The QE at this stage was measured to be 3.4% compared to 0.1% for the sample grown at RT.
Figure 28: XRD spectra taken during the growth of K$_2$CsSb indicating relevant diffraction peaks. Sb layer grown at TS= RT (a) and TS=100ºC (d) in 2 nm steps. K deposition on Sb films shown in (a) and (d) at TS =RT (b) and TS=100 ºC (e) in 10 nm deposition steps. Cs deposition on preceding K-Sb phase from (b) and (e) in 10–20nm steps for T$_S$ =RT (c) and T$_S$ =100ºC (f)[5]

Three things are clear based on the study:

1. The conversion of K$_3$Sb to K$_2$CsSb through the deposition of Cs seems to take similar paths regardless of sample temperature. The cubic structure of K$_3$Sb converts first followed by the hexagonal phase much later. However, the substrate temperature is shown to play a role in the conversion of the hexagonal phase. This is so because transforming the hexagonal structure involves not only the
exchange of atoms but also the breakdown of a very stable crystal structure which would require energy and the rebuilding of a new structure.

2. The additional thermal energy provided by the higher substrate temperature aids in the reaction between Sb and K; however, it also increases the mobility of the K atoms and impedes the sticking properties of K causing faster and different reactions which result in a mixed K\textsubscript{5}Sb phase that quickly transforms to cubic K\textsubscript{3}Sb and finally to hexagonal K\textsubscript{3}Sb.

3. The higher growth temperature promotes certain surface reaction affecting the final quantum efficiency of the resulting photocathode film.
12. EXPERIMENTAL APPROACH

In order to successfully understand the film growth mechanisms that yield Cs$_3$Sb photocathodes with high quantum efficiency and low emittance, it is necessary to determine the roles of each individual species flux and various processing parameters and their interactions in the nucleation and growth of the films. The growth and characterization capabilities available in the ACERT laboratory (Applied Cathode Enhancement & Robustness Technologies) at Los Alamos National Laboratory consist of various in-situ, ex-situ, and real-time techniques. All thin cathode films were deposited by molecular beam epitaxy (MBE) in an ultra-high vacuum (UHV) chamber with a base pressure of $\sim 4 \times 10^{-10}$ Torr. The metals were supplied by solid source effusion cells (for Sb) and a modified J-tube effusion cell (for Cs).

12.1 Equipment specifications

The ACERT Lab at Los Alamos National Laboratory has direct access to a wide range of powerful techniques whose specifications will be discussed in the following section. The instrument that will be discussed consists of three interconnected UHV chambers (one for cathode growth, one for analysis and one for emittance measurements), effusion cells, custom built J-Tube effusion cells, surface science characterization tools Auger electron spectroscopy (AES) and X-ray Photoelectron spectroscopy (XPS), and the Momentatron system.

12.1.1 Ultra high vacuum chambers

Film growth and characterization was performed in three 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 cathode growth chamber but separated by a UHV compatible gate valve. The load lock chamber is independently pumped by a turbo pump (Leybold, Turbovac 160) and is equipped with a standard European-style transfer mechanism with a sample mount flag placed on a load lock arm that locks in place when rotated for loading. Once a sufficiently low pressure is obtained, (approximately $3 \times 10^{-8}$ Torr, as measured by a nude ion pressure gauge) the sample is transferred on to a custom built sample heater in the growth chamber by use of a magnetic linear transfer arm. The custom built heater is on manipulator platform that can be moved in 5 directions, x, y, z, θ, φ (azimuthal rotation) and is capable of temperatures ranging from room temperature up to 1300 °C, as measured by a type C thermocouple located between the heater wires and located within 2 mm of the back of a stainless steel plate (1.5 mm thick) that accepts the sample mounting flag to which the substrates are attached. Precise and accurate sample temperature measurements were performed using an optical pyrometer that typically read 50 – 75 °C below the thermocouple reading. The pyrometer reading was calibrated against the heater temperature using the melting point of Indium (157 °C) as a standard. The heater temperature versus equilibrium (steady-state) temperature as read by the pyrometer is plotted in Figure 29 and the fit to a simplified Stefan-Boltzmann radiation law is shown. At operational temperatures, the cathode sample assembly heating was found to be dominated by conductive cooling thru the mounting copper block. The equation fitted is a steady-state power equation based on the Stefan-Boltzmann radiation law:

$$T_{surface} = \sqrt{\frac{T_{heater}^4 + 2T_{room}^4}{3}}$$ (10)
Figure 29: Calibration curve of heater temperature vs. cathode temperature and comparison to theoretical radiative heat transfer

The growth chamber is pumped with a Pfeiffer TPU 330 turbo pump and a Varian 500181B ion pump (400L/s) that maintain a background pressure of approximately $4 \times 10^{-10}$ Torr (as measured by an ion gauge). The growth chamber is also equipped with an anode assembly (also referred to as electron collector), a quartz-crystal microbalance (QCM), a residual gas analyzer (RGA), and a two laser diode assembly.

The growth chamber is connected to an adjoining UHV surface science chamber, separated by a UHV-compatible manual gate valve, which allows for sample transfer between those two chambers without breaking vacuum thereby minimizing contamination and preserving the cathode photoemissive surface lifetime for surface science analysis. Transfer between the two chambers is again performed using a magnetic linear transfer arm onto a manipulator stage with 4 axis movement, x, y, z, θ. The surface science chamber is equipped with a Leybold Turbvac 160 turbo pump and a Perkin-
Elmer sublimator ion pump with a pumping speed of 200 L/s that can be isolated with the chamber by a gate valve. Further, the surface science hemispherical electron energy analyzer is lined with a $\mu$-metal shield that is designed to absorb stray magnetic fields that could deflect electrons during Auger electron spectroscopy characterization (AES).

The surface science chamber is then connected to a third adjoining UHV surface chamber, separated by a UHV-compatible manual gate valve that allows sample flag transfer between those two chambers without breaking vacuum. This third chamber is used for emittance measurements and is equipped with two Varian triode ion pumps (40L/s). Figure 30 shows the UHV system configuration that was used for photocathode growth and characterization.

![Figure 30: UHV system consisting of three interconnected chambers with two load lock chambers. The chambers are separated by UHV compatible gate valves. The photocathode growth chamber consists of a QCM, an Anode, an RGA and solid source effusion cells (Sb) and alkali J-tubes. The Surface Science consists of an AES hemispherical energy analyzer and the Electron Beam Diagnostics chamber contains a momentatron.](image-url)
12.1.2 Primary growth equipment

In MBE, thin films grow occurs following the reactions between thermal-energy molecular or atomic beams of the constituent elements that are deposited onto a substrate surface that is maintained at a selected film growth temperature. The constituent elements are supplied by effusion cells sources that play a key role in the quality of materials grown by MBE.

12.1.2.1 Solid source effusion equipment

For film growth, antimony metal shots (99.9999% shots from Alpha Aesar) were inserted into an modified Mcallister Technical Services low temperature evaporator cell. In an effusion cell, a pure solid material is placed in a ceramic crucible and heated to generate a local vapor pressure characteristic of the materials temperature and vapor pressure. The effusive source is oriented toward the substrate so the evaporated material’s vapor exits the source towards the substrate. The effusion cell consists of a pyrolytic boron nitride (PBN) ceramic crucible wrapped around by a tantalum wire, a type C thermocouple in the back, integrated water cooling, and a manual shutter. The antimony cell was calibrated against voltage in order to correlate heater power, cell temperature, and antimony flux. The absolute antimony flux was monitored via a QCM that was put into the sample position and via a RGA that measured the equivalent antimony pressure.

12.1.2.2 J-tubes

The alkali metals (Cs, K) were supplied using a custom-built J-tube effusion cell assembly. The concept of a J-tube is very similar to that of a valve cracker that are common evaporator system sold commercially by MBE system suppliers. Typically valve crackers have two heating zones and a valve that separates the two zones depending
on the specific design. The design of the J-tube was based on a rough model from Jefferson Labs and collaborator at Brookhaven. The custom-built J-tube consists of two heating zones. Zone 1 is the section where the volume of Cesium resides and is set at Temperature $T_1$. That section attaches to an assembly thru a valve with a narrow tube attached to the outlet that delivers the evaporated flux of alkali metal to the film growth surface. The section after the valve is the second zone (Zone 2) and is set at Temp $T_2$, where $T_2 > T_1$. The Gas flow is regulated through a high-temperature UHV compatible all-metal ball valve that separates the two independently heated zones. The valve is used as an on/off valve rather than a leak valve, to initiate or stop the alkali flux delivery to the substrate. The equilibrium vapor pressure above the liquid cesium is set in the cold zone (zone 1 of the J-tube source) and the valve is then used to deliver the vapor thru a long delivery tube (3/16” ID) that goes into the UHV growth chamber. The hot zone (zone 2 of the J-tube source) is heated to a temperature above that of zone 1 to prevent the cesium from sticking to the inside walls. By increasing the temperature of zone 1 (thermocouple resolution of 1°C), the absolute flux of the alkali metal can be increased in a very controlled manner. 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 and vary them with a few percent accuracy. The desired film growth rates and thicknesses were used tp calculate the fluxes that were monitored using a quartz crystal microbalance (QCM) that could be place into growth position. Once calibrated, the QCM provided an absolute number for the deposition rate of the Cs or Sb with a resolution of 0.01A/s. Calibration of the Cs J-tube was necessary to establish
the relationship between heater power, temperature, and Cs flux. The Cs flux was also measured using a residual gas analyzer.

![Figure 31: Calibration curve for Cs deposition rate vs. Cs cold zone temperature comparing the measured QCM rate and equivalent RGA pressure](image)

**12.1.3 Primary analysis equipment**

Cathode film characterization could be performed both *in-situ* (Quantum Efficiency Spectral Response, and AES) and ex-situ (AFM). The typical characterization techniques that were used will now be discussed.

**12.1.3.1 Quantum efficiency and Spectral response measurements**

The measurement of the quantum efficiency of a photocathode is quite simple in concept and involves the collection of the photocurrent from the illuminated film at a given incident laser power. The photocurrent can then be converted using the electric charge and photon energy to a ratio of emitted electrons to incident photons, the QE. The
measurement set up consists of an anode made of a stainless steel wire that is electrically isolated from the chamber. The anode is biased between 40-90 V with a combination of batteries that provide different DC voltages between the anode and a picoammeter. The electron current emitted from the sample sitting at ground is then measured by a picoammeter.

**12.1.3.2 Laser diodes**

The measurement of extremely low quantum efficiencies requires light sources intense enough to produce measurable photocurrent. Two laser diodes were chosen to span the blue and green region of visible light. The diode lasers have modest power requirements and can output a few mW of optical power. The photocurrents were generated using two laser diodes at a wavelength of 405 nm (1.46 mW and 0.52 mW incident power) and at a wavelength of 532 nm (0.39 mW incident power). Laser spot sizes on the growing sample surface were 0.5-1 mm radius in order to avoid unwanted heating effects or space charge limited emission that could result from too high of an intensity. Table 3 gives the lasing wavelength and corresponding photon energy, color, and power from the lasers.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Ephoton (eV)</th>
<th>color</th>
<th>Power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>405</td>
<td>3.06</td>
<td>Blue</td>
<td>1.46-0.52</td>
</tr>
<tr>
<td>532</td>
<td>2.33</td>
<td>green</td>
<td>0.39</td>
</tr>
</tbody>
</table>
12.1.3.3 Quartz crystal microbalance (QCM)

Effusion cell and J-tube evaporated flux calibrations were performed using a quartz crystal microbalance (QCM) deposition monitor. The QCM was mounted inplane next to the substrate heater assembly and directly facing all the evaporative sources. The QCM could be translated into the same position as the film growth surface to accurately determine the deposition rates, and then moved to the side to monitor the rates during photocathode growth. Any material deposited on the cathode is likewise deposited on the deposition monitor crystal.

The principle of operation of the deposition monitor is the following. The initial resonance frequency of an installed quartz crystal is 6 MHz. This frequency is reduced when additional mass is deposited on the crystal. The instrument measures the frequency shift, and with appropriate known materials properties (density, Z-factor, etc) the added mass can be determined. Using standard densities available for evaporated metal films, the mass is converted within the Inficon XTM/2 controller to an equivalent film thickness (Ångströms), which is displayed with 0.1 Å precision and recorded by LabVIEW with 0.1 Å precision. During flux calibration the QCM is positioned at the growth position to get an accurate reading of the fluxes. However during film growth the QCM is moved to the side to allow the substrate to be placed in the growth position. Therefore, the film thickness recorded during photocathode growth is a fraction of what is deposited on the substrate since the evaporation sources have a relatively broad angular flux distribution.

12.2 General experimental approach

In order to successfully engineer a process capable of reproducibly growing a Cs$_3$Sb photocathode material with controlled stoichiometry and high QE, the role and
interactions of each individual species flux and processing parameters during growth of the photocathode were studied. The photocathodes were grown primarily focusing on a co-deposition mode by depositing antimony and cesium onto a silicon substrate. The controlled parameters included the substrate temperature, the fluxes of the antimony and cesium delivered to the growth surface, and their arrival rates that determined the growth rate. The QE of the photocathode was evaluating by measuring photocurrent when the photocathode surface was illuminated with with alternating 405 nm and 532 nm lasers. The influence of flux ratio, substrate temperature, and grow rate on the QE of the films were varied in controlled ways to optimize the films photoemissive properties.

13.0 RESULTS AND DISCUSSION

All Cs₃Sb films grown in this study were deposited using standard MBE techniques with the focus on a co-deposition (or co-evaporation) process that involved evaporating the two elements (Cesium and Antimony) at the same time to allow them to react on the surface of the growing film to directly form the photoemissive material. This co-deposition process is an alternative to the sequential layer deposition growth process that relies on the inter-diffusion of a sequentially deposited cesium layer into a previously deposited antimony film to form the photoemissive compound. As described in the previous section, the cathode growth chamber allows repeated depositions of cathode materials while monitoring QE at multiple wavelengths during the film growth process. In this study we report the effects of substrate temperature, individual fluxes of Cs and
Sb, flux ratio (Cs/Sb), and growth rate on the optical properties (QE, spectral response) during film growth of Cs$_3$Sb film on Si (100) substrates in real-time.

### 13.1 Cs-Sb Photocathode growth process

Photocathode growth experiments were performed on silicon (100) substrates. The substrates were mounted onto a stainless steel sample plate flag assembly using clips and transferred into the UHV chamber and onto the manipulator heater assembly. The substrate temperature was measured near the front of the heater using a type K thermocouple. For cleaning, the sample temperature was raised to ~760 °C for ~20 min. The substrate temperature is then lowered to 250 °C or lower for Cs-Sb film growth. Typically the Sb effusion cell is raised to the selected temperature by controlling the heater power supply voltage, and the Cs J-tube cold-zone temperature was raised to a previously calibrated value to establish an equilibrium vapor pressure at a fixed temperature with the isolation valve closed. Once both cell temperatures were stable, the shutter for the antimony evaporator and the Cs valve were opened for co-deposition. All of the temperatures were actively monitored during the Cs-Sb film growth. The photocurrent generated by illuminating the sample with the laser diodes at 532 nm and 405 nm was then monitored in real-time as the deposition cycle took place. Adjustments to the fluxes were mostly made by varying the temperature or the Cs J-tube while monitoring the photo response.

Figure 32 shows the real-time photocurrent response during the growth process for a thick Cs-Sb cathode, and illustrates the ability to tune the QE of the photocathode in real time. Initial studies into the nucleation and growth mechanisms of Cs$_3$Sb focused on the impact of flux ratios and temperature on the QE. The stoichiometric flux ratio for
forming Cs$_3$Sb was determined based on carefully measured calibration cures using a QCM and the known density and other parameters for Cs and Sb. The growth rate for the initial Cs-Sb growth studies were calculated and chosen based on published literature [12].

![Figure 32: The time evolution of the photocurrent using two wavelengths (black curves) and the Cs cell temperature (red curve) during the production of cathode #1 (Cs$_3$Sb)](image)

One of the project goals was to perform the overall growth at low (near ambient) temperatures while still ensuring high QE for relatively thin photocathode films, especially at the green excitation wavelengths that are particularly attractive for next
generation accelerators and FELs. Thus, the overall growth rate was set at a relatively low value of ~0.002 nm/sec. It was hypothesized that at low substrate temperature, slower growth rates with the correct flux ratios of the Cs and Sb constituents would provide adequate time for the reaction to form the desired Cs$_3$Sb compound and yield photocathodes with high ~20% QE at 405nm excitation and >5% QE at 532nm.

The first photocathode was grown with the substrate heater at 250 °C (~ 82 °C on the Si surface). The antimony flux was held constant at a voltage of 3 V (2.07×10$^{12}$ atoms/cm$^2$.s) and the flux ratio (Cs/Sb) was varied by increasing the Cs flux (from 5.83×10$^{12}$ to 1.42×10$^{13}$ atoms/cm$^2$.sec). The film growth system and various parameters are controlled using LABVIEW, and the software interface allows monitoring the time evolution of the photocurrent, the QE, the overall deposition rates, the evaporation rates and temperatures of the two different elements, and the substrate temperature. The data shown in Figure 32 was obtained for a photocathode grown over an extended period of ~90000s (~25hr). The first 50,000s were grown at a constant Cs/Sb flux ratio of 2.82, likely resulting in the cathode being slightly Cs deficient since the stoichiometric ratio for Cs$_3$Sb is 3. At the beginning of the growth, the photocurrent generated by illuminating the film with a laser light at 405 nm (blue) is seen to start almost immediately without any nucleation time. This is a different response than previously reported for the sequential growth of Cs$_3$Sb photoactive films [13]. It is observed that the slope of the photoelectric current measured using the green laser (532 nm) does not increase as quickly as the photocurrent measured with the blue laser. This observation suggests that as more photoemissive material is being grown on the substrate, the green photoemission response from the material is worse. Previously, the green photoemission intensity has been correlated with the
formation of fully stoichiometric Cs$_3$Sb, implying that in the initial growth stage in Figure 32 the film stoichiometry may be deviating from Cs$_3$Sb and is most likely Cs deficient. It has been established that the best spectral response of Cs-Sb photocathodes is associated with generally higher QE values at lower photon energies (moving from blue to green to red wavelengths) and that this improved QE is strongly correlated with formation of fully stoichiometric Cs$_3$Sb vs. Cs deficient material.

When looking at the first 50000s of the growth where all the rates are constant and stable, the photocurrent using the blue laser light is seen to gradually increase from 0 to 30 μAmps (30 μAmps corresponds to a QE of ~3%). If the change in photocurrent and QE was a function of the thickness of the cathode only, the photo response would start out linear then it would peak at a saturation value. However, the slope observed in figure 32 during the first 50 000s of the growth suggests that the cathode is changing its stoichiometry and crystal structure over time under a constant flux of incoming Cs and Sb.

The last 40000s of the growth illustrated in figure 32, show the effect of increasing the Cs flux (Cs: Sb flux ratio) while keeping the antimony flux constant on the QE of the resulting cesium antimonide films. Increasing the Cs/Sb flux ratio by increasing the Cs flux systematically has an immediate (within 1 minute) impact on the QE at both wavelengths suggesting that the photo response is very sensitive to subtle changes in the surface stoichiometry. Furthermore, as the new flux ratio stabilizes, the photocathode is growing thicker and the light is sampling further into the newly established stoichiometry. The continuous increase in QE results from the photocathode getting thicker and with the new flux ratio yielding and improved photoresponse. The QE
at 405 nm increased from 3% to 21% with an increase in Cs/Sb flux ratio from 2.82 to 6.85, and the QE at 532 nm is also substantially increased likely reflecting the formation of more fully stoichiometric Cs$_3$Sb.

Unfortunately the experimental apparatus is not yet fitted with the ability to perform detailed in situ surface diagnostics which might confirm that the stoichiometry of the cathode is in fact 3:1 Cs:Sb. Variations in stoichiometry have been reported in the literature [14] and the best indication in literature that near-ideal stoichiometry has been achieved is that the QE was peaked and the QE ratio, $\frac{\text{QE (at 405 nm)}}{\text{QE (at 532 nm)}}$ is about 2. Figure 33 shows the QE ratio during film growth. Figure 33 (a) is the corresponding QE measurements from the photocurrent data shown earlier in figure 32 and figure 33 (b) shows the QE ratio changes as a function of changes in the flux ratio. As the flux ratio was systematically increased, the QE ratio decreases to a value below 2 which is a good indication of the growth of high quality stoichiometric Cs$_3$Sb film.
Figure 33: (a) Corresponding QE progression measurements of the cathode shown previously when the photocathode surface was illuminated with a 532 nm laser (green) and 405 nm (blue) (b) The QE ratio progression with respect to flux ratio

13.2 Growth Rate Study

The initial growths were primarily used to narrow the operating window in which stoichiometric, photoactive Cs$_3$Sb can be obtained at a heater temperature of 250 °C (82°C at the surface). Once the desired flux ratio was obtained, the influence of growth rate on the QE and photoresponse of the initial layers of Cs$_3$Sb photocathode was investigated as shown in Figure 34. By increasing the Sb flux from $2.07 \times 10^{12}$ atoms/cm$^2$ sec to $5.06 \times 10^{12}$ atoms/cm$^2$ sec and the Cs flux from $1.42 \times 10^{13}$ atoms/cm$^2$ sec to $3.54 \times 10^{13}$ atoms/cm$^2$ sec the effective growth rate was increased from ~0.03 Å/s to ~0.075 Å/s (a factor of 2.5) while keeping the Cs:Sb ratio constant. The relatively fast response in QE at 532 nm and the lower QE ratio from the start indicates that high quality material is being grown. However, at longer times the QE at 405 nm and 532 nm is seen to level out at around 3% and 1% respectively. One hypothesis may be that growing at a faster rate may not provide enough time for the Cs$_3$Sb material to nucleate and form large grains thereby impacting the QE at 532 nm. Since at these longer growth times an ~45 nm thick cathode is formed, the QE at 405 nm also saturates. Higher growth rates becomes more important when growing for large scale application, but in order to understand the growth mechanism and surface dynamic lower thin film growth rates for Cs$_3$Sb are preferred.
The observed immediate green (532 nm) response at the higher growth rate can also be correlated to the increase in Sb flux, where having more antimony available to react from the beginning may allow the accelerated formation of high quality Cs$_3$Sb. This observation means that the amount of antimony arriving at the surface largely determines how quickly it reacts with Cs to form a film that is photoactive, indicating that the film growth is Sb flux dominated. If Cs was the limiting factor for the growth rate of Cs$_3$Sb, then increasing the Sb flux would have no impact on the surface reaction.

### 13.3 Impact of fluxes on film growth mechanism

The next step to understanding the mechanism for growing a stoichiometric and photoemissive Cs$_3$Sb was to investigate the importance of flux ratio (Cs/Sb) on the resulting quality and QE of the Cs-Sb films. The effect of the flux ratio on the QE of three different samples was compared. The flux ratio for sample 1 was established on a 150 nm thick cathode. After a systematic increase of Cs illustrated in Figure 32
illustrated earlier, a flux ratio of 6.85 was established to give a Cs$_3$Sb film with a QE of 21%. The flux ratio (6.85) for sample 2 was established on a 45 nm thick cathode and the flux ratio for sample 3 was established on a Si (100) substrate with no previously grown Cs-Sb film. All QE measurements were taken at a thickness of roughly 200 nm. The table below summarizes the QE measurements.

**Table 4: QE measurements normalized to thickness of three cathode grown using the same flux ratio on different starting surfaces**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux ratio (Cs/Sb)</th>
<th>starting surface</th>
<th>QE at 405 nm</th>
<th>QE at 532 nm</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>6.85</td>
<td>150 nm thick cathode</td>
<td>21%</td>
<td>9%</td>
<td>200</td>
</tr>
<tr>
<td>Sample 2</td>
<td>6.85</td>
<td>45 nm thick cathode</td>
<td>2%</td>
<td>0.02%</td>
<td>200</td>
</tr>
<tr>
<td>Sample 3</td>
<td>6.85</td>
<td>Si(100)</td>
<td>4%</td>
<td>1%</td>
<td>200</td>
</tr>
</tbody>
</table>

The resulting QE using the same flux ratio is different for each Cs-Sb film, which may suggest that the resulting QE might be dependent on the path whereby it was grown. Considering the fact that sample 2 and 3 were given a continuous flux of Sb and Cs over a period of 13 hours and the QE observed remained unchanged it is safe to assume that enough time was given for the reaction to occur. After the period of continuous flux of Cs and Sb, the Cs flux was then increased and the QE was seen to also increase. Based on this observation, it is apparent that the Cs-Sb films were Cs deficient therefore the reaction leading to stoichiometric Cs$_3$Sb could not occur. This may suggest that the sticking coefficient of Cs changes as the film grows and might be a factor of how much Cs is already present on the surface. Cesium has one of the lowest melting points of any metal at 28.44 °C, second to mercury. Therefore, it is not surprising that it has high vapor pressures and evaporation rates even at modest temperatures (~5x10$^{-3}$ Torr at 150 °C).
These bulk properties provide an indication that monolayer and sub-monolayer films of cesium should be prone to evaporation, but the evaporation rates of such at the surface will differ from the bulk because cesium bonds differently to various surfaces. For instance, cesium on polished, polycrystalline tungsten has been measured to have a sub-monolayer evaporation rate of 0.009 Å/s and a multiple-monolayer evaporation rate of approximately 0.214 Å/s at temperatures less than 200 °C [19]. This hypothesis is furthermore supported by QCM rate data during flux calibration. The rate of thickness increase (Å/s) for Sb at a constant temperature was found to be constant over time while the rate of thickness increase for Cs started at 0.1 Å/s and ended at 0.03Å/s over a period of 10 mins. Although the QCM is cooled and sitting at a chilled water temperature (20°C), the corresponding Cs vapor pressure at that temperature is $10^{-7}$ (0.1 monolayer per sec), which is equal to the impinging rate at the surface and therefore may justify the lower sticking coefficient of Cs even at room temperature.

### 13.4 Impact of Substrate temperature on film growth

In order to investigate the role of temperature on the dynamic of Cs$_3$Sb formation, growth at room temperatures was explored. The flux ratio was held constant at Cs/Sb value of 6.85 which is the value that was seen to promote the highest QE (20%). Figure 35 shows the QE at 405 nm and 532 nm. Part I represents the QE during growth and Part II represents the QE after growth over a period of 11 hrs (38900s). During the growth at room temperature (from 0 to 11000s) the QE at 405 nm is seen to slowing increase then slowly saturating at a QE of < 1%, however no real increase in the QE at 532 nm is observed. The increase in blue (405 nm) response correlates to an increase in thickness
however the fact that there was no green (532 nm) response suggested that the film that was forming was not stoichiometric. After the growth the film was left in the UHV chamber and the QE was monitored over a period of 11hrs after the growth. Immediately after the growth was stopped, QE at both wavelengths was seen to increase and over the period of 11hr, the QE at 405 nm increased from <1% to over 6% and the QE at 532 nm increased from zero to over 2% giving a QE ratio of approximately 3. This suggests that at such low temperature the flux ratio of 6.85 created a Cs rich environment quenching formation of the Cs$_3$Sb reaction product.

![Figure 35: QE measurements at 405 nm and 532 nm of the co-deposition of Cs3Sb at room temperature. Part I: during deposition. Part II: after deposition.](image)

In order to further investigate the role of flux ratio and temperature on the dynamics of Cs$_3$Sb formation, growth at three substrate temperatures (RT, 60°C, 85°C)
using a lower flux ratio (Cs/Sb = 2.82) was explored. The substrate temperature in this case is defined as the Si surface temperature. The flux ratio, slightly Cs deficient from the stoichiometric flux ratio, was held constant at Cs/Sb = 2.82 to enable effective comparison from sample to sample. First, Figure 36 shows the QE at 405 nm and 532 nm of three different growth runs at three different temperatures during the first 3000 s.

The results show that at room temperature, Figure 36 a), no green (532 nm) response was observed during the initial stages of film growth. As the temperature increases, the slope
of the curve representing QE at 532 nm follows that of the QE at 405 nm suggesting that more Cs$_3$Sb is formed at the initial stages. However the highest QE at 405 nm (1.4 %) was observed at a surface temperature of 60 °C. These results support a growth mechanism that requires precise tuning of both flux ratio and substrate temperature to minimize Cs depletion and drive the reaction to form stoichiometric Cs$_3$Sb and also promotes the nucleation of grain sizes that will minimize electron scattering.

**13.5 Cs$_3$Sb thin film photocathode degradation**

The degradation of two Cs$_3$Sb photocathodes was compared and Figure 37 shows the results of leaving the thin film Cs$_3$Sb photocathode sitting in UHV for 13hrs. The data in Figure 37 was taken after deposition when all the fluxes were stopped. Film deposition for both samples (1 and 2) was done at 250 °C (as read from the heater TC). After film deposition, sample 1 was heated to 360 °C for one hour (3600s) then cooled to room temperature while sample 2 was immediately cooled to room temperature. As the thin film in sample 1 was heated the QE at 405 nm decreased as seen in Figure 37. This decrease in QE is attributed to cesium depletion from the surface that makes the cathode non-stoichiometric. When the film cooled down the QE recovers for a short period of time then degrades fast. On the other hand, the QE of sample 2 experiences a short increase, then barely degrades over 13 hrs. The rapid decrease in QE over time for sample 1 due to its non-stoichiometric composition made the film sensitive to accelerated degradation from loss of Cs. This observation suggests that the structure of a stoichiometric Cs$_3$Sb photocathode is more stable.
Figure 37: Degradation progression of two Cs-Sb films over 14hr. Sample 1 was annealed to 360°C after growth and sample 2 was not.
14.0 Conclusion

The goal of this research was to effectively understand and explore the co-deposition of Cs$_3$Sb thin films by molecular beam epitaxy in order to develop atomically smooth thin film photocathodes for next-generation X-ray light sources. The specific objectives included growing Cs$_3$Sb on a silicon substrate via co-deposition to form stoichiometric films, understanding and linking the effects of deposition process conditions to the growth mechanism of Cs$_3$Sb by analyzing in real-time the resulting photoactive performance. By successful demonstrating the ability to grow stoichiometric Cs$_3$Sb with high QE at room temperature, high-brightness, low intrinsic emittance and high quality electron beams can be developed and optimized for next-generation X-ray light sources.

The highest photoactive Cs$_3$Sb thin film has been grown on silicon via co-deposition at a substrate temperature of 82°C generating a QE of 20% at 405 nm and QE of 8% at 532 nm. A systematic study of the impact of growth parameters shows that the chemistry, and possibly the crystallinity of the co-deposited Cs$_3$Sb films highly depends on a balance between substrate temperature, initial flux ratio and growth rate. This balance is necessary to minimize Cs diffusion, Cs depletion and Cs$_3$Sb dissociation, which are competing mechanisms observed during film growth. Although the growth mechanism of Cs$_3$Sb was found to be antimony controlled, the sticking coefficient of Cs was seen to decrease over time leading to the deterioration of the QE of the Cs$_3$Sb films at a surface temperature of 82°C. Upon subsequent Cs supply, the deficient films may deplete the surface, triggering Cs diffusion into the film that can lead to an increase in surface roughness. At room temperature, establishing initial flux ratio is seen to be
critical for determining full stoichiometry and good crystallinity of Cs$_3$Sb. However, the low temperature limit is thought to promote nucleation of smaller grain size crystals constraining the QE values at both wavelengths to levels less than 10% because of likely electron scattering via grain boundaries.

The dynamics leading to formation of the Cs$_3$Sb reaction product are complex. Optimization of the co-deposition of Cs$_3$Sb will require a deeper understanding of those dynamics. Specifically, a comprehensive time-dependent theory of cesium diffusion through the film and across the surface, with the inclusion of evaporative effects and their proper functional dependence, will serve to strongly support the development of a consistent process capable of growing high QE and atomically smooth Cs$_3$Sb films.

The operational lifetime measurements suggested that non-stoichiometric thin films are more sensitive to degradation. In addition, the final films need to be studied by XPS/AES analysis in order to further validate the conclusions relating the observed QE performance to stoichiometry. Possible mechanisms of degradation of the cathode photoemissive properties have also been speculated. However, XPS/AES analysis will allow the investigation of the film surface composition with respect to the formation of oxides, a possible degradation mechanism. Despite the high QE obtained with the co-deposition process for Cs$_3$Sb thin films, information on the morphology of the final film surface has yet to be investigated. This can be accomplished via UHV- AFM measurements of the surface roughness of the resulting thin film with correlations to deposition conditions.
15.0 RECOMMENDATIONS

This study demonstrates the potential of Cs₃Sb photocathodes for next-generation X-ray light sources. The progress made through this research can be extended beyond understanding the mere co-deposition of Cs₃Sb to building correlations between processing parameters and film properties by studying structure and composition evolution during film growth in order to engineer the desired photocathode thin film. One recommendation is geared towards the focus on structural characterization techniques during growth (Reflection High-Energy Electron Diffraction- RHEED) and after growth (Low Energy Electron Diffraction-LEED). By using RHEED and LEED, it will be possible to monitor the crystal quality of the top surface of the photocathode film and enable the correlation between processing parameters, stoichiometry and crystal quality. Further, in the process of using RHEED, time should be spent to allow for real-time growth rate determination this can be of great importance when determining the sticking coefficient of each individual species.

A second recommendation is focused towards an in depth understanding of the competing mechanisms that govern the growth of Cs-Sb photocathodes and how each processing parameter quenches or enhances each mechanism. bonding mechanisms between MgO/6H-SiC and BTO/MgO, and to demonstrate

grain size control through the epitaxial growth of the mentioned films exploring the use of lattice matched substrates and/or template layers.
16.0 REFERENCES


**Appendix A**

**A.1: Fundamental principle behind thermoelectricity**

Thermoelectricity is a phenomenon discovered and developed back in the nineteenth century. It is the direct conversion between heat and electricity. The observed phenomenon is called the thermoelectric effect. The term "thermoelectric effect" encompasses three separately identified effects: The Seebeck effect, the Peltier effect, and the Thomson effect. The Seebeck effect is the conversion of temperature differences directly into electricity. The second of the thermoelectric effects named the Peltier effect is described as a temperature gradient generated when an electrical current is applied [4]. Figure A1 illustrates the two phenomena.

![Figure A1: Schematic of a p-n junction used as a thermoelectric couple based on two major thermoelectric effects: Peltier effect on the right and Seebeck effect on the left. [5]](image)

Shortly after the discovery of the Peltier effect, W. Thomson established a
relationship between the Seebeck and Peltier effects and also introduced the existence of another thermoelectric effect called the Thomson effect. This effect is simply the heating and cooling in a conductor when current passes in a presence of a temperature gradient. All materials exhibit thermoelectric effects but the name 'thermoelectric materials' is used to describe the materials that are good at converting heat to electricity.

Any electrically isolated conducting material that is subjected to a temperature gradient generates an electrical potential (voltage) called the *Absolute Seebeck Effect* (ASE). The instantaneous rate of change of the ASE with respect to temperature is defined as the *Absolute Seebeck Coefficient* (ASC) of that material. Two dissimilar conducting materials can be connected in a junction to form a thermocouple. The application of a temperature at the junction, that is different from the electrically isolated ends of the individual wires, will produce a voltage across the unpaired terminals. This voltage is called the *relative Seebeck electromotive force*, RSE and it is a consequence of the difference between the internal potentials, ASE’s, of the individual materials forming the thermocouple junction [6]. The instantaneous rate of change of the absolute Seebeck emf is the absolute Seebeck coefficient which is described in Eqn 1

\[
ASC = \left[ \frac{d}{dT} (ASE) \right]_T
\]  

The Seebeck effect is present as long as there is a temperature gradient regardless of whether current flows or not. The open circuit voltage \(V_{oc}\) with no current flowing is also called the Seebeck voltage given by the following equation:

\[
V_{oc} = S_{\text{diff}}(\Delta T)
\]
The constant of proportionality, $S_{dif}$, also called the differential Seebeck coefficient defined as the Seebeck coefficient of the thermocouple. The performance of any thermocouple as an energy convertor depends on the thermal and electrical properties of the two materials forming the junction. However, in the search improved thermocouples, it is uncommon to investigate a pair of materials at the same time. Therefore, single material properties will be the focused in the following discussions including relationship between materials development and system requirements.

To understand how TE materials generate electricity from a temperature difference it is necessary to understand how electrons move in a material. An electron in a solid is an elementary particle that carries electric current. When electrons in a material are subjected to a temperature difference they flow from the hot end to the cold end causing an electric current. The larger the temperature difference the more electrical current is produced. This implies a coupling between thermal and electrical phenomena in the material. Therefore a high flow of electrons is necessary to maximize the electrical current going through a material and a low flow of heat carrying particles is necessary to maintain a large temperature gradient.

The key parameters that impact the magnitude of the Seebeck voltage are the Seebeck coefficient, the electrical conductivity and the thermal conductivity. The Seebeck coefficient, $S$, of a material is defined by the following equation

$$S = \frac{8n^2k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \quad (3)$$

Where $k_B$ = Boltzmann constant
n = carrier concentration
$m^*$ i= effective mass of the charge carrier
h = plank’s constant
A high Seebeck coefficient, $S$, is required to get the maximum output voltage per degree of temperature difference. A detailed derivation of a material’s Seebeck coefficient may be found elsewhere [7]. Electrical conductivity is the ability of a material to conduct an electrical current. This value needs to be at its maximum in a thermoelectric material to minimize the loss of charge energy due to joule’s heating which is the process where the energy of an electric current is converted to heat as it flows through the material. The energy conversion occurs through scattering events, in which the kinetic energy of a carrier drifting in the applied electric field is transferred to the lattice [49].

In the Drude model, the electrical conductivity is defined in terms of the elastic scattering time, $\tau$, and the effective mass of the electrons, $m^*$ in the materials in the following equation:

$$\sigma = \frac{nq^2\tau}{m^*} \quad (4)$$

Where $n$ is the carrier density
$q$ is the charge of the electron

When the material is subjected to a temperature difference, a fraction of heat will be directly transport from $T_h$ side of the couple to the $T_c$ side of the couple through thermal conduction rather than being carried by charges. The part of the heat carried directly from one side to the other will not produce electricity hindering the achievement of high conversion efficiency while maintaining a high temperature difference. Heat is carried in solid materials by lattice vibration waves (phonons), and by free electrons. Therefore, the ability for a solid to conduct heat, the thermal conductivity, is the summation of the lattice contribution $k_l$ and the electron contribution $k_e$. A low thermal conductivity, $\kappa$, is highly favored to enable restriction of the diffusion of the heat across the device in order
to maintain a large temperature gradient. The Seebeck coefficient, the electrical conductivity and the thermal conductivity of given material are referred to as its transport properties and are embodied in the so-called figure-of-merit, $Z$. Since $Z$ varies with temperature, a useful dimensionless figure-of-merit can be defined as $ZT$. The Figure of Merit of a single material is given by:

$$Z_i T = \frac{\sigma S^2 T}{\kappa_{lattice} + \kappa_{electronic}}$$  

(5)

Where:

- $S$ is the Seebeck coefficient of the material
- $\sigma$ is the electrical conductivity
- $\kappa_{lattice}$ = phonon contribution to the thermal conductivity
- $\kappa_{electronic}$ = electronic contribution to the thermal conductivity.
- $T$ is the absolute temperature

Based on the relationship describe in (5), obtaining a high Figure of Merit for thermoelectric materials requires maintaining high electrical conductivity and large Seebeck coefficient while simultaneously limiting thermal conductivity.

In a simple material, an increase in Seebeck coefficient, $S$, leads to a simultaneous decrease in electrical conductivity, $\sigma$. Comparatively, an increase in electrical conductivity $\sigma$, leads to an increase in thermal conductivity, $\kappa_{electronic}$. The dependence of the parameters is illustrated in Figure A2.
Figure A2: Illustration of the interdependence of the Seebeck coefficient, the Figure of Merit, the electrical conductivity and the thermal conductivity with respect to the change in carrier concentration for a bulk material. [8]

Figure A2 confirms that the carrier concentration needs to be at a minimum for the Seebeck coefficient to be at its maximum. While increasing the carrier concentration is unfavorable to the Seebeck coefficient, Figure A2 shows an increase in electrical conductivity due to the increase of available carriers. On the other hand as the carrier concentration increases in metals the electronic contribution to the thermal conductivity becomes dominant [9]. Metals are usually known for their low values of Seebeck coefficient, high thermal conductivity and high electric conductivity, which cannot compensate for the former two setbacks. The insulators are characterized by high Seebeck coefficient and low electrical conductivity. Semi-conductors seem to have a
carrier concentration in the range where the Figure of Merit is at its maximum while parameters compete with each other.

To better understand the interrelationship of parameters, the Figure of Merit can also be rewritten in terms of electrical resistivity ($\rho$).

$$ZT = \frac{s^2T}{\rho \kappa} \quad (6)$$

Where $\rho$ = electrical resistivity

As stated before, the thermal conductivity has both an electron and a phonon (lattice vibration) component. Around room temperature and above, these contributions to $\kappa$ are independent and have the following relationship:

$$\kappa = \kappa_e + \kappa_{ph} \quad (7)$$

In insulators and low carrier density semiconductors $\kappa_{ph} >> \kappa_e$, while in metals $\kappa_e > \kappa_{ph}$. $\kappa_e$ is related to the electrical conductivity by the Widemann-Franz law: $\rho \kappa_e = L_0 T$ where $L_0$ is the Lorentz number (2.22 x 10^{-8} watt-Ohm/K^2) for free electrons. Eqn (8) can then be rewritten in terms of the two contributions of the thermal conductivity as followed:

$$ZT = \frac{s^2}{L_0 (1 + \frac{\kappa_{ph}}{\kappa_e})} \quad (8)$$

For $ZT$ to be at its maximum, it is highly recommended to have $\kappa_e > \kappa_{ph}$ as in the metals but as stated earlier metals usually have low Seebeck coefficient. A simple calculation using Eqn 8 indicates that $S$ must be 156 $\mu$V/K to have a $ZT$ of 1, which is a very high number compared to 10 $\mu$V/K, a typical Seebeck coefficient value for metals. Because the Seebeck coefficient’s contribution is dominant in determining the overall figure of
merit, metals are not used as thermoelectric materials. On the other hand, semiconductors have their Seebeck coefficient increasing as carrier density decreases. [10]. However, this behavior happens in the region where $\kappa_{ph} >> \kappa_e$ making semiconductors with low lattice thermal conductivity, $\kappa_{ph}$ and high Seebeck coefficient one of the target thermoelectric materials.

**A.2 Thermoelectric material for device integration**

The challenge in high-efficient TE materials is the decoupling of the four parameters mentioned above due to their interdependency. There is no thermodynamic limit to the ZT of a material, however, the highest ZT found in a commercially available product is reported as ZT~2. PbTe- based materials dominate the commercially available power generation applications at high temperatures, and Bi$_2$Te$_3$-based materials dominate for the refrigeration applications need at room temperature [11]. However a value of 1 for the ZT, falls short of the generally desired threshold value of 3 needed for device integration. The ultimate objective of TE material research are to increase the performance of TE devices. Along with continuing to improve the material’s figure of merit, device efficiency is also important. The efficiency of a thermoelectric device composed of two thermoelectric materials is given by Eqn 9

$$\eta_{\text{max}} = \frac{T_H - T_C}{T_H - T_C + \frac{1}{M + \frac{T_C}{T_H}}} (9)$$

$$M = \sqrt{1 + \frac{1}{2} ZT (T_C + T_H)} (10)$$
\[
ZT = \frac{(S_1-S_2)^2 T}{\left(\frac{k_1}{\sigma_1} + \frac{k_2}{\sigma_2}\right)^2}
\]  
(11)

Where:
- \(T_H\) is the temperature at the hot end of the device, K
- \(T_C\) is the temperature at the cool end of the device, K
- \(ZT\) Figure of Merit of device, dimensionless
- \(S_i\) = Seebeck coefficient, V/K
- \(k_i\) = thermal conductivity of species i, W/m K
- \(\sigma_i\) = electric conductivity of species i, Siemens/m

Note by Ohm’s Law and Definition of Power within an electrical circuit:
1 V^2 = 1 Watt/Siemen

The maximum overall conversion efficiency of a thermoelectric material integrated in a device is the product of the ideal reversible thermodynamic process efficiency and a factor describing the energy losses within the device due to Joule heating and non-ideal thermal conductivity [49]. The ideal reversible thermodynamic process efficiency is called the Carnot efficiency and the energy losses associated with the heat conduction and Joule heating of the two dissimilar materials connected is given in Eqn 10 and Eqn 11. As there is no theoretical limit for ZT of a material, it approaches infinity as the device efficiency approaches the Carnot limit. Therefore, a thermoelectric power conversion device with materials having ZT of 3 operating from 303 K to 773 K would yield \(~50\%\) of the Carnot efficiency [12]. Consequently, what is needed to make this application possible are new material designs to enhance the ZT. For a device, \(ZT\) is defined for a pair of thermoelectric materials, rather than single materials, but the potential for a material to be used in thermoelectric applications depends on the conversion efficiency of that single material. Therefore, it is convenient to select materials on the basis of the maximization of material ZT given earlier in Eqn 5. To avoid any confusion, the use of ZT in the rest of the document will be strictly to describe the figure of merit of a single material.
A.3 Historical work on Semiconductor Thermoelectric materials

Two predominant approaches have been adopted to improve the material’s Figure of Merit. The first approach is called the “Phonon glass electron crystal” (PGEC) and the second approach is nanostructuring. The first one suggests that an ideal thermoelectric material should be the combination of glass-like thermal conductivity and crystal-like electronic properties [13]. This concept led to the engineering of complex materials with distinct region aimed at providing different functions. The second approach involves the decrease in size of the material from bulk to the nanometer scale forming what is called low dimensional materials. They possess at least one physical boundary small enough to confine the electrons or phonons [13]. From there, different methods were used to further the theories concerning PGEC and nano-structuring:

1. The field of low dimensional structures makes use of nano-structuring to control targeted parameters achievable by causing differences in the density of state of a material near its Fermi level allowing opportunities to vary the Seebeck coefficient, the electrical conductivity and the thermal conductivity almost independently [14]

2. The reduction of the lattice contribution to the thermal conductivity through nanostructuring introduces a large number of grain boundaries at the nanoscale capable of scattering different portion of the heat-carrying phonons spectrum.

3. Band-gap engineering which allows the transport properties of electrons and holes to be independently and continuously tuned. [15]

The use and exploration of families of bulk thermoelectric with complex crystal structures which have high electronic conductivity due to their highly crystal structure and low thermal conductivity due to their complex structural features [13]. This approach
is the most achievable in materials with complex crystal structures, where voids (vacancies) and heavy element atoms located in the voids would act as effective phonon scattering centers and reduce the lattice thermal conductivity significantly.

**A.4 Figure of merit (ZT) enhancement at the nanoscale-theory**

Low dimensional thermoelectric materials were introduced as a mean to improve the Figure of Merit. Before demonstrating the potential enhancements that low dimensional structures can bring to the ZT of a thermoelectric material, the definition of low dimensional samples must be introduced. If a sample is made with dimensions of length, $L$, width, $W$ and thickness $t$, then the dimensionality of the system and the appropriate transport regime for electrons or phonons is inferred by comparing the sample dimension to the various scattering lengths and characteristics lengths. [16]

The concept of low dimensionality goes from 3D crystal solids to 2D (quantum wells) to 1 D (quantum wires) and finally 0D (quantum dots). [17] The unique ability to tune material properties by reducing the size, to low dimensional structures designed brought the introduction of nanoscale polycrystallines and interfaces into bulk materials which have the potential to reduce the lattice thermal conductivity by increasing the phonon scattering without compromising carrier mobility values. This is possible at the nanoscale because the transport of electrons and phonons are affected by quantum size effects and interface effects. The idea is that if the device dimension of a material is made smaller than the mean free paths of electrons and low frequency phonons, the boundary of the material confines the mean free paths to those of high and medium frequency phonons, essentially screening out low frequency phonons. Since low frequency phonons are usually the highest contributors to the thermal conductivity of materials, the thermal conductivity should decrease when these phonons are screened without touching the
electrical conductivity. A theoretical model on the contribution of phonon scattering to the lattice thermal conductivity, as a function of mean-free path for Silicon generated by Henry et al. calculated that 90% of the thermal conductivity accumulation in Si is due to phonons that have mean free path greater than 20 nm. Which means a decrease in the grain size to 20 nm could achieve a 90% reduction in lattice thermal conductivity [18].

To understand how low dimensional systems can improve ZT, we first need to find the energy solutions for a low dimensional system. It is required to solve the time independent Schrodinger equation:

\[
-\frac{\hbar^2}{2m_e} \frac{d^2\psi(x)}{dx^2} + V(z)\psi(x) = E\psi(z) \quad (16)
\]

For a 3-D bulk system the energy equation is given by:

\[
E = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z} \quad (17)
\]

For a 2D quantum well the solution becomes

\[
E = \frac{\hbar^2 k_x^2}{2m_e} + \frac{\hbar^2 k_y^2}{2m_e} + \frac{\hbar^2 \pi^2 n^2}{2m_e w^2} \quad \text{for } n = 1, 2, 3\ldots \quad (18)
\]

The integers \( n = 1, 2, 3 \) are quantum numbers and the solution provides quantized energy level restricting the energy of the electron to subband states. This indicates free-electron like motion in the x-y plane and a bound state in the z-direction. Using the same method the energy of the electron for a 1D system is given by:

\[
E = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 \pi^2}{2m_y w^2} + \frac{\hbar^2 \pi^2}{2m_z w^2} \quad (19)
\]
This indicates free-electron like motion in the x-direction and a bound state in the y and z direction. The energy solution of electrons is then used to derive the density of states giving information about electron behavior.

A.5 Fermi Level and Density of states

Electrons are particles that have half-integer intrinsic angular momentum. Therefore, they cannot exist in identical energy states. At absolute zero they pack into the lowest available energy states and build up what is known as a “Fermi Sea” of electron energy states. The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface. The concept of the Fermi energy is an important concept for the understanding of the electrical and thermal properties of solids. Both ordinary electrical and thermal processes involve energies of a small fraction of an electron volt. But the Fermi energies of metals are on the order of electron volts. This implies that the vast majority of the electrons cannot receive energy from those processes because there are no available energy states for them to go to within a fraction of an electron volt of their present energy. Limited to a tiny depth of energy, these interactions are limited to ‘ripples on the Fermi sea”. At higher temperatures a certain fraction, characterized by the Fermi function, will exist above the Fermi level. In doped semiconductors, the Fermi level is shifted by the impurities, illustrated by their band gaps. In metals, the Fermi energy gives us information about the velocities of the electrons, which participate in ordinary electrical conduction.

The density of states refers to the number of quantum states per unit energy. In other words, the density of states denoted by \( g(E) \) indicates how densely packed quantum states are in a particular system. To understand the importance of the density of
states the expression $g(E) dE$ needs to be evaluated. Integrating the density of the quantum states over a range of energy will produce a number of states.

$$N(E) = \int_{E}^{E+\Delta E} g(E) dE \quad (20)$$

Where $g(E) dE$ represents the number of states between $E$ and $dE$.

In a 3D system, we know the total energy is given by (20) giving a solution in k-space similar to the plot in Figure A3

Figure A 3: Schematic of the solution in k-space of the energy of the electron. The value of k is given by the dots and the number of allowed state is the number of these points contained in the blue shell of radius k and thickness $dk$
In 2D, an electron is confined along one dimension but able to travel freely in the other two directions. An electron would then be confined in the $z$-direction but would travel freely in the XY plane just like illustrated in Figure A4.

![Visualization of the movement of the electron in a quantum well (2-D)](image)

Figure A4 Visualization of the movement of the electron in a quantum well (2-D)

Instead of finding the number of k-space within a sphere, in 2D, the calculation becomes easier because we only need to operate in two dimensions. Instead of using the volume of a shell, the area of a ring with width of $dk$ is used. Analogous to the sphere in three dimensions, the circle is used because all points on the circle are an equal distance from the origin; therefore, the circle indicates equal values of energy. The radius becomes $k = \sqrt{k_x^2 + k_y^2}$ and the solution in the k space given in Figure A5.
Figure A5: Illustration of the k-space in 2-D which is given by the donut-shape annulus. The density of state is the number of available state in the annulus of radius $k$ and thickness $dk$.

The density of states for a 1D quantum mechanical system exhibits a unique solution which has application in things such as nanowires and carbon nanotubes. In both the x and y directions, the electron is confined, but it moves freely in the z direction.

Figure A6: Schematic of the motion of the electron in a 1-D system
With this restriction in the motion of the electron the k-space becomes a length and the area of the annulus changes to a line. In a 0-D structure, the values of k are quantized in all directions. All the available states exist only at discrete energies described. The derived density of states for each dimension can then be plotted vs. energy similar to Figure A7.

![Figure A7: Density of state of 3-D structures (blue), 2-D structures (red) 1D structure (green) and 0-D structures (black) [19]](image)

It can be noticed that the density of states of a bulk material is gradually dependent on the energy where as the 2-D density of states does not depend on energy. Immediately as the top of the energy-gap is filled there is a significant number of available states. When we take into account the other energy level in the quantum well, the graph becomes a staircase.

**A.6 Thermal and electrical properties at the nanoscale.**

The reduction in thermal conductivity which is one target method used to increase the Figure of Merit of TE materials takes new scopes at the nanoscale because heat
transfer at nanoscale may differ significantly from that in macro and micro-scales. With device and characteristic length scales becoming comparable to the mean free path and wavelength of heat carriers (electrons and phonons) the classical laws are no longer valid [20]. For nanoscale materials, the thermal conductivity is no longer a material property: the physical size of the material starts to have an impact on its properties. Electrons exhibit both wave and particle properties which is called wave-particle duality and this behavior is more significant at the nanoscale. Two length scales, namely De Broglie wavelength, $\lambda$, and mean free path $l$, have been identified to characterize the transport of energy carriers with wave-particle duality. The wavelength, $\lambda$, is defined as

$$\lambda = \frac{h}{p} \quad (21)$$

where $p$ is the momentum and is a measure of the significance of wavelike behavior.

When the characteristic length is much larger than the wavelength $\lambda$, then the energy carrier can be treated as particles. When the characteristic length is at the same order of the wavelength $\lambda$, these carriers will exhibit significant wave behavior and when the characteristic dimension is comparable to or even smaller than the wavelength of the carriers, carriers “feel” the presence of particle boundaries and responds to changes in particle size by adjusting their energy. These quantum confinement effects result in the alteration of the energy spectrum and decrease the group velocity of the quantum wavepackets which have a direct impact on the thermal conductivity. This impact can be seen in Eqn 22 where a more general form of the thermal conductivity is defined
\[
\frac{1}{3} v^2(\varepsilon) \left( \frac{f_0}{T} \right) D(\varepsilon) d\varepsilon
\]  
(22)

where \(v_{\text{g}}\) is the group velocity, \(\tau(\varepsilon)\) is the scattering time.

Since many forms of phonon scattering are present in a solid, the net relaxation time is determined by considering all the scattering methods in parallel. This formulation is called Matthiessen’s Rule such that the effective scattering time is given by:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{phonon}}} + \frac{1}{\tau_{\text{impurities}}} + \frac{1}{\tau_{\text{boundary}}}
\]

(23)

Where the effective scattering \(\tau_{\text{eff}}\) are scattering rate due to different processes.

Eqn 23 implies that the scattering process with the shortest time will dominate.

For nanostructures, boundary scattering is dominant because the ratio of the wavelength of phonon, \(\lambda\), to the characteristic dimension, \(L\), is greater than 1 which means that the characteristic dimension is smaller than the wavelength of the carriers indicating that specular interface scattering is dominant [21]. For perfect specular scattering the phase of wavepackets and thus the coherence are preserved. The coherence between those wavepackets will produce interference effect in which the superposition of several coherent wavepackets will result in a new energy band for electron and phonons or the changes in the energy dispersions and group velocities [22]. Therefore boundary and interface scattering rate are enhanced in low-dimensional structures leading to increasing resistance to heat flow.

The quantum size effect on phonons observed in low-dimensional structures can
be extended to the transport of electrons and has been utilized to improve the electron energy conversion capability. Having laid the background for understanding the thermoelectric phenomenon, and some of the research approach used on the traditional semiconductor thermoelectric materials, the next section will introduce oxide thermoelectric materials and a detailed look at the potential control of Seebeck coefficient due to metal oxide tunability.

**A.5 Introduction to thermoelectric materials**

This section presents an introduction of oxide thermoelectric that will set the theoretical foundation behind the proposed research and the important factors affecting oxide TE transport that will eventually be important when correlating processing parameters to film properties. The largest figures of merit reported above have been achieved with materials containing lead, tellurium, antimony and germanium [44]. However, many of these compounds present stability and toxicity issues for some applications and are expected to be replaced by non-toxic and relatively abundant materials, namely metal oxides.

Metal oxides are a vast but conventionally less studied family of TE materials. Metal oxides are known to exhibit a wide range of electronic properties ranging from insulating to semiconducting to conducting which make them quite promising in terms of tuning their electrical property [45]. However, this class of compound was initially overlooked in the search for high ZT materials because, typically insulators, they exhibit very low electrical conductivity and most also have a low average atomic mass relative to many traditional thermoelectric materials and therefore a higher atomic vibration frequency and thermal conductivity. However, a case can be made for the use of metal
oxides as thermoelectric materials based on a large value of the Seebeck coefficient that can potentially be obtained, as well as the electrical tunability available in the typically complex structures.

A.6 Advantage of thermoelectric oxides

By far, the most widely used state-of-the-art TE materials are bulk materials. They are complex alloys of Bi$_2$Te$_3$ (n-type) and Sb$_2$Te$_3$ (p-type) for cooling and refrigeration applications (T< 200 C). Peak $zT$ values for these materials are typically in the range of 0.8 to 1.1, with p-type materials achieving the highest values. The summary of the materials used for different temperature range is illustrated in Figure A8 a)

![Figure A8](image)

**Figure A8: a) Figure of merit of state-of-the-art materials used through a wide range of temperature. b) New classes of materials that are found to have good $zT$ c) The effect of tuning the carrier concentration in PbTe compounds.**

The driving force in optimizing the $zT$ for most of the bulk alloys presented above is tuning of carrier concentration. An example of this effect is found in Figure A8 c) where changing the dopant concentration of compound PbTe changes not only the peak $zT$ but also the temperature at which the $zT$ peaks[46]. The reliance on these materials is troublesome partly because of their toxicity (Sb, Se, Pb), which will limit some applications, but more so because of the scarcity and cost of tellurium which at 1 ppb in the earth’s crust is even rarer than platinum (37 ppb). The USGS classifies tellurium as
one of the nine rarest metals [47] and the DOE lists it as a critically scarce energy material [27]. Because of its scarcity the cost of tellurium has risen from $3.86/ lb in 2000 to $127/ lb as of 2015 [48]. In comparison, oxide thermoelectrics are generally non-toxic and rely on more abundant transition metals, having excellent high temperature stability and corrosion resistance.

The increasing attention towards oxide TE materials is largely due to the discovery of a cobalt oxide crystal (NaCo$_2$O$_4$) exhibiting metallic electrical conductivity (0.2 mΩ cm) while having a large value of 100 µV/K as Seebeck coefficient[49] . This cobalt oxide crystal with its large Seebeck coefficient along with the metallic electrical conductivity was shown to be part of a class of compound called strongly correlated systems (ones where the charge carrier interactions must be included in studying their properties) and it was concluded that the layer of CoO$_2$ serves as the electronic-transport layer, the Na$^+$ ions act as phonon scattering centers limiting the thermal conductivity and the large Seebeck coefficient was attributed to what is called spin entropy, a concept that will be explained shortly. This modular structure provides opportunity to tune the atomic configuration of each layer allowing the independent manipulation of thermal conductivity, electrical conductivity and Seebeck coefficient. Figure A9 shows the layered structure of the cobalt oxide.
A.7 Strongly correlated systems and Seebeck coefficient

In a solid, the flow of electrons is accompanied by both a charge current and an entropy current. This entropy current is also part of the Seebeck effect, and in oxide materials, the electronic spin entropy (or in other words the energy carried by moving spin) is predicted to dominate the entropy current thus, impacting spin entropy in oxide materials is believed to impact the Seebeck effect. When any material is subjected to a temperature gradient, electrons flow from the hot side to the cold side generating an electric current. This implies that there is a coupling between electrical and thermal phenomena, which can be described by two equations. The equation for the electric current density (24) describes the electron flow and the equation for the thermal current density (25) describes the heat flow transferred by the electrons.

\[ j = \sigma(-\nabla V) + S \sigma (-\nabla T) = \sigma E - S \sigma \nabla T \]

Where \( j \) is the electric current density defined as the charge per area per time, \( \sigma \) is the electrical conductivity.
V is the electromotive force (emf) generated  
S is the Seebeck coefficient, and  
E is the resulting electric field  
∇T is the temperature of material as a function of time and position

\[ q = ST\sigma(-\nabla V) + \kappa(-\nabla T) = ST\sigma E - \kappa\nabla T \]  

where all definitions are the same as above and  
q is the thermal current density  
κ is the thermal conductivity

Equations (24) and (25) can be combined to give

\[ S j = \frac{q}{T} \]  
The right side is the entropy current density, which makes the Seebeck coefficient, S, equivalent to the ratio of the entropy current density to the electric current density. In other words the Seebeck coefficient is the entropy per charge carrier. As electric current caused by charge accumulation is indifferent to spin, a magnetic field should have virtually no effect on the Seebeck coefficient. However, Wang et al. [50] found a suppression of the Seebeck coefficient under a longitudinal magnetic field at low temperature (10K) in NaCo$_2$O$_4$. These experimental results and many other investigations disclosed that spin entropy plays some sort of role in influencing the Seebeck coefficient. Thus, this is more evidence of the possibility of controlling spin entropy in order to influence the Seebeck coefficient.

**A.8 Seebeck coefficient due to spin of electrons**

Seebeck coefficient is frequently used as a mean to determine the sign and concentration of carriers in metals and semiconductors. An oversimplification often occurs where only the entropy from charge is considered ignoring the fact that the
carriers also have spin and orbital degrees of freedom. This oversimplification was present in the mathematical high temperature formula used for Seebeck coefficient proposed by Heikes in 1961[51], which was later modified by Koshibae et al. [52][53] to include the spin and orbital contributions to entropy in the calculation for Seebeck coefficient. In metals the spins are tied to delocalized electrons but in compounds like NaCo$_2$O$_4$ the spins are not fixed to specific atoms within the lattice, and instead they are free to move around. This class of compound in which spins are delocalized is called strongly correlated systems. In strongly correlated systems the behavior of one electron is not independent of the behavior of the others, thus making electron-electron interaction a significant factor in material properties. Strongly correlated electron systems have degenerate 3d orbitals due to electron spin and orbital degree of freedom. This degeneracy of electronic state is due to a competition between crystalline field and Hund’s rule of coupling. This orbital degeneracy permits the material to either be in a high spin state or a low spin state. For example, cobalt oxide NaCo$_2$O$_4$, is composed of a layered of edge shared CoO$_2$ octahedra where each Co ion is surrounded by six O$^{2-}$ ions arranged in an octahedral geometry. Because of electron shell overlap from the 2p orbitals of the surrounding oxygen atoms, the 5 d shells orbital for the cobalt ion split into two bands: a lower energy, triply degenerate d-orbitals ($d_{xy}$, $d_{yz}$ and $d_{xz}$) and a higher energy, doubly degenerate d-orbitals ($d_{x^2-y^2}$ and $d_{z^2}$). For the stoichiometric NaCo$_2$O$_4$ compound there is an equal amount of Co$^{3+}$ and Co$^{4+}$, which can arrange their electrons in the bands. The different electron configurations are shown in Figure A10 along with the electronic degeneracy calculated as the product of spin and orbital degeneracy.
In Figure A10, the triply degenerate (d_{xy}, d_{yz} and d_{xz}) are denoted t_{2g} and the doubly degenerate d-orbitals (d_{x^2-y^2} and d_{z^2}) are referred to as e_{g}. The configuration that contains the maximum number of unpaired electrons with the same spin is called high-spin. The other is called low-spin because it contains the minimum number of unpaired electrons. Experimentally, low-spin cobalt ions have been observed to enhance the Seebeck coefficient while high-spin iron ions substituted in the cobalt ion site in transition metal oxides demonstrated a suppression of the Seebeck coefficient [55]. Understanding the mechanism by which the Seebeck coefficient is being suppressed at the atomic level opens up possibilities for tuning.

**A.9 Spin state of a material**

Theoretically, three interacting factors affect the spin state of a material: The field effect geometry, the oxidation state of the metal center and the electron d-configuration.

1. Field geometry:

   Whether a crystal is high spin or low spin depends on the relative size of the pairing energy (P), which is the energy needed to pair two electrons and the
splitting energy ($\Delta$) defined as the energy distance between bands. If $P \gg \Delta$, the crystal will be high spin because promotion of an electron to the anti-bonding $\sigma^*$ requires less energy than pairing an electron. If $P \ll \Delta$, the complex will be in low spin. The energy distance between the split bands is different for a tetrahedral, dodecahedral, cubic and octahedral arrangement of atoms around a metal ion (crystal fields). In general the splitting energy increases in the same order, $\Delta_t < \Delta_d < \Delta_c < \Delta_o$. Accordingly, metal ions in an octahedral field are more likely to have the option to be in high-spin or a low-spin state. The above relationships assume that the environment around the metal ion is perfect. However, distorted geometry of an octahedron or tetrahedron can also be present around the metal ion and is expected to have an effect on the splitting energy of that metal, thus impact spin state.

2. Oxidation state of metal.

It has been observed that the greater the charge on the metal ion, the greater the magnitude of the splitting energy, $\Delta$. For a given metal ion, $M^{n+}$, $\Delta$ is always larger for $3^+$ charge than for a $2^+$ charge. This is due to the fact that the ligands surrounding the metal ion are pulled more strongly toward the metal in the $3^+$ ion. This allows the electrons of the ligands surrounding the metal to split the energies of the metal d orbital more effectively.

3. Electron d-configuration

The splitting of $d$ orbitals in the crystal field model leading to the degeneracy of the orbitals depends on the geometry of the crystal formed around the metal. Octahedral bonding geometry-of materials with electron configuration of d1, d2, d3, d8, d9, d10 only
have one way to arrange the electrons. As a result, only when there are four, five, six, or seven electrons in the $d$ orbitals, can the electrons be rearranged in ways to change from high-spin to low-spin materials [56].

Understanding how those three key interacting factors can be manipulated in metal oxides and how they influence the spin state of metal oxides can allow further correlations between spin state and Seebeck coefficient. The goal is to understand what parameters affect BTO single crystal film growth in order to later make correlation between spin interaction in thin film which opens up possibilities for spin state tuning.

**A.10 Thermoelectric Barium titanate (BaTiO$_3$, BTO)**

The absence of lead and the physiological inertness of Barium Titanate (BTO, BaTiO$_3$), has made it an ideal material for many applications in environment-friendly material to replace chalcogenide TE materials. Due to its high temperature stability Barium titanate has the potential advantage over conventional semiconductor for thermoelectric devices operating at very high temperatures of 1000K and above. Adversely, BTO like most of the metal oxides is known to have a high thermal conductivity compared to the threshold value wanted for ideal thermoelectric materials. Therefore in order to enable BTO as a practical thermoelectric material, we need to take advantage of the influence of spin state on the Seebeck coefficient.

As discussed previously, spin-state in a bulk material, can be influenced by three factors. The manipulation of the three factors can be most directly impacted by the following means:

1. The field effect geometry, which involves change in crystallinity, relative atom placement (substitution site), substrate, and dimensional constraints.
2. The oxidation state of the metal center or the bonding of oxygen (O) to metal

3. The d configuration, which involves the choice of a dopant metal of 4 to 7 electrons in the d orbital.

Experimentally, the transition between high-spin and low-spin state in inorganic bulk materials has been attributed to the incorporation of dopants (including iron, cobalt, and manganese which have magnetic moments) that impact the spin, or by applying pressure leading to a thermal spin switch. However, in thin films, the low dimensional geometry creates a localized effect (discussed in appendix A) that may enable tuning of the desired properties.

A.11 Influence of dopant concentration on spin state and Seebeck coefficient

Experimentally, high-spin metal ions in transition metal oxides demonstrate a suppression of the Seebeck coefficient while low-spin metal ions enhance the Seebeck coefficient. This has been observed in Terasaki et al. [57]. They found that NaCo$_2$O$_4$ bulk crystals exhibited metallic electrical conductivity (0.2 mΩ cm) and a large Seebeck coefficient of 100 μV/K at room temperature with an increase in the Seebeck coefficient (200 μV/K) at high temperatures. The bulk crystal Na ions and CoO$_2$ are alternately stacked along the c-axis. In the layer-structured cobalt oxide NaCo$_2$O$_4$ with high Seebeck coefficient, the cobalt ions exist in a mixture of Co$^{3+}$ and Co$^{4+}$. The magnetic measurements of both Co ions revealed that they are in a low spin state and the spin state may be the source of the enhanced Seebeck coefficient [58]. The low spin state of cobalt ions enables the hopping of an electron from one oxidation state to another resulting in a large entropy exchange between Co$^{3+}$ and Co$^{4+}$. This entropy exchange was added to the
original Heikes formula given in equation (24) and a new modified version of the Heikes Formula was derived and is given in equation (27)

\[
S = \frac{k_B}{q} \ln \left( \frac{g_I}{g_{II}} \frac{\gamma}{1 - \gamma} \right)
\]

(27) 

Where the subscripts I and II denote the conduction sites and \( g_I \) and \( g_{II} \) denote the electronic degeneracy associated with each site respectively. Equation (27) demonstrates that not only the fraction of conducting sites \([y/(1-y)]\) but also the ratio of the degeneracies for the ions involved in conduction is equally important. Therefore, for a stoichiometric compound \( \text{NaCo}_2\text{O}_4 \) with cobalt ions \( [\text{Co}^{3+}] = [\text{Co}^{4+}] = 0.5 \) \( = \gamma \) in low spin states, applying the electronic degeneracy \( g_{3+} = 1 \) and \( g_{4+} = 6 \) and substituting in equation (34) we get a Seebeck coefficient of 154 \( \mu \text{V/K} \) which is in good agreement with the low-temperature experimental Seebeck coefficient of 100 \( \mu \text{V/K} \) in bulk crystals of \( \text{NaCo}_2\text{O}_4 \) [59]. The large Seebeck coefficient stems from the presence of the low-spin state of \( \text{Co}^{3+} \). Along the same line, if both low spin and high spin states are available to \( \text{Co}^{4+} \) ions then the total contribution of \( \text{Co}^{4+} \) ion is the sum of the contribution of the low spin and the high spin state given by \( g_{4+} = 6+6 = 12 \) which when substituted in Eqn. 34 gives a calculated Seebeck coefficient of 214 \( \mu \text{V/K} \). This value of the Seebeck coefficient also is in good agreement with the high-temperature transition observed in the Seebeck coefficient which suggests that having a low spin state may not be the only route to a high Seebeck coefficient but rather, having a high degeneracy ratio is necessary to an increase in Seebeck coefficient.

Similarly, Kobayashi et al. [60] found that bulk \( \text{Sr}_{1-x}\text{Y}_x\text{CoO}_{3-y} \) (SYCO) is also a layered structure where octahedral \( \text{CoO}_6 \) and tetrahedral/pyramidal \( \text{CoO}_{4.25} \) layers are alternately stacked with insertion of the ordered \( \text{Sr}_{0.75}\text{Y}_{0.25}\text{O} \) layer. The Co ions in the
CoO$_6$ layer occupies the intermediate spin state (refer back to figure 10) and those of the CoO$_{4.25}$ occupies the high spin state. In an attempt to understand the driving force behind the spin state transition of Co$^{3+}$ calcium ions, Ca$^{2+}$ was used as a dopant and Seebeck coefficient was observed to be strongly dependent on Ca$^{2+}$ content. Figure A11 shows the results of the magnetization, the Seebeck coefficient and the resistivity of the Ca$^{2+}$ doped SYCO.

![Graph showing magnetization, resistivity, and Seebeck coefficient](image)

**Figure 39:** a) shows the magnetization of Sr$_{3.1}$-xCaxY0.9Co4O10.5 in 0.1T. b) shows the resistivity of Sr$_{3.1}$-xCaxY0.9Co4O10.5 c) shows the Seebeck coefficient, S.[60]

With increasing dopant content from $x = 0$ to $x = 0.8$ the magnetization drops from 4.5 emu/g to 1 emu/g with a decrease in the transition temperature which is associated with the spin state cross over between intermediate spin and low spin. The
Seebeck coefficient changes with the Ca content in Figure A11. At 100 K, the Seebeck coefficient for x= 0 is 60 μV/K where as that for x = 1.2 is 200 μV/K. Since the resistivity is essentially the same value between x = 0 and x= 1.2 the Seebeck coefficient and perhaps the thermoelectric Figure of Merit \( Z = S^2/\rho\kappa \) are enhanced by a factor of \( (200/60)^2 \sim 13 \) because nothing is said about the thermal conductivity. The Seebeck coefficient enhancement can be understood in terms of the spin-state cross over driven by chemical pressure in other words pressure due to strain induced by the dopant. In Equation (34), let (I) and (II) ions be Co\(^{4+}\) and Co\(^{3+}\), respectively. Then the degeneracy \( g_{3+} \) is 1 and 15 respectively, for the low and high spin states of Co\(^{3+}\). Given a constant x, the Seebeck coefficient should change by \( (k_B \ln 15/e) = 230 \) μV/K when the Co\(^{3+}\) experiences a cross-over from high to low spin state. This value was consistent with the observed value of 220-60 = 160 μV/K, assuming that about 70 % of the Co\(^{3+}\) ions go to the low spin state. Since the Ca ion is divalent, its substitution acted as a chemical pressure which drives the spin state of Co\(^{3+}\) from the high/intermediate spin state to the low spin state as is similar to many other oxides \([61][62]\). Also one interesting outcome from the results in Figure A11 is that the electrical resistivity seems to be almost independent of the Ca substitution. At 800 K, the resistivity is as low as 2-3 mΩ cm which corresponds to that of conventional metals. The resistivity increases with decreasing temperature but is independent of the Ca content. This can be used to help isolate interdependent properties.

In order to understand how the doped transition metal Fe affects the spin entropy, Tang et. al \([63]\) studied the magneto-Seebeck coefficient, Mössbauer spectra and magnetic properties in Fe- doped NaCo\(_2\)O\(_4\) in detail. They found that high-spin Fe\(^{3+}\)
doping suppresses the spin entropy in NaCo$_2$O$_4$ and reveal the reason for the decrease in thermopower. Bulk polycrystalline samples NaCo$_2$–xFexO$_4$ were synthesized by conventional solid-state reaction. The temperature dependences of the Seebeck Coefficient for NaCo$_2$–xFexO$_4$ (x = 0, 0.1, 0.4, and 0.6) was generated. The Seebeck coefficient for all samples was seen to increase monotonically with the elevated temperature. However, the Seebeck coefficient decreased with the increase in Fe content across the entire temperature range. If the charge carriers retain a spin degree of freedom, a spin entropy term, $(k_B/q) \ln 2 \approx 60 \, \mu\text{V} / \text{K}$, will contribute to the Seebeck coefficient [64]. Once the spin is forced to align with a magnetic field, the spin entropy will be suppressed and hence its contribution to the Seebeck coefficient reduced. In order to disclose the effect of Fe doping on spin entropy Mössbauer spectra and magnetic properties were also studied for these materials. Below in Figure A12 is the report of the observed magnetic properties observed.

Figure 40: (a) susceptibility $\chi$ measurements as a function of temperature for NaCo$_2$–xFexO$_4$ for x = 0, 0.1, 0.4, and 0.6 (b) The effective magnetic moment of these samples [65]
For all Fe-doped samples, the molar magnetic susceptibility, $\chi$, is enhanced by Fe doping in the studied temperature range. This can be attributed to the substituting of high-spin Fe$^{3+}$ ions for nonmagnetic Co$^{3+}$ ions. In Figure A12 (b) we can see that the effective magnetic moment, $\mu_{\text{eff}}$, decreases with decreasing temperature for all samples, suggesting antiferromagnetic coupling in the (Co, Fe) O sublattices. Previous X-ray absorption spectroscopy studies in NaCo$_2$O$_4$ showed that Co$^{4+}$ and Co$^{3+}$ ions were in low-spin states t5 and t6, respectively [66] The $\mu_{\text{eff}}$ for the undoped sample is 1.29 $\mu_B$ at 40 K, in good agreement with the low-spin configuration of Co$^{4+}$ ($S = 1/2$) and Co$^{3+}$ ($S = 0$) ions. The $\mu_{\text{eff}}$ for all doped samples with $x = 0.1$, 0.4, and 0.6 is enhanced across the entire studied temperature regime. The $\mu_{\text{eff}}$ at 55 K is 5.27 and 5.43 $\mu_B$ for $x = 0.1$ and 0.4 samples respectively, which is close to the spin-only value of Fe$^{3+}$, i.e., 5.92 $\mu_B$. The authors suggest that partial nonmagnetic Co$^{3+}$ ions are replaced by high-spin Fe$^{3+}$ ions, inducing the increase in the average quantum number of spin and then the increase in $\mu_{\text{eff}}$. The studies of Mössbauer spectra and magnetic properties confirmed that high-spin trivalent iron ions are doped into octahedral Co$^{3+}$ sites. Therefore, the ratio of Co$^{4+}$ ions to total Co ones increases with the increase in Fe content [63]

Based on the above studies, it can be concluded that both the concentration of metal ions and the oxidation state in which it is present contributes to the spin state of the material. While, the effect of doping with transition metals on thermoelectric property of NaCo$_2$O$_4$ is generally studied [67][68], studies about the effect of transition metal doping on the spin entropy are very few. In cobalt oxides, the spin entropy contribution to the Seebeck coefficient is related to the Co$^{4+}$ concentration and degeneracy [63] [58] but this relationship needs to be explored in other metal oxides. As discussed previously one of
the major advantage of MBE and UHV is the ability to control atomic level control, which makes it an effective tool to relate dopant concentration to spin state. Investigating the effect of transition metals doping on the spin entropy may promise an effective way for improving the Seebeck coefficient

Appendix B
The custom furnace where H$_2$ cleaning is performed consists of a welded aluminum cube with an outer dimensional side length of 7.5 inches and a wall thickness of 0.75 inches. 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.

B.1 SiC Cleaning Procedure

The n-type research grade 6H-SiC substrates use in this study are on-axis (±0.5°) supplied by Cree Inc. The SiC are first degreased in heated solvents of trichloroethylene, acetone, and methanol and then loaded in a custom-built hydrogen furnace. In order to have effective cleaning procedure for substrates it is necessary to find the balance for possible cleaning variables including heating and cooling rate, ultimate temperature,
cleaning time and gas flow rate. A typical H₂ cleaning procedure consists of the following steps.

1. Remove loading section, install a Ta boat between Cu clamps and tighten down the Cu clamps
2. Place the SiC sample (< 0.7 × 0.7 cm²) at the center of the Ta boat and secure loading section
3. Purge furnace with hydrogen for 5 minutes (ignite exhaust burner) and turn on cooling water
4. Adjust hydrogen to a desired flow rate (11.4 lpm, reading of 35-45 from the flow meter)
5. Turn on power supply (Sorenson DCR 20-115B) and increase current 5 A/30 sec (100°C/30 sec); monitor temperature with optical pyrometer (two color) with filter on
6. Once desired temperature (1600°C) is reached, maintain desired hydrogen flow rate and temperature for 30 minutes. Typical current is around 70-80A, depending on the width of Ta boat
7. Reduce power (2.5 A/30 sec) while maintaining H₂ flow.
8. Turn off power supply, hydrogen, and cooling water; remove loading section and retrieve sample
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