Integrating RHEED-TRAXS and Molecular Beam Epitaxy for Real-time Compositional Control of Functional Oxide Deposition Processes

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ABSTRACT

Real-time chemical analysis during film growth by Molecular Beam Epitaxy (MBE) has been unattainable because traditional Ultra High Vacuum (UHV) tools such as X-ray Photoelectron Spectroscopy (XPS) or Auger electron spectroscopy (AES) cannot be used at pressures above $10^{-8}$ Torr, and MBE growth pressure are typically $10^{-6}$ to $10^{-5}$ Torr. Real-time chemical analysis and stoichiometry control is important, however, because stoichiometry changes of less than one percent in materials such as functional oxides can cause measurable changes in their physical properties\(^1\). Indirect measurements of stoichiometry, such as surface Reflection High Energy Electron Diffraction (RHEED) pattern, are often misleading. RHEED - Total Reflection Angle X-ray Spectroscopy (RHEED-TRAXS) has been shown in this work to be a viable real-time relative stoichiometry analysis tool for MBE deposition processes. Despite the limitations in detecting low atomic number elements ($Z<10$), this work showed that RHEED-TRAXS could be useful for collecting chemical information during the deposition of multi-element metal oxides such as barium hexaferrite ($\text{BaM, BaFe}_{12}\text{O}_{19}$). While progress has been made through this work to qualify relative atomic ratio, real-time quantitative stoichiometry measurement still faces challenges.

This RHEED-TRAXS study first involved designing a detector positioning system compatible with the UHV environment and the existing MBE chamber. Systematic factors that can influence the measured x-ray intensity were identified and isolated to provide consistent spectrum evaluation and data processing. Critical angle of the substrate signal, such as the Si K\(\alpha\) line, was established as a reference for calibrating the measurement geometry and determining elemental sensitivities. Using this reference, increases in film elements intensities such as the Mg x-ray K\(\alpha\) line,
were measured during film growth such as magnesium oxide (MgO) deposition and related to the growing film thickness. Substrate Si Kα x-ray intensity attenuation through the MgO layer also provided a way for film thickness approximation. In the deposition process of BaM, RHEED-TRAXS was used for monitoring the Fe Kα line, Ba Lα line, Mg Kα line and Si Kα line signal intensity variations during deposition. The intensity changes were related to the film stoichiometry changes during MBE processing. The correlation between thickness and composition with absolute and relative x-ray intensities based on calibrated geometry in this study is an excellent example of the potential of RHEED-TRAXS for real-time compositional analysis, and motivation for further quantitative development.
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1. Introduction

Molecular Beam Epitaxy (MBE) is a preferred method for depositing epitaxial thin films due to its precise control of relative atomic fluxes and surface reactions. MBE systems operate under Ultra High Vacuum (UHV), with base pressure of $10^{-9}$ Torr to $10^{-10}$ Torr with operating pressures up to $10^{-5}$ Torr. The base pressure enables the incorporation of UHV-based analytical techniques such as Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS) and Reflection High Energy Electron Diffraction (RHEED) to achieve both stoichiometry and structure control. However, XPS and AES cannot be operated at pressure higher than $10^{-8}$ Torr, and thus they cannot be used during real-time nano-scale deposition. RHEED electron beams with an energy of 12.5keV and 2° glancing incidence can diffract from the sample surface providing a pattern on a phosphor screen that indicates the surface atom structure of the sample. However, although the structure information provided by RHEED patterns can be used to imply the approximate chemistry of the film, changes in chemistry that do affect properties are often not observable by changes in the RHEED pattern.

Multifunctional heterostructures of functional oxides, such as ferrimagnetic barium hexaferrite and piezoelectric lead zirconate titanate, integrated on semiconductor platforms are of interest to the development of smarter, smaller and more energy-efficient multifunctional electronic devices that take advantage of the coupling between magnetic, electric, and stress-induced responses. Either structure or stoichiometry changes of less than one percent of multi-element oxide materials can cause measurable changes in their functional properties. Real-time stoichiometry control technique is necessary but not yet available.
RHEED - Total Reflection Angle X-ray Spectroscopy (RHEED-TRAXS) was proposed as a technique that can offer real-time stoichiometry control during MBE growth. When the RHEED electron beam impacts the sample surface, part of the electrons can promote the excitation of characteristic x-rays that are representative of the film’s consisting elements within the excited volume. RHEED-TRAXS takes advantage of the total reflection of x-rays by detecting x-rays at the critical angle geometry. As refractive indices of materials for x-ray are less than one, total internal reflection happens at the vacuum/sample interface where a sharp increase of x-rays intensity can be detected at their specific critical angles. Below the critical angle of a specific element, no x-rays from this element can be detected, however, at the critical angle, peak intensity of the elemental x-ray will be observed and is believed to consist of x-rays mostly excited near the surface \(^3\). As a result, observable changes in the x-ray intensity near the critical angle can be expected and detected when stoichiometry changes at the film surface\(^4\). By detecting x-rays at critical angles during film deposition process, elemental x-ray intensity variation from deposited single or multi elements can be followed by RHEED-TRAXS to predict surface composition.

The potential of RHEED-TRAXS as a tool for \textit{in-situ}, real-time stoichiometry monitoring has been discussed by several groups working with different materials systems such as AlAs/GaAs(001)\(^4\), InAs/GaAs(001)\(^4\)\(^5\), YBa\(_2\)Cu\(_3\)O\(_{7-x}\)/MgO(100)\(^6\). In these studies, RHEED-TRAXS was used to assist the understanding of the growth process of the various semiconductor film systems. Yamanaka \textit{et al.} applied Monte Carlo simulation to quantify the atomic depth distribution by deconvoluting x-rays excited. At varying RHEED electron incidences, variation in the intensity of x-rays can be related to the layered structures in Au, Ag, Ga, In or Sn metal layers covered Si (111) surfaces\(^7\). The purpose of these studies was to quantify the atomic depth
distribution by deconvoluting the excited x-rays at different RHEED incident angles. Recent work by Sandeep et al. used reciprocity theorem to calculate the film thickness and the interface roughness through interface reflectivity with Y/Mn films deposited on GaN substrates\textsuperscript{8}. This rigorous approach demonstrated the potential of RHEED-TRAXS as a tool for measuring real-time stoichiometry during epitaxial deposition of multi elements film with MBE. However, quantification of the RHEED-TRAXS signal for chemical analysis and growth mechanism studies on oxide systems is still in its preliminary stage\textsuperscript{9}, study on using RHEED-TRAXS quantitatively for oxide systems and for thickness measurement during oxide deposition is limited.

To achieve a practical real-time analysis and control of stoichiometry, the RHEED-TRAXS system needs to be made compatible with the MBE and UHV environment. This involves re-designing the commercially available equipment by engineering a way to insert the X-ray detector into the UHV environment while maintaining UHV quality, reliably protect the detector during film growth, and effectively and conveniently maintain the RHEED-TRAXS system. Secondly, as RHEED-TRAXS is a technique that is highly sensitive to geometries, the capability of the system to include angle resolution, real-time applicability and line-of-sight X-ray detection needs to be optimized so that the spectrum evaluation and data processing can be consistent and effective. Moreover, to determine the surface sensitivity, the geometry impact (take-off angle dependence) on stoichiometry and the surface roughness impact on intensity measurements, a comprehensive calibration methodology needs to be established and the relative impact of all the systematic influences need to be determined. The final goal of quantification of RHEED-TRAXS is to relate the absolute and relative x-ray intensities with the compositional information of the growing film to enable real-time stoichiometry control.
2. Background

Functional oxide materials are a group of complex oxide materials that possess a wide range of crystal structures and functionalities. These materials consist of multiple elements and can only achieve their functionality when certain specific stoichiometry and complex crystal structure are met. The key of understanding these functional oxides is to understand the interaction between chemistry and structure, and their impact on the electronic structure within the material. Various methods have been used to grow these complex oxides including sputtering, milling, spin coating, pulsed laser deposition, sol–gel processes, metal-organic chemical vapor deposition, molecular beam epitaxy.

MBE processing is an effective approach to achieve precisely controlled interfaces. The process takes place under Ultra High Vacuum (UHV) where no gas phase reaction is possible and reactions only happen on the substrate surface. Reactants are controlled separately using individual effusion cells. Real-time crystallographic monitoring technique RHEED is available for monitoring the surface crystal structure changes during growth. Although these structural changes may be linked to changes in stoichiometry, RHEED does not provide a direct link between the structure change and the stoichiometry change. Reflection High Energy Electrons Diffraction-Total Reflection Angle X-ray Spectroscopy (RHEED-TRAXS) is a technique that has potential to provide researchers with in-situ real-time control of the stoichiometry.

The idea of using RHEED electron excited X-ray emissions for elemental analysis was first proposed in 1967 by Sewell et al.; the theory was further investigated and presented by Ino et al. in their work of using Ag films deposited on
Si substrates where the concept of critical angle in RHEED-TRAXS application was introduced; its applicability was further approved by recent researches\textsuperscript{13,3}. In order to implement RHEED-TRAXS with MBE and enable real-time stoichiometry control, understanding of the physics of the RHEED technique and the x-ray emission is indispensable. In addition, comprehensive knowledge of the UHV system and MBE process is necessary for establishing an effective calibration method.

2.1 Functional metal oxide thin films

Functional oxides are widely used in dielectric capacitors, ferroelectric random access memories, sensors, micro-electromechanical systems, antireflective coatings, thin film solid-oxide fuel cells, and photoelectrocatalytic solar cells\textsuperscript{14}. Thin film oxide heterostructures can sense various changes in the environment factors such as temperature, pressure and external electromagnetic field with different mechanisms. The functionality of these multi-element oxide materials depends on their structure and stoichiometry.

2.1.1 Structure, stoichiometry and functionality

The importance of both stoichiometry and crystal structure on the physical properties can be illustrated by the MBE processing of barium titanate (BTO, BaTiO\textsubscript{2}). BTO is a type of ferroelectric materials that can change its electric polarization in response to external electric field. The ferroelectric property of BTO is directly related to its Ba/Ti atomic ratio in the crystal structure. The most sensitive ferroelectric response can only be achieved when the BTO is at the right stoichiometry.
During the MBE process of BTO deposition, when Ba/Ti ratio is at one, crisp RHEED pattern as shown in Figure 1 can be observed. As a result, when a RHEED pattern shown in Figure 1 (b) is observed during MBE process, this is a good indication of the correct stoichiometry in the growing surface. If the ratio is off, where either Ba or Ti rich surface develops, RHEED pattern can change into what is representative of polycrystalline surface under both situations (Figure 1 (a) and (d)). If the chemistry situation can be correctly identified, the corresponding element flux can be adjusted to bring the film back to the right stoichiometry. Otherwise, if the film continues to grow under unbalanced Ba/Ti flux, the film will turn into amorphous state and cannot be recovered.

Figure 1: Comparison of RHEED patterns under different Ba/Ti ratio during BTO deposition (Courtesy Trevor Goodrich).
The physical properties of materials such as functional oxides are highly sensitive to the stoichiometry of the consisting elements. For example, shown in Figure 2 above is the hysteresis loop measured of a series of PZT samples with different crystal orientation and slightly different Pb/Zr ratio. On one hand, it can be observed from the comparison between (a) and (b) that, same materials with different crystal structures exhibit very different response profiles to external electric field. On the other hand, a closer look at each of the figures reveals the differences in polarization caused by the different Pb/Zr ratio.

Figure 2: P-E hysteresis loops for PZT (a) (001) and (b) (111).
2.1.2 Relevant measurement techniques

While structure and chemistry are of equal importance in determining the functional properties of the grown film, real-time chemistry information is less easily obtained. Non-destructive chemical analysis techniques such as XPS, X-ray Fluorescence (XRF) and Energy Dispersive X-ray Spectroscopy (EDXS) can provide useful information of the surface of interest, however, their application as real-time technique are limited based on their specific working theory and relatively high cost to integrate into a MBE processing chamber.

XPS uses x-ray induced photoelectrons for chemical bonding and compositional analysis. Due to the low kinetic energy nature of the photoelectrons, XPS needs to be operated under low ambient pressure (\(<10^{-7}\)) and tight measurement geometry. Oxide growth environment usually involves oxygen environment and thus limit the potential of using XPS for real-time chemical analysis. Besides, typical XPS systems with hemispherical analyzers work under swept mode and require certain data acquisition time. These aspects are all challenges for developing XPS into a real-time measurement technique.

XRF is commonly used for quick and accurate chemistry information of various specimens. It uses x-ray to promote the excitation of characteristic x-rays and relates the x-ray intensity to their specific atomic composition. Development of using XRF for real-time measurement can be seen in literature\(^{15}\). Operation of XRF apparatus usually involves a highly geometry-sensitive calibration process before each run. Due to the long penetration depth of the primary x-rays, conventional XRF usually excites a relatively deep range of sample surface and thus is not surface sensitive. This is not favorable for real-time chemistry control as the technique is not
sensitive to the changes happening at the growing surface and thus cannot improve the ability to control the quality of the film. To improve the surface sensitivity, Total Reflection X-ray Fluorescence (TXRF) can be considered for real-time measurement. This requires an additional x-ray tube and an x-ray detector, in addition to the precise geometry calibration that is necessary before each run in order to interpret the results.

EDXS works under a different type of physical process. It uses electron beam to radiate the sample surface at a 90-degree angle and detects the x-ray excited by incident electrons. Due to the normal incidence of the electrons, in EDXS measurement, x-rays are generally excited from the bulk of the sample instead of the surface. As a result, EDXS is usually used as a compositional analysis tool for bulk samples. Similar with the XRF, this is not sufficient to monitor the chemical changes happening at a dynamically growing sample surface when the majority of the x-ray signal comes from below the surface.

2.2 MBE growth technique and characterization techniques

The word epitaxy comes from Greek roots and means the arrangement (-taxis) of atoms on (epi-) an ordered substrate. Common epitaxy methods include Liquid Phase Epitaxy (LPE), Vapor Phase Epitaxy (VPE) and Molecular Beam Epitaxy (MBE). Molecular beam epitaxy (MBE) is a method of depositing atoms on the substrates layer by layer under ultra high vacuum and relatively low temperatures. It is a versatile technique for the research and development of thin epitaxial structures made of materials including semiconductors, metals or insulators. MBE has the advantages of clean growth environment, precise control of reactant species and their growth condition, capability of integrating in situ diagnostic techniques and its compatibility with other high vacuum thin film processing methods.
2.2.1 UHV system and MBE process

Ultra High Vacuum refers to the vacuum level of lower than $1 \times 10^{-8}$ Torr (1 millibar = 1 Torr = 1 mmHg = 133.3 Pa, one atmosphere is 760 Torr)$^{16}$. Compared with atmospheric pressure of 760 Torr, UHV contains much less molecules and particles in the same space. UHV is necessary for surface science and measurements, as particles attached on the surfaces can change their properties. At pressures of $10^{-6}$ Torr, one monolayer of particles can be formed on any surface within seconds. However, under UHV conditions, this process take thousand times longer, as the number of gas atoms in UHV environment is at least as small as $10^{-12}$ times this number under atmospheric pressure. Accordingly, as long as the UHV condition is reached, it takes hours before the sample is covered or recovered by molecule layers. This provides a clean environment that makes atomically clean surface possible and enables the maintenance of a contamination-free state for performing the experiments$^{17}$.

Besides, as a result of the long mean free path, UHV also enables the interactions between electrons, surface atoms, excited atoms and ionized particles without interference from environmental gas phase molecules. The mean free path $\lambda_{\text{mfp}}$ is defined as the mean distance needed by molecules between two successive collisions. The calculation of mean free path under vacuum is shown below. Since the number of molecules $n$ is directly proportional to pressure $P$ (Torr), the calculation of $\lambda_{\text{mfp}}$ in centimeters can be simplified (Equation 1). When the pressure is at $10^{-9}$ Torr, the mean free path is as long as 50 kilometers, in which case the molecules have little probability of colliding with each other before reaching the substrate surface$^{18}$. 


\[ \lambda_{\text{mfp}} = 5 \times 10^{-3} \frac{1}{P} \]  

(1)

**where:** \( \lambda_{\text{mfp}} \) = Mean free path (cm)

\[ P = \text{Pressure (Torr)} \]

MBE is a processing technique invented in the late 1960s that takes advantage of the UHV environment. MBE processes usually deposit films at a relatively slow rate, which is essential for the film to grow epitaxially. In solid source MBE, reactants are stored in crucibles in separate effusion cells (Knudsen cells). In MBE chambers, all the effusion cells are designed to focus on the substrate position. When the crucibles are heated up to certain temperatures, atoms start to evaporate, traverse across the chamber and eventually reach the substrate surface. During the process, because of the long mean free paths of the particles and atoms, evaporated atoms do not interact with each other until they reach the substrate. As a result, MBE prevents any gas phase reaction and thus provides more control over the reactions. Temperatures of the effusion cells can determine the kinetic energy of the particles in the flux thus has a direct impact on the growth rate and the film composition. By controlling the temperature of the effusion cells, atomic flux can be precisely controlled.

A schematic drawing of the typical MBE system is shown in Figure 3. All the components including effusion cells, RHEED, heater, transferring mechanism and load lock for sample loading operate under ultra high vacuum environment in a stainless steel chamber. All the components can undergo up to 200°C for extended period of time during bake-out operation.
As a technique of vapor phase deposition in ultra high vacuum conditions, MBE provides a wide range of growth conditions. Combined with in-situ and real-time surface diagnostic technique RHEED, MBE offers the researches with the best possibilities and test systems to establish the concepts and theories for comprehensive understanding of crystal growth from the vapor phase.

2.2.2 RHEED electron diffraction

Electron diffraction was first observed in the 1930s, which leads to the development of molecular beam epitaxy technique. Since the invention of Reflection High Energy Electron Diffraction (RHEED), it has been used as a standard real-time surface structure monitoring technique in almost all the MBE systems.

RHEED uses a beam of high-energy electrons (greater than 10 keV) to probe the sample surface. This beam of electrons hit the sample surface at a grazing incident angle of about 2°. The diffracted electrons can be absorbed by a phosphor
screen on the other side of the apparatus where patterns of the interfered electrons can be observed. The pattern reflects the interference of electrons due to the atoms in the surface, thus can be used to predict the structure of the atoms in the surface (Figure 4).

Figure 4: RHEED apparatus is consisted of a phosphor screen and an electron source that are positioned 180° apart.

Due to the glancing incidence of a few degrees and the small electron penetration depth at this angle, RHEED is sensitive to the atomic structures of the very top few layers of film surfaces. Through different RHEED patterns, it is possible to determine the growth mode. Spotty RHEED patterns suggest 3-D growth where small, isolated three-dimensional nuclei occur on the surface; while 2-D growth usually exhibit streaky patterns that suggest continuous layer-by-layer growth.

Only an electron gun and a phosphor screen are required to perform the basic functions of a RHEED apparatus. The simple design and the flexible geometry make it an ideal approach for real-time surface study during atom deposition and can be combined with other surface probing techniques such as AES, STM and SEM25 26.

2.2.3 XPS surface analysis

X-ray Photoelectron Spectroscopy (XPS) is a technique that uses photoelectrons excited by x-ray to provide chemistry information of a solid sample
surface. The excited photoelectrons come from specific core electrons in their originating atoms, as a result, their kinetic energies are determined by the energy of the incident x-ray photons, the binding energy specific to the particular level and the work function. Due to the low energy of the photoelectrons, only these excited from within the top 10 nm of a sample surface can escape the sample surface and eventually be detected by the hemispherical electron analyzer for chemistry information. Therefore, XPS is widely used in surface characterization due to its high sensitivity to surface.

2.3 RHEED-TRAXS

The physics of RHEED-TRAXS is based on electron induced characteristic x-ray emission and the phenomenon of total reflection. In order to design the RHEED-TRAXS apparatus, determine the sensitivity of the technique, establish effective calibration methodology and enable real-time stoichiometry control, understanding of the physics is necessary.

2.3.1 Electron induced characteristic x-rays

When incident primary electron of sufficiently high energy is scattered by the atoms in the sample, it causes core electrons to be ejected from the K-shell of the atoms within the excited volume and leaves a vacancy in the orbitals behind. When the atom relaxes, electrons from higher energy orbitals will fill into the lower energy orbitals. During this process, excess energies from the relaxed electrons can be emitted in the form of x-ray photons. These x-ray emissions can be defined according to the transition from which they are generated (Figure 5).
Figure 5: Diagram for energy levels, absorption edges, and characteristic x-ray line emissions for a multi-electron atom \(^{28}\).

For example, when an L shell electron fills a vacancy in the K shell, the x-ray photon emitted can be defined as K lines. Based on the fine structure of the L shell orbitals, these x-rays can be further named as K\(\alpha_1\) and K\(\alpha_2\) lines. If the transition happens between M shell and K shell, these x-ray emissions can be named as K\(\beta\) lines. Meanwhile, these electron transitions can also take place between M shell and L shell, the x-rays emitted from which will be called as L lines. Depending on the atomic number of the atom excited, all or part of these transitions can happen.

Electron induced x-ray emissions are characteristic of all the originating orbitals, and thus are the fingerprints of elements in the elements identification process. Their energy can lead to their originating atom, and their intensity can be related to the number of atoms within the excited volume. Auger process is a competing process that happens when one electron makes a transition into the core vacancy. Instead of x-ray photons, secondary electrons can also be emitted. The
possibility of these two processes depends on the atomic number of their originating atom. For atoms with atomic number less than 15, Auger electron emission is dominant. For elements with higher atomic number, x-ray fluorescence is the major effect (Figure 6).

![Graph showing Auger effect and x-ray fluorescence yields vs. atomic number]

**Figure 6: Auger effect and x-ray fluorescence depends on the atomic number of the elements**

### 2.3.2 Total external Reflection X-ray spectroscopy

For x-rays, their refractive indices in vacuum are all unity, and in any other medium, their refractive indices are very small and close to unity. The result of this is when x-ray travels from any medium into vacuum, total reflection can happen at the interface. Figure 7 shows a refracted beam divided from the original incoming x-ray being deflected toward the boundary plane. When $\alpha_1$ decreases, intensity of the refracted beam decreases while the intensity of the reflected beam increases. When $\alpha_1$ reaches the critical angle, the refractive beam diminishes and the incident beam gets completely reflected. The angle $\alpha_1$ which refraction is just possible is defined as
critical angle $\alpha_{\text{crit}}$. When this angle $\alpha_1$ keeps decreasing past the critical angle, all the x-ray remains completely reflected. The boundary will become an ideal “mirror”, totally reflects the incident beam back into the original optical dense medium.

As the light path can be reversed, total external reflection can be understood through the same scheme shown in Figure 7. When light incident from the less optical dense material into the optical dense material, incident angle $\alpha_2$ is less than the refraction angle $\alpha_1$. When $\alpha_2$ approaches zero, $\alpha_1$ approaches the critical angle. If an x-ray detector were to be placed at $\alpha_1$, the closer it reaches the critical angle, the smaller $\alpha_2$ gets until when $\alpha_2$ reaches zero and incident beam becomes parallel to the surface.

![Figure 7: Refraction of light at material interface. When light incident an interface, the intensity of the reflected and the refracted light increase oppositely. When incident angle $\alpha_1$, equals critical angle angle, refracted light diminishes and total reflection happens.](image)

Critical angle is a function of the density of the material, energy and stoichiometry of the material, and is inversely proportional to the energy of the x-ray (Equation 1). With energy being given in keV and density in g/cm$^3$, the angle calculated is in degrees.

$$\alpha_{\text{critical}} = \sqrt{2 \delta} = \frac{1.65}{E} \sqrt{\frac{Z}{A \rho}} \quad \text{(1)}$$

where: $Z = \text{atomic number, dimensionless}$
In the case of vacuum/film interface, the significance of the total external reflection at critical angle is shown in Figure 8. When x-rays travel across the vacuum/film interface, due to the total reflection effect, on the vacuum side, theoretically no x-rays will be observed in the space between the critical angle and the surface plane.

![Figure 8](image)

**Figure 8:** When x-rays excited in the crystal propagate into the vacuum, critical angle ($\theta_c$) can be observed on the vacuum side where a high intensity of x-ray can be observed. When the take-off angle $\theta_t$ is below the critical angle, no x-rays can be detected.

### 2.3.3 X-ray escape depth

When x-ray enters a thin film, its intensity gets attenuated by the scattering of x-ray photons. Elastic scattering (Rayleigh scattering) only changes the direction of the x-ray photons, while inelastic scattering not only changes the direction of the photons but also consumes the energy of the photons\(^ {28, 27} \). Photoelectric absorption and scattering result in the attenuation of x-rays in materials. Because of the energy
loss, the x-rays can only travel a certain distance in materials before its intensity attenuates below certain level. This depth or distance is commonly referred to as the penetration depth. If the process is reversed, where x-ray propagates through the medium to the vacuum, the deepest depth that x-rays originates from can propagate through to the vacuum is usually referred to as the escape depth.

Understanding the x-ray escape depths is key to the determination of the surface sensitivity of x-ray techniques. Escape depth is a similar concept as penetration depth, but of the reversed direction. Penetration depth can be defined by the depth of a homogeneous medium an x-ray beam can penetrate before its intensity is reduced to 1/e, or 37% of the initial value. If the x-ray beam were to start propagating from this penetration depth inside the material towards the vacuum/film interface, the photon will reach the interface if its intensity is not completely attenuated. Attenuation is due to the reabsorption by other atoms along the path. When only 1/e (37%) of the original photons can escaped the surface, the total distance that the x-ray have propagated through the medium is the escape depth. Both the escape depth and penetration depth concepts can be used for other particles including electrons.

Escape depth of x-rays depends on the energy of the x-ray photons and the mass attenuation coefficient of the material the x-ray is propagating through. When the incident angle equals to or is greater than the critical angle of specific x-ray in this material, the penetration depth can be calculated with the Equation 2. Notice that at critical angle, the escape depth equals zero, which suggest, all the x-ray at critical angle comes from the very surface of the film.
\[ Z_n = \frac{\lambda}{4\pi \sqrt{\beta}} = Z_n = \frac{\lambda}{4\pi} \frac{1}{\sqrt{\frac{\lambda}{4\pi} \left(\frac{\mu}{\rho}\right)^\rho}} = \sqrt{\frac{\lambda}{4\pi}} \frac{1}{\sqrt{4\pi \xi \left(\frac{\mu}{\rho}\right)^\rho}} = \sqrt{\frac{hc}{4\pi E}} \frac{1}{\sqrt{\left(\frac{\mu}{\rho}\right)^\rho}} \]

where, \( Z_n = \) Penetration depth (cm)

\[ \lambda = \frac{hc}{E} = \text{Wavelength of the x-ray (nm)} \]

\[ \beta = \frac{\lambda}{4\pi} \left(\frac{\mu}{\rho}\right) \times \rho = \text{Imaginary component of refractive index, dimensionless} \]

\[ \left(\frac{\mu}{\rho}\right) = \text{Mass attenuation coefficient of materials} \]

2.3.4 Electron penetration depth

Distinction between electron penetration depth and x-ray penetration depth is of key importance to the understanding of the physics behind RHEED-TRAXS. As electron beam is the primary excitation to promote the emission of x-rays, its penetration depth into the film determines from how deep inside the sample x-rays can be excited. For RHEED electrons, when the electron beams hit the sample surface with a fixed kinetic energy, penetration depth of the electrons is determined by the electron incident angle (Figure 9). When the incident angle decreases, the penetration depth decreases accordingly. On the other hand, x-rays emission will be generated on the electron path into the material. If the x-ray escape depth is greater than the penetration depth of the primary incident electrons, electron penetration depths will be the determining factor for surface sensitivity.
Figure 9: The penetration depth of electrons varied with the incident angle. Electrons with normal incidence can penetrate a greater depth (a) than electrons with grazing incident angle (b).

Similar to the estimation of x-ray escape depth, the penetration depth of RHEED electrons is angle-dependent, and it can be related to the energy of the electrons and the material system being studied. However, estimation of electron penetration depth is more complicated. According to T.E. Everhart et al. 29, the probability of an electron with energy $E$ traveling through a material with atomic number $Z$, density $\rho$ and atomic mass $A$ scattered through an angle $\phi$ in a distance $\Delta x$ can be determined with the equation below.

$$
p(\phi, E) = \frac{N_A e^4}{16} \left( \frac{Z \rho}{A} \right) \left( \frac{Z}{E^2} \right) \frac{\Delta x}{\sin^4(\phi/2)} \tag{3}
$$

where: $E =$ energy of electron (keV)

$Z =$ atomic number

$N_A =$ Avogadro constant

$\Phi =$ Scatter angle (°)

At the surface, the incident beam has not been scattered, the ratio of angular scattering probability to fractional energy loss $\Delta E/E$ can be estimated as a function of $I$ (mean excitation energy for electron energy loss in the solid) and the scattering
angle.

$$
\frac{p(\phi, E)}{(\Delta E / E)} = \frac{1}{32\pi} Z \frac{1}{\ln(aE / I) \sin^4(\phi / 2)}
$$

(4)

According to related literature, at given scattering angle \( \phi \) and energy \( E \), the path through the material will be more irregular at higher atomic numbers\(^{29-30}\).

For different material at different electron energy, penetration depth varies in a wide range. X-ray penetration depth and electron penetration depth both can determine how surface sensitive RHEED-TRAXS can be. In another words, electron penetration depth and x-ray escape depth can be the limiting factor when determining the sensitivity of RHEED-TRAXS. Under the same experimental condition, the shorter of these two will determine the thickness of the sample that RHEED-TRAXS can probe. According to the study by Vanmil \textit{et al.}, for Al K\( \alpha \) x-rays in GaN, the limiting factor is the electron penetration depth\(^{31}\).

There is no straightforward calculation to determine how far electron beams can go into the sample. Approximations are made on the basis of probability theory, and according to some reports, the electron penetration depth vs. energy curve approximation worked well only under certain circumstances\(^{29-30}\).

T.E. Everhart \textit{et al.} derived the relationship between kilovolt electron energy and penetration depth in solid materials using Bohr-Bethe energy-loss relation, and shows that it is in the form of \( R = kE_B^\alpha \) and are valid over limited energy range. According to their study, in the same energy range the exponent \( \alpha \) is determined by the atomic number of the material.

Assumptions were made by Ino \textit{et al.} to simplify the calculation of electron penetration depth\(^3\). Their assumption includes that the intensity of the electron beam diminishes with the distance traveled, intensity of x-ray emission is proportional to the intensity of the electron beam, and that intensity of the outgoing x-rays would not
diminish before escaping the surface (Figure 10).

Figure 10: Schematic of a simplified penetration depth approximation method in Ino et al.’s work.

With these assumptions, the intensity of the beam can be expressed by

$$I = I_0 e^{-s/l} \quad (5)$$

Where $I_0$ is the intensity of the incident beam, and $I$ is the intensity of the beam in the film; $l$ is the total distance electron beam traveled (take the distance when intensity is reduced to $e^{-1}$ as the end of the distance); $s$ is the distance to be calculated. Both $s$ and $l$ are geometrically shown in Figure 10. As shown in Figure 10, if the penetration depth were to be measured vertically as $\alpha$, then at a glancing angle the depth $\alpha$ can be calculated with the following equation:

$$\alpha = l \sin \theta \quad (6)$$

where $\alpha$ = penetration depth (nm)

$l$ = total length of travel (nm)

$\theta$ = glancing incident angle

The approach developed by Ino et al. is based on several assumptions; especially the assumption that claims the intensity decrease of the electron beam has an exponential relationship with the distance traveled. According to T.E. Everhart’s work, the exponent changes with the atomic number of the material being bombarded.
And the exponential relationship also has limitations on both the applicable electron energy range and the atomic number of the material involved. The applicable range are 5-25 keV and 10<Z<15 respectively. Specific applications should find out their own relationship between electron penetration depth and x-ray penetration depth with the very specific energy range that applies since both the electron energy and energy of the x-ray emission of interest are all part of the equations to determine the electron penetration depth.

Another approach by measuring the glancing angle dependence of x-ray emission under RHEED-TRAXS conditions was carried out by Yamanaka et al. According to their research, the general trend of dependence curves was explained well by applying Monte Carlo electron trajectory simulations to the analysis. Monte Carlo calculation was also used by Joseph et al. on the calculation of x-ray generated within the sample as a function of depth. And their quantitative analysis result shows that the electrons are confined at a depth of 80 MLs.
3. Critical Literature Review

RHEED-TRAXS is not commercially available and needs to be tailored for each MBE system based on the existing chamber design. To build a RHEED-TRAXS system that can be used in-situ during MBE, accurate angular positioning control and ultra high vacuum compatibility are of primary importance. After the system is in place, analytical strategies, including calibrations of the spectrum and intensity, data collection methods, determination of the chemistry in real-time need to be established for the specific material systems.

3.1 RHEED-TRAXS application in different material systems

Early studies of Hasegawa et al. observed the increased surface sensitivity of RHEED induced x-rays near critical angles where they deposited Ag on Si surface and introduced the concept of RHEED-TRAXS. After the introduction of the concept, literature on using RHEED-TRAXS has been focused on two major material categories: functional metal oxides and III-V/II-VI materials. A significant number of studies were focused on metal deposition on semiconductor substrate for modeling purposes and quantitative analysis\textsuperscript{4, 6, 8, 22, 31, 34}.

Early reports of Ino et al. focused on the single metal element deposition on Si substrates. These single element material systems can be used to confirm the theory of RHEED-TRAXS. Their work provided ample information on modeling of layer distribution of RHEED electron induced x-rays with varying RHEED incident angle. The adsorption, desorption and epitaxial growth processes of Au, Ag Ni, Sn, Si, Ge, InSb Au-Ag alloy on Si and Ge substrates with different orientations were intensively reported\textsuperscript{35}. 
Liu et al. investigated the islands deposition on Cu/Ag/Au coated surface. Chandril et al. applied RHEED-TRAXS on deposition of Mn/Y multilayered structures on GaN/Al₂O₃ (0001) and explored the possibility of using the distorted-wave approximation to estimate the thickness and interfacial roughness.

Using the elemental x-ray intensity changes measured by RHEED-TRAXS for monitoring growth study in III-V/II-VI systems was widely seen in a number of literature. Ohtake et al. applied RHEED-TRAXS to evaluate the growth rate and surface-chemical composition of ZnSe (001) deposited on GaAs(001) substrate where take-off angle close to the Se Kα line was used for all measurement. Wolfgang Braun’s group investigated the growth process of AlAs/GaAs (001) and InAs/GaAs(001) using RHEED-TRAXS and demonstrated its applicability in assisting the study of growth mechanism. Shigetomi et al. used RHEED-TRAXS to observe the isothermal desorption of In atoms under different As pressures after a 10ML of InAs was deposited onto GaAs substrate.

For application in oxide systems, research is still in preliminary stage. Aoki et al. applied RHEED-TRAXS on the system of high temperature superconducting oxide (HTSC) YBa₂Cu₃O₇-x and demonstrated the element specific critical angle dependence of RHEED-excited characteristic x-rays. They also applied the measurement to deposition of films with thickness ranging from 0.8Å to 800Å to observe the intensity change of individual elements. Kashiwakura et al. investigated the thermal oxidation of LaSix on Si (100) substrate using Si Kβ line. By varying the incident electron energy, they measured the corresponding spectra and compared with probing depth approximated by an empirical model.

RHEED-TRAXS initially attracted attention and became popular among researchers working with III-V/II-VI systems. Meanwhile, with the development of
functional oxides, the need for a real-time, \textit{in situ} compositional control technique in the oxide system became pressing as in these complex oxides, small variation in stoichiometry can cause significant changes in physical properties of the material. Furthermore, understanding the mechanism of thin film deposition in MBE processing is important for achieving a better process control and further improving the film quality for device applications. In order to more effectively implement RHEED-TRAXS in the Interface Engineering Laboratory, understanding from related literature using RHEED-TRAXS to study thin film deposition processes in various perspectives are essential for gaining the knowledge needed in designing, building and developing RHEED-TRAXS effectively.

3.2 Qualitative analysis

The intensity of the characteristic x-rays excited by RHEED electrons can be impacted by various factors including electron energy, electron beam current, incident angle of the electrons and azimuthal angle of the electron with respect to the crystal structure orientation and take-off angle of the x-rays. When the impacts from factors other than the film chemical changes are controlled during experiment and excluded from the observations, x-ray intensity information from the RHEED-TRAXS can be used to provide qualitative monitoring of the film deposition.

Ohtake \textit{et al.} investigated the deposition of ZnSe on GaAs(001) substrate with the assistance of RHEED-TRAXS positioned at the critical angle of the Se \( Ka \) line. Oscillations of Zn x-ray K line intensity were observed during deposition under island growth when the substrate was exposed to Zn and Se alternatively, however, the Se intensity stayed relatively constant throughout. Under layer by layer growth, it was
observed that the Se intensity showed an oscillation that corresponds to the ALD cycles (Figure 11)\textsuperscript{37}. Thus RHEED-TRAX can be sensitive to growth modes.

Figure 11: Zn K\textalpha{} and Se K\textalpha{} lines intensity variation under (a) island growth mode and (b) layer-by-layer growth mode during ALE growth of ZnSe.

Based on the energy of the Zn K\textalpha{} line (8.64keV) and the Se K\textalpha{} line (11.22keV), in the same material (ZnSe), Se x-rays would have a smaller critical angle than that of the Zn x-rays. This critical angle is also smaller than that of the substrate x-rays Ga K\textalpha{} line (9.25keV) and As K\textalpha{} line (10.24keV). Theoretically, if the detector was positioned at the Se critical angle, it will not be able to see the x-rays coming from the other elements in the film. However, experimentally, some x-ray can still be observed at angles under the critical angles where maximum intensity can be observed. In practice, critical angles can be located by measuring the x-ray intensity distribution to find the maximum intensity angle. However, Se was the deposited element in Ohtake’s work, as a result, without depositing the film to a certain thickness, the practice of measuring the intensity for locating the critical angle was not possible. It was not mentioned in the paper that how the critical angle of Se was determined. If the theoretical calculated angle was used for the work, some
inconsistency can be expected from the results due to the flexibility of MBE system’s positioning mechanism.

Shigetomi et al. investigated the desorption processes of deposited InAs on GaAs substrates under different As pressures and substrate temperatures\(^{5a}\). It was observed that at a relatively higher As pressure \(P_{\text{As}} = 3.0 \times 10^{-8}\) Torr, desorption process of As atoms was different from that at a lower As pressure \(P_{\text{As}} = 1.0 \times 10^{-8}\) Torr (Figure 12). X-ray intensity of As stayed relatively constant at the initial \(~50\) min of desorption, suggesting a constant number of As atoms within the excited sample volume. The intensity only started to drop at around 60 minutes and quickly decreased from 10 MLs to approximately 3 MLs within less than 20 min. In contrast, intensity of As under a lower \(P_{\text{As}}\) started decreasing from the beginning of desorption and linearly decreased to the same extent (3 ML) after about 60 minutes. It was observed that the As pressure plays a key role in altering the desorption process.
Figure 12: InAs isothermal (450°C) desorption process tracked with RHEED-TRAXS by Shigetomi et al.

Under the same As pressure of $3.0 \times 10^{-8}$ Torr, substrate temperature was shown to also play a role in determining the desorption rate of As as shown in Figure 13. When temperature was varied from 510°C to 550°C, total time taken to desorption to the same amount decreased from about 30 min to <10 min. Changes in corresponding RHEED patterns confirmed the observations in RHEED-TRAXS x-ray intensities.
Similarly, adsorption process can also be studied with the assistance of RHEED-TRAXS. Ohtake et al. also investigated the adsorption states of both Zn and Se on GaAs (001) substrates under different temperatures (Figure 14)\(^40\). The coverage of Zn decreases with the increase in substrate temperature until a plateau was reached. At different temperatures, the thickness of the plateau varies which suggests a temperature controlled adsorption mode. At lower temperature (200°C), intensity of Zn increased significantly with the exposure to the Zn beam, and gradually slowed down after 10 minutes of growth. As the temperature was increased, the increase of Zn into the film slowed down and reaches a plateau at an earlier time.

Figure 13: Desorption of As from InAs film under same As pressure but different temperatures.
Figure 14: Adsorption of Zn to GaAs substrates under different temperatures tracked by RHEED-TRAXS.

These works suggested the application of RHEED-TRAXS during real-time deposition to assist the study of process parameter impact on the growth mechanism. It has been observed that RHEED-TRAXS measurements are highly sensitive to chemical changes and can reflect these changes in the characteristic x-ray intensity immediately. These results confirmed the feasibility to provide chemistry information in real-time, and RHEED-TRAXS’ potential to assist deposition monitoring and mechanism studies. Confusions arise when critical angle measurements were involved. Due to the element-dependent property of total reflection angle x-rays, measurement at random angles can only provide qualitative information of the monitored process. Unless the relationship between the critical angles and the detection angles are specified, interpretation of the data will be greatly limited.

3.3 Quantitative studies
The goal of quantification efforts on RHEED-TRAXS is to relate the absolute x-ray intensity or relative x-ray intensity ratios into information useful for chemical analysis. As part of the technique development, the quantification can be approached by first calibrating the RHEED-TRAXS intensity against a known technique such as XPS. XPS is a surface sensitive technique that measures the atomic composition of the top 10nm of materials. As a result, if RHEED-TRAXS signal comes from deeper than top 10nm of the sample surface, composition from XPS will not be comparable and cannot serve the purpose of the calibration. In this case, other techniques such as Secondary Ion Mass Spectrometry (SIMS) can be used for further quantification instead. However, due to the geometry sensitive nature of the x-ray detection, there’s not yet a concrete theory in explaining the x-ray signal distribution in the RHEED electron excited sample volume. Quantitative analysis in the RHEED-TRAXS aspects is still limited. More thorough modeling of the process is in need to further advance the development of RHEED-TRAXS.

3.3.1 Compositional Analysis

Kamei et al. applied the preliminary study of RHEED-TRAXS to the deposition process of Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ superconducting films in conjunction with inductively coupled plasma emission spectroscopy (ICP)$^6$. In their study, films with different stoichiometry ratio were used to construct a calibration curve where the stoichiometry ratio measured with ICP was used as a standard. RHEED-TRAXS characteristic x-ray (Y La, B La, Cu Ka) intensities were normalized against the Cu Ka peak intensity as the stoichiometry ratio. By relating this ratio to the measured ratio in ICP, the calibration curve was achieved. Later, the calibration was used to predict the stoichiometry of a deposited film.
The predicted value deviates the measurement of ICP by about 10% less, while this result is encouraging, the authors failed to comment on systematic issues such as the detection geometry, comparison of sampling depths, signal-to-noise ratio of different elements, impact of overlapping peaks and differences between using peak area and peak height; all of which have been shown to impact x-ray intensity. The authors attributed this deviation to the fact that RHEED-TRAXS measures intensity at near critical conditions where ZAF correction commonly used for SEM-EDX may not apply. Hence, the author suggested further study with ZAF correction to improve the RHEED-TRAXS prediction. However, calibration with ICP should not require the usage of ZAF since it is a direct comparison. It was not clear but would be interesting to know how ZAF corrections were applied in the calibration process.

The second reason the authors provided was the impact of the surface roughness. Discussion of the impact of the surface roughness was also reported in other publications and it was indeed a possible factor. However, based on the experience in this work, there were other possibilities that could contribute to the deviation on a higher level. For example, it was noticed that the low level of Ba and La in this particular film was mentioned in the paper. Based on the work conducted in this thesis, the intensity of Ba and Y characteristic x-rays is a function of the acquisition time of the spectra or the peak to noise ratio of the spectrum. Error can be introduced when the acquisition time is shortened. In Kamei et al.’s work, the details of RHEED-TRAXS spectrum collection was not introduced for either the calibration measurement or the sample deviated from the calibration. It is possible that for the sample measured, same settings of collection parameter was used which was not sufficient to provide a signal-to-noise ratio as high as that of the calibration samples which has a higher Ba and Y content. The peak intensity difference can also be
spotted in the Figure 15, where Y and Ba L line peaks are of lower intensity and more influenced by the high counts in background.

![Figure 15: Energy-dispersive X-ray spectra of three Y-Ba-Cu-O films with different stoichiometry taken using RHEED-TRAXS and compared with their respective ICP measurement. In the figures, p.h. and comp. denote X-ray peak height and composition, respectively.](image)

In order to use RHEED-TRAXS for chemical analysis, the x-ray intensities first need to be free of systematic impacts such as RHEED parameters and detection geometry, and then they need to be calibrated with the corresponding and known composition. As soon as a correlation between the x-ray intensity excited and the number of atoms in the excited volume are established, accurate composition can be realized. To build this correlation, RHEED-TRAXS can be used on standard samples or it can be calibrated against the measurement from an established technique such as XPS, ICP or SIMS. Since different techniques have different sampling depth in specific material systems, the sampling depth of RHEED-TRAXS at the total
reflection geometry needs to be determined before choosing a method to set the calibration. When these issues are addressed, intensity from RHEED-TRAXS should be able to provide composition monitoring during real-time processing.

3.3.2 Surface impact on the RHEED-TRAXS x-ray angular distribution

Liu et al. studied SrTiO$_3$ “islands” deposited on Si substrate using RHEED-TRAXS and claimed that the intensity (number of beams) of the x-rays is directly proportional to the number of islands. After depositing each SrTiO$_3$ layer, a Cu layer was deposited as a cap, and used for x-ray measurement. By measuring the intensity of Cu Kα x-ray coming from this cap layer at a continuous range of take-off angles, the critical angles can be found. It was found that this critical angle is different when Cu is deposited on different surfaces (Si or SrTiO$_3$).

Assuming a glancing incidence and glancing exit of the characteristic x-ray scattering process (GIEXS), the authors suggested a method of determining surface density by measuring the actual critical angle, and calculate backwards to find the density using equation shown below

$$
\theta_c = (2\delta)^{1/2} = 1.14\sqrt{\rho/E}
$$

(7)

where:

- $\theta_c =$ critical angle ($^\circ$)
- $\delta =$ real component of refractive index
- $\rho =$ density of propagation medium ($g/cm^3$)
- $E =$ energy of x-ray (keV)

As a result, the difference in critical angle (Cu intensity peak position) can be related to the density of the surfaces (Si or SrTiO$_3$), hence to the density of the islands. This unique perspective could point to a novel way of investigating the growth mode.
Another aspect of the energy-density-critical angle equation is that, for x-rays with lower energy, the critical angle is more sensitive to the surface density. From this point of view and by comparing the critical angle of both Ag and Cu coming from the same substrate (SrTiO$_3$), Ag L$\alpha$ line, which has a lower energy and a higher critical angle as shown in Figure 16, was chosen for surface density measurement.

![Figure 16](image)

**Figure 16:** Angle dependence curve of characteristic x-rays coming from Cu and Ag cap layers deposited onto SrTiO$_3$.

By processing SrTiO$_3$ film with two different terminations, the critical angles were measured and compared as an application for the previously mentioned theory (Figure 17). The authors found that the surface atomic layer density, instead of the surface bulk density, determined the position of the peak. X-ray angle dependence measurement was used to confirm this finding and suggested the difference between TiO$_2$ terminated surface and the annealed surface that was composed of mostly TiO$_2$ and small portion of SrO.
Figure 17: Measurement of Au M line x-ray intensity coming from Au capping layer deposited onto (a) TiO$_2$ terminated film surface and (b) annealed surface where TiO$_2$ and SrO coexist.

This work provided an interesting perspective by tracking back the surface sensitivity with the variation in critical angle measurements. However, this is based on the assumption of incidence and exit of the x-rays at a glancing angle. Also, other factors such as x-ray emission from Cu capping layer, surface roughness, optical path resolution and geometry repeatability were not discussed. The author could not explain why the density of a surface as thin as one atomic layer thick impacted the critical angle, while the assumption was based on x-rays refracting off island like SrTiO$_3$ surfaces. Besides, results from a critical angle comparison from different thicknesses suggested that the Cu peak did not vary significantly from 0.2nm to 1nm (Figure 18), which raises question into the legitimacy of the assumption and the value of the statement.
Figure 18: The exit angle dependence of the Cu K-α x-ray intensity varies with the thickness of the Cu film.

Similar trend was observed in Liu et al.’s work with deposition of Cu onto SrTiO$_3$ surface. The author attributed this to the coalescence of the surface due to Cu deposition and believed that the decreasing amount of bare surface reduced the scattering intensity from the SrTiO$_3$ surface. $^{36}$ Thus, surface features such as roughness, surface layer composition can all impact the angular distribution of the characteristic x-rays.

Figure 19: Intensity of Cu K-α x-ray intensity from Cu adlayer of different thicknesses deposited on SrTiO$_3$ surface. Take-off angle was fixed at Cu K-α x-ray $\theta_c$. 


3.4 Glancing angle dependence and atomic depth distribution analysis

When electrons incident the sample surface at certain angle, the penetration depth of the electrons can be described as a function of the energy of the electron and the physical properties of the material. By changing the incident angle of the electrons, x-rays from atoms in different depths of the sample surface can be excited selectively and measured. A number of literature on quantification of RHEED-TRAXS are focused on this aspect, which provides a different perspective in utilizing the electron-induced x-ray for layered structure analysis.

3.4.1 Electron trajectory

Electron penetration depth in any medium can be determined by angle of incidence, magnitude of the current, accelerating voltage and average atomic number (Z) of the sample. Popular methods for approximation with empirical models include these of Everhart & Hoff Model (1971) and Kanaya & Okayama (1972), or Monte Carlo Simulations. Calculation based on model by Kanaya & Okayama (1972). A semi-empirical equation was provided by Kanaya et al. in their 1972 paper as shown below.

\[
r(\mu m) = \frac{2.76 \times 10^{-2} AE_0^{1.67}}{\rho Z^{0.89}}
\]

(8)

where: \(\rho\) = Density of the material (g/cm\(^3\))

\(Z\) = Atomic number

\(A\) = Atomic mass (g/mol)

\(E_0\) = Accelerating voltage (keV)
Table 1: Theoretical electron penetration depth in different materials with 12.5 keV electron acceleration energy at 90° and 2° incidences.

<table>
<thead>
<tr>
<th>Incident Angle</th>
<th>Magnesium Oxide (MgO)</th>
<th>Barium Ferrite (BaFe_{12}O_{19})</th>
<th>Barium Titanate (BaTiO_{3})</th>
<th>Fe</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°</td>
<td>1.466 µm</td>
<td>1.503 µm</td>
<td>1.183 µm</td>
<td>0.7335 µm</td>
<td>1.618 µm</td>
</tr>
<tr>
<td>2°</td>
<td>51.18 nm</td>
<td>52.47 nm</td>
<td>41.29 nm</td>
<td>25.6 nm</td>
<td>56.47 nm</td>
</tr>
</tbody>
</table>

Energy of incident electron beam and the incident angle are the key factors in determining the electron trajectory in a given medium. RHEED-TRAXS can be compared with Energy Dispersive X-ray (EDX) spectroscopy where electron beams incident the sample surface at a 90° angle. In EDX measurements, penetration depth of electrons is usually in the micron range. In the case of RHEED induced x-rays, as the electrons penetrate the sample surface at a glancing angle of a few degrees, electron penetration depth reduces dramatically. Monte Carlo simulation was used in literature 8 to simulate electron trajectories in different conditions. More details will be introduced later in section 4.8 of this dissertation. These empirical models were adopted in this work to calculate the approximate penetration depth of electrons at certain kinetic energies in specific materials. Monte Carlo simulation was also used in this work to simulate the projection of electrons after they enter the surface at 2° incident angle.

3.4.2 Glancing angle dependence of x-rays

Depth distribution of atoms in the surface was investigated by changing the glancing angle of the incident electrons and used to predict the growth mode. For thin
film deposited at the initial stage, while RHEED incident angles were increased, both the RHEED pattern and the composition of the excited x-rays changed. It was generally observed that with the increase of the glancing angle, the peak position of the emitted x-ray intensity moves to higher angles due to the increased contribution from bulk x-rays. This method was reported to have an atomic layer depth sensitivity and especially sensitive of layers close to surface region.

Ino et al. investigated the dependence of the excited x-rays on the glancing angle of the incident electrons. Electron gun was rotated above the sample surface to change the incident angle while x-ray detector was fixed all the time at a constant angle. By using Monte Carlo simulation to simulate the electron trajectory, a sample with 10 monolayers of Ag deposited on Si was measured and analyzed (Figure 20). The contribution of x-rays coming from each layer was shown in the simulation result.

According to the simulation, the intensity coming from the first monolayer showed a $1/\sin \theta_g$ dependence with the glancing angle ($\theta_g$). When $\theta_g$ increases, $\sin \theta_g$ increases thus the intensity decreases by $1/\sin \theta_g$, with the incident electron beam moved towards higher glancing angles. By measuring the glancing angle dependence of x-ray intensities of different element during stages of deposition, the growth mode was predicted. The dependence curve was matched with the simulated curve from the layered structure. For example, if the Ag glancing angle dependence showed $1/\sin \theta_g$ dependence, it can be predicted that Ag stayed on top of the surface (top layer).
Figure 20: Simulated result of glancing angle (θ_g) dependence of x-rays as a sum of emissions from each individual layers in a film. X-ray emission was assumed to be proportional to the total length of the electron trajectories.

In this study, it was observed that the Si signal coming from the substrate did not exhibit a sharp increase according to the critical angle phenomenon. Instead, the intensity of Si increased to a saturation value and stayed relatively constant. A qualitative explanation by the authors attributed this feature to the summation of x-rays coming from a wide range of depth that covers several layers of Si. Especially the author briefly mentioned that the position of the peak indicate the average depth of the Si signal observed. As there’s no further explanation or theoretical reference of how this conclusion came from, it is difficult to extract more information beyond the statement.

In another publication from the same group by Yamanaka et al., the deposition process of In on 1ML Ga covered Si(111) substrate was studied using glancing angle dependence with x-ray detector fixed at critical angles⁴³. In their work, the x-ray intensity profiles of 1ML In and 7 ML In deposition were compared (Figure 21).
Results from 1 ML deposited In agrees well with simulation predicted trend in that In intensity exhibit a $1/\sin\theta_g$ dependence and the underlying Ga monolayer showed a profile matching that of the predicted 2nd layer. The x-ray intensity from the 7ML deposition resembled the prediction from Ino’s work as shown in Figure 20 where Ga intensity peak moved towards higher glancing angles as it is then buried as the 8th layer.

In the findings of this paper, after 2ML of In was deposited, the Ga K line x-ray intensity peak position shifted by 1°; however, after more In was deposited, the Ga intensity peak position stayed relatively at the same position as shown in Figure 21, which suggested a surfactant-mediated layer by layer growth mode where the previously deposited Ga layer was riding the near surface (3rd layer) during growth 43.

**Figure 21:** RHEED electron glancing angle dependence of the emitted x-rays measured from (a) In(1ML) on Ga (1ML) and (b) In (7ML) on Ga (1ML) at room temperatures.
In another work published by Ino et al. on the same topic, the authors suggested the application of the glancing angle method in the study of the deposition modes with different elements including Sn, Ga and In onto Si (111) substrates\(^{46}\). In general, by analyzing the glancing angle dependence curves, different growth modes can be deduced by the difference in the dependence curve (Figure 22). When two different elements are mixed during deposition, they will exhibit similar curve shape. When different elements form distinctive layers during deposition, the glancing angle dependence of each element will resemble the corresponding layers as shown in Monte Carlo simulation. However, since the electron-induced x-ray is element specific and has different sensitivities with different element, the practicality of this theory is uncertain.

Overall, the disadvantage of this glancing incident method is that it is limited to application with distinctive layered structures. If the underlying layers are composed of same elements as that of the top layer, the emitted x-ray at different RHEED incident angles cannot be distinguished. If the growth modes involve mixing of atoms in the same layers, it is not clear whether or not this method would be able to extract the correct information from the intensity change. As the simulation parameters or conditions are not clear in published papers, it is not easy to estimate the possible impact of fitting factors in the simulated results. If more information can be acquired, this could provide a powerful function for RHEED-TRAXS in analyzing composition of complex layer structures.
Figure 22: Growth modes of metals on Si (111) substrates using two-step deposition. The two-step process refers to the method where metal deposition onto the Si substrates at elevated temperatures followed by room temperature deposition.

3.5 Take-off angle dependence

Take-off dependence of the x-rays near the critical angle in different materials systems can be seen in literature. In Aoki et al.’s work on superconducting YBa$_2$Cu$_3$O$_{7-x}$ films, the angle dependence of each element was observed and compared with theoretical calculated values. Ba La line was observed to increase sharply at near its critical angle whereas Y La line intensity slowly increased till a saturation point was reached. Similar behavior of different elements in the same structure can be observed from other literature and this work as well, although the explanation of these observations is still limited in scope.
Ino et al.’s work reported the different behavior of substrate x-ray and characteristic x-rays of the deposited layer. Ag was deposited onto Si substrate and the take-off angle dependence was measured. Several aspects are worth noticing in this plot. First of all, Si intensity does not follow the theoretically expected sharp increase around critical angle. However, intensity of Si reached a maximum then plateaued as shown in Figure 23. In contrast, intensity of Ag L line increased sharply to its maximum and slowly dropped past critical angle. Similar findings were also observed in the experiments conducted in this work. When the thickness of the deposition layer is at least a few nanometers, the substrate x-ray did not exhibit the intensity pike. The reason for this and its impact on x-ray intensity are not clear yet. Second, RHEED-TRAXS is believed to be surface sensitive due to the external reflection and the shallow penetration depths of the excitation electrons. Similar situation was also observed in Chandril’s work. When the overlayer thickness is of several nanometers, angular distribution of substrate x-ray do not show a spike, but reach a plateau instead. This suggested a sampling depth of RHEED-TRAXS at the level of nanometers.
Figure 23: Intensity of x-rays coming from the deposited layer exhibited a pronounced peak, which was not observed with the x-ray excited from the substrate.

Besides, in Figure 23, intensity of Ag is significantly lower (by 9 times less) than that of the Si. Efficiency of the electron excitation could be related to this intensity difference, but it also raises the question about the actual sampling depth of the technique since the intensity can be related to the volume of the sample excited.

Take off angle dependence of the excited x-rays were widely reported in various RHEED-TRAXS systems. This need to be characterized in any system designed as a first step because measurement at critical angle is what makes RHEED-TRAXS suitable for real-time monitoring of the sample surface chemistry.

3.6 Reported Sensitivity

Sensitivity of RHEED-TRAXS involves two concepts. On one hand, RHEED-TRAXS was reported to be sensitive enough to pick up signal from atoms in very low amount. Aoki et al. reported that signals of Y La, Ba La and Cu Ka x-rays were picked up from a deposited YBa$_2$Cu$_3$O$_{7-x}$ film with mean thickness of approximately 0.8Å which is less compared with the height of a unit cell (11.68Å) $^{47}$.

On the other hand, the probed sample volume of RHEED-TRAXS is of interest to controlling the surface chemistry during real-time. As previously discussed (3.3.2), surface sensitivity of RHEED-TRAXS is related to both the electron penetration depth and x-ray escape depth. At the critical angle, the detected x-rays come mostly from the surface of the film within the volume that’s excited by the RHEED electrons at glancing incidence. As a result, the excited volume of the sample is confined to the top few nanometers of a sample surface by the electron trajectory and even further the probed depth of the x-rays is constrained by the total reflection.
angle measurement. Although qualitative analysis indicates high sensitivity of RHEED-TRAXS to the surface chemistry, experimental discussion of this aspect is not much reported.

For real-time chemical analysis purpose, the later aspect of the sensitivity is of more importance. Functionality of a thin film depends highly on the stoichiometry of the film. Correct stoichiometry also guarantees the right crystal structure. If stoichiometry of a growing surface can be tracked in real-time, the stoichiometry and structure can be expected to be uniform throughout the film. As reactions happen at the sample surface only, control of the stoichiometry of each freshly deposited layer using surface sensitive RHEED-TRAXS will be essential. If RHEED-TRAXS can provide the stoichiometry of the newly deposited surface layers, the chemistry of the deposited film can be compared with the desired chemistry. Any variation brought by fluctuations in the growth parameters such as substrate temperature and reactant flux can be corrected by adjusting the individual fluxes.

Aoki et al.’s work presented the thickness dependence of each deposited element x-ray intensity with the thickness of deposited film (Figure 24). A common trend of the increase among different element can be observed from the plot. The thickness where all the increases start to slow down is similar. It was commented in the paper that after 80 Å of film was deposited, the slope of the increasing trend decrease.
Figure 24: Y L\(_\alpha\), Ba L\(_\alpha\) and Cu K\(_\alpha\) elemental x-ray intensity variations with YBa\(_2\)Cu\(_3\)O\(_{7-x}\) film thickness.

Deposition process is a complicated process through the perspective of x-ray propagation process. X-ray intensity is not only proportional to the number of atoms but also related to the attenuation effect brought in by layer thickness. During the deposition process, the sticking of the atoms on ever evolving surface can also change with time. In the simplest case, two assumptions with extreme cases will be made here to provide a comparison look at this change as an attempt to identify the reason behind the decrease in the slope.

First, assuming that RHEED-TRAXS does not possess surface sensitivity and can probe the whole sample volume, the intensity of the detected elemental x-rays should be proportional to the number of atoms deposited. If attenuation of the most bottom layer of the deposited material can be ignored, the increase should be linearly proportional to the increase of the deposition time. If not neglecting the attenuation of the x-ray through the deposited material, the intensity increase should be a function of...
both the proportional increase with atomic concentration and the attenuation of the x-ray coming from the bottom of the deposited layer. The fact that researchers found the trend is linear within certain range.

Braun et al. ’s work indicated that by tracking the Al signal decay time in the overgrowth of AlAs surface by GaAs, an approximate thickness of 20Å can be deduced based on the growth rate. Kashiwakura et al. reported a sensitivity of 0.1 Å - 0.2 Å in thickness and a probe depth of about several tenth of an angstrom.

RHEED-TRAXS has been reported to be sensitive enough to reveal chemical changes in sub-monolayer ranges. But this does not mean that RHEED-TRAXS is detecting chemical changes of the sub-monolayers only. Without more information on how the sampling depth was determined, how surface sensitive RHEED-TRAXS is remains a challenging question to be answered.

3.7 Impact of surface roughness

The impact of the surface roughness on the RHEED-TRAXS measurement is not widely reported, but certain perspectives can be found through the qualitative discussion by Ohtake et al. and the more rigorous work by Chandril et al.

In Ohtake et al.’s work on deposition ZnSe on GaAs (001) by ALD, it was mentioned that the critical angles of the Zn Kα and the Se Kα x-rays emitted x-rays from rough surfaces (island growth) have different critical angles compared with that emitted from layer by layer growth conditions (Figure 25). Critical angles measured with films grown under layer by layer mode were greater than films grown under island growth mode. As different growth mode can result in different surface
roughness, it can be expected that the change of critical angle can be related to the change in surface roughness.

**Figure 25:** Intensity of the Zn Kα and Se Kα x-rays measured from both island growth mode and layer by layer growth mode, plotted against the take-off angle.

Although the intensity of the detected x-rays in RHEED-TRAXS setup depends highly upon the relative detection angle with respect to the elemental critical angles, the authors commented that the intensity of the x-rays from a growing film at the very initial stage of growth is less impacted by the growth mode but more determined by the absolute number of atoms deposited. However, a clear definition of “initial stage” was not provided.

Braun’s work also discussed the impact of the surface roughness on the RHEED-TRAXS signal intensity. It was observed that at the very beginning of the growth, intensity all increased abruptly and gradually relaxed after the growth. The
relaxation process was not simultaneous for all elements but turned to be faster for more mobile GaAs than AlAs. The authors believed this maybe related to the growth related surface roughness change but did not further explore this phenomenon\(^4\).

Most recent work by Chandril et al. incorporated the surface roughness factor into their theoretical model and quantitatively modeled the x-ray emission using structural parameters\(^8\). Considering the process of x-ray generated from certain depth propagate through and exit a material at certain angle can be equivalent to the process of x-ray impinging the same material at the same angle and reaching to the same depth\(^4\)\(^9\)\(^50\), theoretical methods such as distorted-wave approximation can be applied to this process.

3.8 Technical limitations

Braun et al. reported the impact on x-ray intensity due to coupling between peaks with close energies. While this situation can be improved with detectors of higher energy resolutions, peak deconvolution may still be necessary for elemental composition analysis of elements with x-ray energies within the high-resolution detectors.

Another difficulty is that the critical angle and the shape of the angular dependence curve are not independent of processing factors such as deposited film thickness and material properties of both the substrate and deposited layer. This was reported in literature and also observed in this work. Experiments are needed to determine the impact of these factors and to seek effective methods compensating for the impact on intensities.

3.9 Summary
The applicability and potential of RHEED-TRAXS in MBE systems for in-situ, real-time analysis have been suggested by several researchers. Early research on RHEED-electron -induced x-ray emission has provided a proof-of-concept for the RHEED-TRAXS theory. However, impacts from various variables in the MBE processing of thin films are still not clear. Before it can be effectively utilized for real-time control of MBE processes, especially for oxides, several specific aspects of RHEED-TRAXS need to be studied including processing impact on intensities independent of elemental composition, thickness approximation in real-time, and depth sensitivity.

Although RHEED-TRAXS has been used for qualitative monitoring of an MBE process, using it for quantitative analysis is still unattainable. Quantification approaches such as calibration methodology, compositional analysis, and determination of the surface sensitivity of RHEED-TRAXS, all need to be investigated and effective methodologies established.
4. Experimental Approach

Enabling x-ray detection in the existing vacuum system is the fundamental step in developing a RHEED-TRAXS system. There are several aspects to be considered in parallel: selection of detector, and incorporation of detector into vacuum system, x-ray flux control according to the selected detector and angular positioning of the detector. After the system can be built and the impact of various factors on the RHEED-TRAXS x-ray intensities has been understood, the x-rays can be further utilized to help improving the process control of thin film deposition using MBE.

4.1 RHEED-TRAX x-ray detector

X-ray detectors based on different sensing materials may vary from each other in spectrum process and analysis. In order to understand the spectrums and to more accurately convert the signal intensity into elemental composition, understanding of how the detector functions is essential.

4.1.1 Multi-channel x-ray detector

All spectrometers are composed of three parts: an excitation source, a mechanism for separating and isolating characteristic lines, and a device for characteristic line intensity measurement. Generally by the number of channels it has, x-ray spectrometer can be defined as single channel or multi-channel spectrometers. Single channels can only detect x-rays at one energy at a time while multi-channel spectrometers have the ability to detect x-rays with different wavelengths or energies at the same time. Compared with multi-channel wavelength-dispersive spectrometers with fixed channels, energy-dispersive spectrometers are all multi-channel detectors.
Two types of detectors are commonly seen for XRF applications, Si-PIN and CdTe detectors. They both have advantages in certain applications. Compared with CdTe, Si-PIN sensor detectors have better energy resolution for energies below 25keV, lower background counts and good efficiency that depends on the detector thickness. Si-PIN detectors almost always have better spectral characteristics, better resolution and better peak to background ratios. For higher energy x-rays (generally above 25 keV), CdTe detector is the detector of choice. There will be some overlap and trade-offs, so the best choice depends on the details of the application.

The specific characteristic x-rays of most of the elements in the periodic table are in the range from 0.052 keV (Lithium) to 136.08 keV (Furmium) for $K\alpha$ lines. Current research in Interface Engineering Laboratory involves the usage of magnesium (Mg), barium (Ba), iron (Fe), oxygen (O) and silicon (Si), the characteristic x-rays of which we will be detecting are all under 25keV. As a result, Si-PIN detector better meets the needs of this work.

A Si (Li) type detector (Amptek XR-100CR) is used for this study. For Si based x-ray detectors, when x-ray photon incidents the silicon sensing element, it will interact with silicon atoms to create electron/hole pairs on an average of every 3.62eV of energy lost for one pair. Depending on the energy of the incoming x-rays, the energy loss or the generation of electron/hole pairs is decided by either the photoelectric effect or Compton scattering. The efficiency (or probability) of the detector to create electron/hole pairs is determined by the thickness of the silicon. The efficiency increases proportionally with the thickness of the silicon.

By applying a 100-200 volt bias voltage across the silicon depending on the detector thickness, the electron/hole collection process can be facilitated. Higher
voltage can also decrease the capacitance of the detector thus lower the system noise. However, this voltage will cause excessive leakage or eventually breakdown for operation at room temperature. Higher temperature of the sensing elements will also cause electronic noise in the system. Thus cooling of the detector is an important aspects that need to be considered in the design and in the operation of the detector. By cooling the detector properly, this leakage current can be reduced considerably and make the high bias voltage possible. A cooler input FET is also preferable because it can reduce the electronic noise of the system.\textsuperscript{52}

The XR-100CR detector from Amptek is a high performance detector using a thermoelectrically cooled Si-PIN photodiode. Other than expensive cryogenically cooled systems, a 2-stage cooler is used to achieve its cooling performance. The input FET and a novel feedback circuit are also mounted to the 2-stage cooler. These components are kept at approximately -55 °C, and are monitored by an internal temperature sensor.

### 4.1.2 Detector Efficiency

The detector efficiency shows the ability of the detector to detect photons. It is the ratio or percentage of the detected photons with respect to the incident photons. For photons with an energy between 6 and 11 keV, the efficiency can reach 100%, but beyond this range, the efficiency is reduced due to the transmission of X-rays in the beryllium window and the absorption of X-rays in the Si (Li). The efficiency of the detector is a function of mass attenuation coefficient, mass density and mass thickness and density. For photons with energy lower than 2 keV, absorption in the Beryllium window is the dominants loss of the efficiency. For photons with energies higher than 20 keV, interaction within the Silicon crystal becomes decisive. Air in the system is
another factor that can reduce the efficiency, which is not a problem in vacuum operation\textsuperscript{53}.

The hermetic TO-8 package of the detector (shown in Figure 26) has a light tight, vacuum tight thin beryllium window to enable soft x-ray detection\textsuperscript{52}. As this beryllium window is a non-replaceable part of the detector, it cannot be exposed to the harsh growth environment during MBE processing. Beryllium has a key application in x-ray detectors. It has the property of blocking all the visible lights and only allows the x-rays to go through. Beryllium window in the detector protects the components from being damaged and provide the detector the ability to detect x-rays with lower energies. The dimension of the beryllium window and its relative dimension within the XR-100CR detectors are shown in the Figure 26\textsuperscript{54}. However, it also brings in limitations due to the cutoff energy of Be for low energy x-rays, which will be discussed in details in section 4.2.2.

![Figure 26: Amptek X-ray detector elements showing the beryllium window, the detector, temperature monitoring and the cooling stage.](image-url)
4.2 General Approach

For each experiment to be tracked with RHEED-TRAXS, certain procedures need to be carried out before the growth to ensure the consistent geometry. Besides, in order for results to be comparable from run to run, factors that impact the x-ray signal intensity need to be calibrated. These factors include the kinetic energy of the electron beam, the emission current of the electron beam and spectra acquisition time. The goal of the characterization or calibration is to provide an effective reference to normalize results (i.e., x-ray signal intensity) between different experiments where these conditions have to be varied for specific needs and to enable comparison of experiment result taken under different settings.

4.2.1 Geometry Calibration

Calibration of the system geometry is achieved by setting the detection angle (or take-off angle) to Si elemental x-ray critical angle where intensity of the Si x-ray reaches the maximum. Different from regular operation of RHEED for its diffraction properties, using the electron excited x-rays require stable emission current in the beam. Prior to each measurement, RHEED was warmed up under operation conditions until the emission current is stable. Gate valve between RHEED-TRAXS chamber and the growth chamber need to be opened during this process to allow the beam to stabilize during equilibrated pressure. Once the beam stabilized, the emission current drift is not observable under the current available equipment setting. Over long period of time (>1hour), change in the emission current by +/- 0.1 μA can be observed.

X-Y stage needs to be reset to 0.000 inch in the X direction, and to origin (middle point) on the Y direction. While changing the position of the detector manually, spectra will be collected at each 0.016” increment for ~10s under consistent
RHEED conditions. For no to low Si counts region (usually happens between 0-0.300”), wider steps (.050” per interval) can be used till an trend of sharp increase is observed (This usually happens after passing 0.300”). The intensity of the Si x-ray is counted as the area under the defined Si peak. By plotting this intensity against the corresponding detection angles, the highest intensity region can be determined and used as the measurement angle for the following experiment. During the RHEED-TRAXS measurement, it is important to make sure that the RHEED pattern and its intensity are stable because this indicates electrons are incidenting at approximately the same spot on sample. The electron beam can shift on the sample surface due to accumulated charge.

4.2.2 Measurement during deposition

After the detector has been aimed at the Si critical angle, real-time data collection can be performed. Higher emission current of 6 µA is normally used due to the increased chamber pressure in oxygen environment. Without oxygen gas in the chamber, 3 µA is sufficient to provide high peak to noise ratio. Beside oxygen pressure, elemental sensitivity to the electron excitation also varies. Generally, lower atomic number atoms are easier to be excited thus gives out more x-rays whereas high atomic number atoms emit less x-ray when excited. Moreover, atomic concentration of atoms in the sample surface can also impact the intensity. Elements at lower concentration will emit less x-rays, thus requires a longer acquisition time to reach a pronounced peak. Based on the characteristics of specific material systems, emission current and the acquisition time can be adjusted to improve the signal-to-noise ratio. In this work, RHEED-TRAXS data collection during BaM deposition is set to be at least 15s under the emission current of 6.0 µA. This is due to the low efficiency of Ba L line emission and its low atomic content in the growing film surface. In comparison,
x-ray collection during MgO deposition on SiC can be done with 5-10s acquisition time.

4.3 Film deposition

RHEED-TRAXS was targeted to provide help on monitoring the film growth in real-time. As a result, film growths including deposition of MgO on SiC, Fe on MgO, Ba on MgO, BaM on MgO were all followed using RHEED-TRAXS. The deposition conditions of these experiments are described below.

4.3.1 SiC substrate preparation

Single-side polished, on-axis 6H-SiC(0001) substrates purchased from Cree Inc. were diced into $0.5 \times 0.5$ cm$^2$ squares and rinsed in heated solvents of trichloroethylene, acetone, and methanol for degreasing purpose. High temperature hydrogen reduction process was carried out on degreased substrates to remove scratches and reduce residual oxygen contamination to 8% atomic concentration of the overall surface composition. Processed substrates were then glued onto a molybdenum sample holder with conductive silver paint and immediately loaded into an ultra-high vacuum system with a base pressure of $1.0 \times 10^{-9}$ Torr.

After the SiC substrate has been prepared and loaded to the chamber, a pre-growth XPS analysis will be performed to find the oxygen content on the surface. Qualifying SiC substrates are subsequently transferred to the growth chamber via an internal transfer mechanism for depositions. RHEED is another characterization technique used to determine the quality of the SiC surface. Successful SiC cleaning will appear crisp under RHEED diffraction, however, “bad” cleanings typically have
higher oxygen content (>13%) from XPS scan, and exhibit less defined RHEED pattern (Figure 27).

![RHEED images of SiC substrate](image)

**Figure 27:** RHEED images of SiC substrate with (a) less than 8% oxygen (b) at least 13% oxygen.

The high temperature reduction process is the key step that determines the crystallinity of the starting surface. Reconstruction of the surface atom happens at the right heating conditions, and hydrogen environment washes off the excess oxygen bonded with the surface atoms. This is a standard procedure in the interface engineering lab carried out with a setup described elsewhere. A self-calibrating Omega (OmegaScope OS3750) pyrometer has been used to monitor the surface temperature as the control variable. As the pyrometer reads the average temperature within the range of the view window, the accuracy can be impacted by inconsistent placement of the sample on the heating element (a tantalum strip in this case), the width of the tantalum strip, and the current and voltage applied to the tantalum strip. Due to these factors complied, consistent SiC preparation result cannot be guaranteed even the temperature reading is consistent from run to run.
Considering that the reconstruction process under high temperature could be impacted by the power input, a different approach was taken. Instead of monitoring the pyrometer reading, power feed through a Sorehonsen DCR 20-115B DC power supply was controlled to be a constant 300 watts. With the tantalum strip in the circuit, the current is usually around 55-60 amps with voltage fluctuate in the rage of 5-6 volts. With this condition, satisfying reduced oxygen content of around 8% can be consistently achieved.

4.3.2 Heteroepitaxy of MgO

MgO works as a template layer between wide-band gap semiconductor substrate SiC and the functional oxide films such as BaM and BTO to reduce the lattice mismatch and prevent interfacial diffusion. Deposition of MgO on SiC substrate was processed in the oxide growth chamber with the assistance of atomic oxygen source (RF plasma).

Conditions to result in high quality MgO films were discussed by Goodrich et al. 56. A CreaTec Dual-LTC-K-Cell in with 10cc crucibles was used to provide the Mg flux. Mg effusion cell was set to 340°C for the growth. Low substrate temperature of 140°C was used to ensure 2-dimensional growth. RF Oxygen plasma (Oxford Applied Research) was used to provide atomic oxygen for the deposition.
Figure 28: Thickness of a series of MgO films were approximated using Si 2p3 core electron attenuation and plotted against the corresponding deposition time.

For the study of MgO deposition mechanism with RHEED-TRAXS, 10-20mins of MgO deposition was done under the exact same conditions and was monitored with RHEED-TRAXS detector. Based on the growth rate study using XPS shown in Figure 28, the acquisition time of 10s means an average of 1-2 Å of newly deposited film if the growth was not paused while x-ray data was being taken. As a result, during the tracking of MgO deposition, growth was temporarily held by closing the main shutter for data collection. During the initial 2 minutes of growth, RHEED pattern transitions from SiC (Figure 27) into what is typical of the MgO (111) pattern (Figure 29) and the corresponding MgO thickness approximately matches that of a MgO unit cell (~2nm).
Figure 29: RHEED images of deposited MgO film (a) (110) orientation and (b) (112) orientation.

4.3.3 Heteroepitaxy of Barium Hexaferrite

Heteroepitaxy of barium hexaferrite (BaM) was studied as a model system with RHEED-TRAXS for the purpose of illustrating the growth mechanism of this complex ferri-magnetic oxide. Temperature of the Ba source is controlled using the same CreaTec Dual-LTC-K cell used for Mg source but with a separate crucible. Temperature of the Fe source is controlled using Veeco single filament high temperature effusion cell with high purity Fe fillings purchased from Alfa Aesar. For BaM deposition, the Fe source temperature used was 1260°C, Ba source temperature used was 470°C. Oxygen plasma was used to provide atomic oxygen to the reaction. Photomultiplier reading of 1500 mV under the oxygen pressure of $3.5 \times 10^{-6}$ Torr was used for most experiments although power was varied under certain cases for plasma strength impact investigation. Substrate temperature was maintained at 720°C for all experiments. All the BaM films were deposited on pre-deposited MgO layers.

4.4 XPS measurements

XPS was used for chemical analysis of samples prepared including pre and post hydrogen cleaned SiC substrates, deposited MgO films and as-grown BaM films.
By comparing the attenuation of signals such as Si 2p3 and Mg 2p photoelectrons, overlayer thickness of MgO and BaM can also be determined.

In order to develop RHEED-TRAXS as a stoichiometry control technique, standards are necessary for quantification of the intensity information acquired by RHEED-TRAXS. XPS serves as a way to relate the collected x-ray intensity with the number of atoms in this work. XPS is generally sensitive to the top 10 nanometers of a specimen. However, as discussed before (Section 2.3.4 and 3.6), RHEED-TRAXS is sensitive at a greater scale of the sample surface that is greater than 10nm. Due to this reason, the accuracy of calibration in conjunction with XPS is limited beyond the top 10 nanometers. In other words, calibration of films less than 10nm thick is relatively reliable.

4.4.1 Chemical composition measurement

Samples are loaded from the load lock for analysis. After the pressure in the loadlock is evacuated to lower than $10^{-6}$ Torrs, the sample can be transferred into the analysis chamber for XPS analysis. A PHI 10-360-4-015 hemispherical analyzer with a PHI 04-173-0-077 Mg/Al dual anode non-monochromatic x-ray source was used for all the analysis. The x-ray source and the analyzer are equipped in an ultra-high vacuum chamber with a base pressure of ~$2 \times 10^{-9}$ Torr. Water-cooled x-ray source produces both Al and Mg x-rays which incident the sample at an angle with the surface normal of 54°. The hemispherical electron analyzer is placed right above the sample surface with an adjustable distance between the detector front and the sample surface. This flexibility allows it to be used for analysis of samples with different thickness, shape or morphologies.
The coordinates of the samples stage are fixed for all measurements so that elemental photoelectron intensity (such as Si 2p3 and Mg 2p peaks) can be compared before and after a film has been deposited for thickness modeling purposes. All films were first scanned with a wide binding energy range (1100eV for Mg anode and 1400eV for Al anode) survey scan to identify all the elements in the sample specimen. Then, for elements that are of particular interests, multiplex scans can be set up to investigate the bonding states with more detail. Compared with survey scan, which generally covers a full energy range of 1400eV to 0eV for Al anode and 1100eV to 0eV for Mg anode in order to identify all possible elements in the sample, each multiplex scan consists of several scans that are targeted at specific energy ranges. Tight scans were performed with 0.05eV per step, as a result, its peak shape can reveal the bonding information of the element. By deconvoluting the overall peak curve into minor peaks each of which represents more specific elemental bonding state, accurate bonding information can be acquired.

For an unknown sample, survey scans provides a list of elements that are present in the sample surface, from which elements of more interest can be selected and investigated in much detail. Materials studied in this work include SiC substrates, MgO template layer, BaM thin films, and occasionally films containing Mg, Ba or Fe.

For SiC substrates, survey scans were performed to give an approximation of the overall oxygen content and the silicon to carbon ratio on the SiC surface. Then, detailed multiplex scans were performed on Si 2p3 transition, C 1s transition, and O 1s transition. By fitting the peaks with 80% Gaussian and 20% Lorentzian, all the component peaks can be revealed and analyzed to explain the possible bonding states of Si and C. With this information, the source of the oxygen content on the prepared
surface can be tracked. Si and C bond with each other, and their “shoulder” peak features if there is any, can be attributed to the residue oxides. This is proved to be highly useful when studying the process factor impact of high temperature SiC cleaning in hydrogen environment (4.5.1).

For MgO films, Si 2p3, C 2p, Mg 1s and 2p transitions, O 1s, are investigated. The use of Si 2p3 peak intensity in approximating the MgO thickness, and the use of Mg2p peak intensity in approximating overlayer film thickness will be discussed in the following section.

**4.4.2 Thin film thickness measurement using XPS**

Similar to photons, when photoelectrons travel through certain medium, their intensity will be annihilated due to inelastic scattering inside the medium after a certain distance span. In this XPS system, this distance is around 10nm for most material systems. To what extent the original photoelectron intensity is attenuated to can be evaluated by the ratio between original intensity of a certain photoelectron transition and the intensity of the same transition after it has travelled through an overlayer. For example, before deposition of MgO layers, intensity of substrate peak Si 2p3 can be measured. After the deposition, its intensity can be measured again with the identical conditions and compared with its original intensity before the deposition. The extent of the attenuation can then be used to approximate the thickness of the deposited MgO layer.

Effective Attenuation Length database (EAL provided by the NIST) is a database that is widely used to approximate overlayer film thickness with the attenuation of under layer substrate elemental electron. The properties of the material
of interest including element, inorganic compound or organic compound are defined in the software at the initial steps. Values for the electron kinetic energy (electron energy subtracted from x-ray photon energy), the photoionization asymmetry parameter (for XPS), and the experimental configuration are also input into the software during initial setup. With these information provided, and the attenuation of the photoelectron intensity before and after the film deposition, film thickness can be approximated. The attenuation ratio is calculated by comparing the peak area under the curve of the interested transition peak before and after the overlayer film deposition.

4.4.3 Angle resolved XPS measurement

In angle resolved XPS, sample is rotated to any angle that is less than perpendicular to the electron detector for measurement (Figure 30). As the electron penetration depth (or escape depth in this case) can be regarded as fixed to be around 10nm, total travel length of the electron is limited to 10nm. When the sample is perpendicular to the electron detector, total length of the trajectory path equals the thickness of the film. When the sample is rotated by $\theta^\circ$, the trajectory of the photoelectrons finally reaching the detector make an angle of $\theta^\circ$ with the surface normal. The result of this is that, the travel length of the detector is more than the thickness of the film. And the thickness of the film sampled equals $10 \times \cos\theta$ nm.

Angle resolved XPS is a non-destructive way to find out the in-depth distribution analysis of the chemical or elemental composition of the sample. It reveals the chemistry information of the near surface of any sample, and can be used to find out the atomic distribution near the surface. As long as the rotation happens only at the sample surface, and that the analysis spot is still the same, AR XPS result
compared with normal XPS result can provide the depth profile information needed. However, it is worth noticing that, when the sample is rotated, the actual analysis spot covers an elongated area on the sample surface. As a result, larger samples are preferred to make sure the electron detector is not detecting signal from surfaces other than the sample.

![Angle-resolved photoelectron spectroscopy](image)

**Figure 30:** Schematic of the setup for angle-resolved XPS measurement\(^{57}\).

### 4.5 Monte Carlo Analysis of Electron trajectory

Monte Carlo is a class of computational algorithms often used in simulation of physical and mathematical systems. It can be used to simulate the electron trajectory in solids. A free software named CASINO (monte \texttt{CArlo SImulation of electronN trajectory in sOlids}) was used in this work to simulate the electron trajectory in materials at different incident angles\(^{58}\). This program is designed for low energy beam interaction in thin foil and bulk, but can also be used for the energy range of 0.1keV.
to 30keV. It can also provide the backscattered coefficient and x-ray excitation under defined conditions. This program can be used for both multi-layer samples and samples with grain boundaries. In this work, multi-layer sample models were used to approximate the electron trajectory in MgO/SiC layered structures.

Monte Carlo Simulation of electron trajectory with 12.5 keV suggested that with a beam size of 70µm, trajectory profile is more spreaded compared with a beam size of 20nm (Figure 31). The range of both trajectory profiles are almost around 1µm scale which means the excited amount of Si atoms are relatively evenly distributed on the sample.

![Figure 31: Monte Carlo simulation performed with CASINO (a) beam size 70um (b) beam size 20nm.](image-url)
5. Results and Discussion

This section will present the findings in the implementation of RHEED-TRAXS in the existing MBE system at the Interface Engineering Laboratory. The results and understanding in the research of using RHEED-TRAXS for thin film thickness and compositional analysis will also be discussed. There are four major sections, encompassing the practical integration of x-ray detection into the existing MBE system, the determination of the factors impacting the x-ray intensity, the results of relating the intensity information with the composition and thickness of thin films determined by other tools and the use of the relative composition to assist the study of oxide deposition.

5.1 RHEED-TRAXS System Design

RHEED-TRAXS systems are not commercially available. With MBE systems equipped with RHEED, an x-ray detector needs to be integrated into the UHV system and accurately positioned to measure the angle-sensitive x-rays. The range of critical angles varies with specific material systems and energy of the x-rays. For example, the element-specific critical angles can vary from less than 0.3° (e.g., Ga Kα in GaN) to up 8° (e.g., C Kα in MgO). As a result, if the RHEED-TRAXS equipment can cover a wide angular range, it will be more flexible for application in different material systems. In addition, accurate positioning and spatial-resolution of the x-ray detection must be considered in the apparatus design so that collected data is repeatable and quantifiable.

In literature, both *ex-situ* and *in-situ* mounting of the detectors were reported for carrying out RHEED-TRAXS measurement. For *ex-situ* systems, emitted x-rays
will transmit through the glass in the view port before reaching the detector. *In-situ* systems incorporate the detector into the vacuum system so that no extra attenuation of the x-rays is introduced. As attenuation of x-rays is a function of the energy of the x-rays, each attenuation barrier will introduce more complexity when interpreting and relating the intensity with chemistry information. In addition, window in MBE chambers can become coated over time, creating a changing barrier to attenuation. Thus the decision was made to engineer and addition to the existing vacuum chamber that would enable *in-situ* integration of the x-ray detection.

If the x-ray detector is not specifically designed for vacuum applications, the system design should resolve aspects including making the x-ray detection UHV-compatible to reduce x-ray attenuation, achieve angular-positioning capability, and enable the x-ray detection in harsh growth environment with minimal x-ray attenuation.

### 5.1.1 Vacuum chamber design

The RHEED-TRAXS system at the Interface Engineering Laboratory was realized through modification of the existing oxide growth chamber, to align the detection-angle starting point on the x-ray detection side-chamber port with focal point of all the effusion cells and the RHEED electron gun, i.e. the position of substrate during film growth (Figure 32).
Figure 32: Setup of the RHEED-TRAXS system with X-ray detector motion in the direction parallel to the surface normal. Source flanges are co-focused on to sample, Angels and distances are not to scale, external Be window, aperture and shutter are not shown.

In order to integrate the non-vacuum compatible x-ray detector into the UHV system, a 6” port was added to the oxide growth chamber. The port center axis is perpendicular to the growth chamber’s vertical axis. The intersection of the center axis of the port and the growth chamber vertical axis is 1” off the focal point on the growth chamber vertical axis, towards the bottom flange of the growth chamber. This offset is necessary for maximizing the movement of the detector and extend the angular range for detection.

Relative geometry of the 6” port and the growth chamber is shown in Figure 33. Green dot inside the growth chamber is the focal point of the added 6” port, which is 0.5” off (along the growth chamber axis) from the substrate growth position and 1.0” off from the RHEED electron focal point (not shown).
The 6” port is immediately connected to a 6” gate valve that can separate the new x-ray detection chamber from the growth chamber. As seen in Figure 34, this gate valve is followed by a four-way-cross (teal), which works as a junction for a turbo pump (blue) and the X-Y stage manipulator (light grey). A Mitutoyo (152-388A) linear stage with a maximum movement range of 2” was acquired for detector movement. This manipulator is used to provide linear motion for the x-ray detector in the direction parallel to the growth chamber axis and perpendicular to the axis. In this research, the parallel direction movement was used to provide take-off angle control of the detector.

By changing the location of the detector in the parallel direction, its relative take-off angle with respect to the substrate growth point changes based on small angle approximation. In Figure 35, the black dash lines indicate the axis of the detection chamber port and the growth chamber axis. The blue dash line connects the substrate growth position and the detector window at any given location. The angle formed
between the port axis and the connection line is regarded as the take-off angle (also shown previously, in Figure 32).

![Diagram of RHEED-TRAXS system]

**Figure 34: Drawing of the RHEED-TRAXS system showing the oxide growth chamber and the RHEED-TRAXS pumping system, detector manipulation stage and detector tube.**

Due to this linear motion, the x-ray detection is not line-of-sight, although line-of-sight measurement would be ideal for minimizing the amount of detected x-rays coming from sources other than the deposited atoms on the growing film surface. The rotational degree of freedom is not practical to incorporate into an existing system. Thus small angle approximation can be adopted for sample analysis as long as careful evaluation of the impact from background x-ray on the intensity of the x-rays of interest is incorporated in system use.

Following the X-Y stage, a custom-made off-center 4.5”-6” reducer flange was designed and built for x-ray detector mounting. If the connection tube between the two end flanges were centered, the detector would not be adjustable to the full range of the manipulator due to space constrictions exerted by the inner diameter and thickness of the detector protection unit. Thus, making the connection tube 0.5” off
center optimized the space usage inside the connection tube in the reducer and the bellow in the X-Y stage and can provide full range movement in the vertical direction.

Figure 35: Geometry for small angle approximation is shown with respect to the chamber.

With all the components mounted, the detector front window and the center of the sample are a fixed distance of 24.6” apart. Using small angle approximation, the 0-2” linear motion corresponds to a range of $0^\circ$-4.65$^\circ$ in detection take-off angle ($\theta_{\text{take-off}}$) with 0.003$^\circ$ precision. This range was sufficient to cover the critical angles of all the elements used in this work. Due to the low energy of the characteristic x-ray lines of low atomic number atoms such as oxygen and carbon ($0.526$ keV for oxygen Kα and 0.282 keV for carbon Kα), these elements will have higher critical angles than higher atomic number atoms in the same material system. Thus when looking at multi-element systems, compromises must be made to balance sensitivity and intensity with compositional monitoring. Also due to their low energy, most Si based x-ray detectors cannot detect elements with atomic number less than 10. In practice,
determination of the range of the detection angle when designing a RHEED-TRAXS system needs to consider these factors.

5.1.2 Detector protection for real-time, in-situ analysis

The x-ray detector used in this work has a detection window that is sealed with a non-renewable thin beryllium foil. Beryllium metal has the property of allowing only x-rays to pass through and as a result, is widely used as x-ray detector window materials. Beryllium can be oxidized at elevated temperatures which would damage the vacuum seal of the detection elements and damage the detector irreversibly\(^\text{59}\). In order to protect this thin window from the MBE growth environment and to extend its lifetime when used in-situ in real-time, a protection mechanism was needed.

When choosing the candidate for the extra layer to protect the detector window, beryllium foil is a preferred candidate since it is generally transparent to x-rays, easy to handle and relatively less expensive than other materials such as Si\(_3\)N\(_4\) membranes. Thickness of the beryllium foil is one of the key criteria in selecting the proper foil for different applications. Although Be is transparent to most hard x-rays, at lower energy levels and low atomic numbers (oxygen to argon), < 10% of the x-rays are passed through the Be window depending on the window thickness. Thus, low atomic number elements such as carbon and oxygen cannot be detected in the system designed in this work.

Figure 36 shows the intrinsic detection efficiencies for the XR-100CR detector used in this work. At around 1eV, transmission drops sharply from 36% and 20% to 4% with 1/3, ½ and 1 mil (1mil = 0.001inch) thick Be foil respectively. Material systems of current interest in Interface Engineering Laboratory include Mg, which has
the lowest energy of the elements of interest and thus in turn experiences the most attenuation. A 0.001” (1mil, 0.305 millimeter) thick Be window was chosen for this work, thus introducing another 50% attenuation to the Mg signal detected. However, the Be window chosen does not have any impact on the intensity of other elements such as Si, Fe and Ba$^{60}$.

![Chart showing intrinsic full energy detection efficiency for the XR-100CR detectors. This efficiency corresponds to the probability that an X-ray will enter the front of the detector and deposit all of its energy inside the detector via the photoelectric effect.](image)

**Figure 36:** Chart showing intrinsic full energy detection efficiency for the XR-100CR detectors. This efficiency corresponds to the probability that an X-ray will enter the front of the detector and deposit all of its energy inside the detector via the photoelectric effect.

This attenuation effect of Be foils with different thicknesses can also be evaluated based on the atomic number of elements. As can be seen from Figure 37, elements with atomic number lower than Si (Z=14) will be attenuated to lower than about 80%, 70% and 60% of the original intensity if they travel through Be foils of thicknesses of 1/3 mil, ½ mil and 1 mil.
Figure 37: $K\alpha$ line x-ray transmission through beryllium window of different thicknesses depends on the atomic number of the elements.

For the most practical and cost-effective solution, thickness of the Be foil, the elements to be measured, attenuation of the characteristic x-rays and the cost of the Be foil of different thicknesses need to be evaluated. Most hard x-rays from higher atomic number elements ($Z \geq 14$) are less impacted than the soft x-rays from lower atomic number elements or the L line x-rays of heavy atoms. The percentage of the attenuation due to the Be window can be accurately approximated with theoretical methods$^{61}$ and taken into account to correct measured intensities. However, signal-to-noise ratio of the impacted x-ray peaks ($Z < 14$) can be decreased due to the reduced counts under the elemental peak, thus compromising sensitivity. In general, thickness of the Be foils need to be chosen carefully with the atom species and the accuracy of the measurement in mind.
5.1.3 Collimation and aperture design

Beryllium foil for coating protection of the beryllium window can be mounted with shutter as described in Vanmil’s work\textsuperscript{31} where a refreshable shutter mechanism was designed and used. However, due to the spatial constraints of the MBE chamber in the Interface Engineering Laboratory, the available space in the added 6” port does not provide enough room for both the shutter mounting and linear movement for angular range. If a 1 1/3” size shutter were mounted, the detector take-off angle range would be too limited to be of value for real-time monitoring.

Although the spatial constrains posed a challenge when a static Be foil window was inserted, it was found out that no obvious accumulation of deposited elements on the extra beryllium foil were observed over a period of ~3 months. This is likely because the x-ray detection chamber is not line-of-sight of any effusion cells. Another factor is that the detector is located about 20” away from the edge of the growth chamber.

The detector window protection design was simplified based on these observations and measurements. In general, however, if the detector in an MBE system needs to be positioned at direct exposure to the effusion cell openings or close to the environment with active species, a renewable option for the beryllium foil without bringing the chamber up to air is necessary. Shown in Figure 38 is the design of the detector support. The detector tube (blue) with the Be window drawn (green block) is inserted into a 2 ¾ inch to 4 ½ inch converter flange which has an extended tube on the vacuum side (extending from the grey flange).
Figure 38: A customized half nipple was designed to cover the detector tube and act as a support for the mounting of both the aperture plate and extra beryllium foil protection.

The photo of the system built is shown in Figure 39. The x-ray detector is mounted to the reducer. The beryllium window of the x-ray detector is secured behind the aperture cap. At the open end of the tubing, a separate aluminum “cap” with four holes is fitted to the tube to cover the detector Be window. Three of the holes are threaded and used for attaching an extra aperture plate onto the cap. As shown in Fig 39, the Be foil can be pressed between the cap and the extra plate with venting screws. The aperture plate is also part of the collimation design. The size of the opening can be adjusted by using different aperture plates of different apertures sizes.

Figure 39: Photo of the x-ray detector protection setup showing the detector, protection tubing and the aperture parts.
5.2 System calibration and characterization

After the RHEED-TRAXS system is designed and installed, practical characterization and calibration of the system is then performed. Characterization of the system checks and confirms the expected total reflection of the x-ray excitation, and provides insight into process factors other than the film stoichiometry that can impact the intensity of the elemental x-rays. These factors then need to be considered in both qualitative and quantitative use of the RHEED-TRAXS information.

Calibration of the system includes x-ray detector calibration and the x-ray intensity calibration for chemical analysis. The purpose of understanding and analyzing the spectrum is to convert elemental peak intensities into useful information of the elemental concentrations. The spectrum energy range from the Amptek XR-100 detector need to be calibrated each time before use in order to identify peaks that appear in the spectrum. Thus, an effective energy scale calibration method is necessary. In addition, after identification of species from the spectrum, relating their intensity with the chemical analysis requires further understanding of the spectrum, and the calibration of the intensity with the atomic concentration.

5.2.1 Energy scale calibration

The Amptek XR-100CR is a multichannel detector that can detect X-rays with different energies at the same time but through different channels. The spectrum output by the detection unit is not calibrated to energy, but displayed by channel numbers which corresponds to energies. The energy level of each channel can be linearly calibrated.
Due to the uncertainty of detector exposure in herent in the non-line-of-sight design of RHEED-TRAXS, samples that was never used in the growth chamber, such as Ge, was used for energy calibration. Ge could then be distinguished from any background peaks.

From knowing the energy of the two Ge peaks (9.89keV and 10.98keV), the overall energy range of the spectra span from around 0.35keV to 12.06 keV (corresponding to channel number 0 to 1024) was determined. Energy of the previously unidentified peaks matches that of the Mg Kα line (1.25keV), Si Kα lines (1.74 - 1.83keV), Fe Kα and Kβ lines (6.4keV and 7.06 keV respectively), an asymmetric peak around 4.5keV can be attributed to the overlapping of Ba Lα line and Ti Kα line since their energies are very close (4.47keV for Ba and 4.51keV for Ti).

Once the elemental peaks have been identified, Si Kα and Fe Kα peak has been used as the reference for each spectrum. The accuracy of the calibration is determined by the deviation of these energies from the linear line formed with 0 keV. The deviation is calculated as the difference between calibrated value and assigned value normalized with assigned value. For Si/Fe calibrated spectrum, the maximum deviation observed is 0.09% (Figure 40).
In summary, in an x-ray spectrum the channel numbers are related with specific consecutive x-ray photon energies and thus known x-ray peaks can be used to calibrate the spectrum. Foreign elements can be used to achieve this goal for preliminary calibration and to locate the peak positions of commonly used elements in any system. After the approximate positions of known elements have been identified, they can be used to achieve accurate calibration prior to each experiment.

5.2.2 System geometry and critical angle

Based on the total reflection of x-rays at the vacuum/film interface, it is expected that any x-ray coming from the surface will exhibit an intensity spike near its critical angle. Tuning the detection of elements near the critical angle will then maximize sensitivity to that element. In order to find the critical angle of element of interest, the detector was moved linearly from in the sample surface plane toward a direction parallel to the surface normal. X-ray spectra were collected at every 0.050”
(0.1°) or 0.016” (0.04°) step. The area under each elemental peak was used to plot the intensity profile over the linear motion range. Based on small angle approximation, this linear distance from the surface plane was converted to the take-off angles between the center of the detector window and center of the sample surface and used as the x-axis for intensity profile distribution.

Figure 41 shows this angular profile of Si x-ray intensity from a SiC substrate was measured according to procedure described in section 4.2.1. The detector was then positioned at the angle where Si intensity reached the maximum (identified as critical angle) to carry out RHEED-TRAXS measurement. After deposition, same procedure can also be performed to locate the Mg intensity angular distribution profile (Figure 41). It can be observed that at close to the surface plane, intensity of elemental x-rays exhibited a steep increase.

![Mg Si K line intensity Angular Distribution](image)

**Figure 41:** Angular distribution of Si x-ray and Mg x-ray intensity measured with ~20nm MgO/SiC film.

As can be seen from Figure 41, intensity of different elemental x-rays changes dramatically with take-off angles. This poses two challenges during real-time
measurement, 1) it is difficult to take all the spectra at all the different critical angles simultaneously with only one detector, and 2) consistency in detecting the angle-sensitive x-rays from experiment to experiment also needs to be ensured and the take-off angle is very sensitive to geometry. These challenges were overcome by fixing detector at the critical angle of the substrate Si Kα x-ray each time before the film deposition. The reason for choosing the substrate x-ray is that even before any deposition takes place, substrate x-ray critical angle can be measured and located. This reduces the impacts of geometric factors due to the near critical angle measurement on the x-ray intensity and thus makes changes in the surface chemistry during film growth as the only variable.

After MgO layer is deposited, Mg intensity increases due to the increasing amount of Mg atoms on the surface, whereas Si intensity decreases as it gets attenuated through the deposited layer. It can be observed that intensity of Mg did not start from zero in Figure 41, this can be attributed to the non-line-of-sight detection of the x-rays.

The oxide chamber involved in this study is used for deposition of MgO, BaFe$_{12}$O$_{19}$ and BaTiO$_3$. The inner chamber wall is coated with elements from accumulated deposition of these metal and oxides. RHEED electrons scattered off the sample surface can hit the chamber wall or the sample holder and excite x-rays from the deposited layer. The detector’s field of view is not limited to the surface of the sample, as a result, the x-rays coming off the chamber wall can be detected by the detector and contributes to the “contamination” peaks in the spectra. As these peaks are not characteristic of Si, it can be easily identified as coming from the environment. Due to this reason, spectrum taken with a SiC substrate usually have Mg peaks at 1.24keV region (Figure 42).
Figure 42: Typical Spectrum from XR-100CR showing the changes in Si and Mg x-ray peak intensity.

For the same reason, certain peaks can also be seen at around 4.5 keV and 6.4 keV, which are the energy levels close to Ba Lα line (4.47keV) and Fe Kα line (6.4keV) respectively. SiC substrates are attached to the sample holder with silver paint, silver paint around the sample can also be reflected in the spectrum as silver peak around 2.98 keV (Ag L lines). Mo peak around 2.29 keV (Mo L lines) is also common in RHEED-TRAXS if the electron beam glances partially on the sample and partially on the Mo sample holder.

The Mo and Ag characteristic peaks that come from chamber background do not interfere with the chemical analysis. However, take Mg for example, Mg x-rays coming from the surrounding forms a part of the total Mg intensity that will be used for composition analysis. Assuming this stray Mg x-rays coming from the environment does not change during growth, it can be subtracted from the total Mg intensity under the Mg Kα peak. Based on studies that was shown in later section (Mg intensity calibration), the results confirms that this method can provide reliable measure of the absolutely gained intensity of the Mg element due to MgO deposition.
According to Figure 42, it is assumed that the background Mg intensity is relatively constant regardless of the growth process, which supposedly could deposit more Mg onto the chamber wall.

Substrates are loaded onto a manipulator in the growth chamber for positioning and heating during growth. This manipulator can be moved in the Z direction and rotated 360° in the plane perpendicular to the Z-axis. Z direction movement of the sample stage enables transferring between the growth chamber and the analysis chamber; however, it also introduces variables into the consistency of x-ray measurement geometry. Highly repeatable Z direction location is necessary to make sure that any pre-calibrated detector stage settings can be repeatedly applied to x-ray detection and provide on-critical-angle measurement. Otherwise, if Z direction location is varied each time, detection geometry has to be re-calibrated.

Another factor impacting the consistency of the pre-calibrated system geometry is the tilted the sample holder stage. After the detector is fixed on the Z location, rotational angle of the stage can also impact the detection angle relative to the critical angle. If the sample holder top plane, where the sample is mounted, is not perfectly perpendicular to the Z axis, by rotating the stage to different incident angles with respect to the RHEED beam, incident angle of RHEED, diffraction angle, diffracted pattern and the angular distribution of the excited x-rays, hence critical angle, will be changed.

Shown in the Figure 43, when the sample stage was rotated around its Z axis, RHEED pattern was observed to shift on the phosphor screen. By measuring the x-ray intensity distribution over certain angle range, it was found that the relative position between critical angle and the detection angle has also shifted with the rotation of the sample stage. X-ray intensity angular distribution shown in green have shifted to the
right by about 0.25 degrees, thus showed a more complete angular distribution profile where zero intensity of x-rays (below take-off angle region) was captured. As a result of this impact, it was preferred to keep a constant rotational angle for each measurement in addition to the constant Z-axis location to ensure repeatable geometry calibration.

Figure 43: Angular dependence curve measured showed observable shift when the sample stage was rotated, suggesting an offset between sample plane and the detection geometry.

5.2.3 Collimation impact

The kinetic energy of RHEED electrons usually ranges from 10keV to 20keV. When these high-energy electrons scatter off the surfaces, they can excite a high volume of x-ray flux. In preliminary investigation of RHEED-TRAXS design in the MBE system in the Interface Engineering Laboratory, it was found that without controlling the incoming flux into the x-ray detector, the XR-100CR detector could not function due to a 100% deadtime. By reducing the x-ray detector view size, the
deadtime situation can be avoided. A series of aperture sizes that are less than the x-ray detector window size (xx) were tested before a final selection of 0.016” was chosen. The 0.016” diameter aperture can effectively reduce the incoming x-ray flux without losing the useful x-ray information from the sample surface.

When the more completed and advanced system described in section 5.1.1 was designed and built, to accommodate the high x-ray flux exited by the RHEED electrons and also control the detector’s field of view, an aperture plate is incorporated to the detector protection window design in this work. When RHEED electrons excite the sample surfaces, x-rays come off the surface in all directions (Figure 8) although only those emitted off the critical angle region are of interest. To limit the field of view of the detector to the narrow range close to the critical angle, collimating the incoming x-ray is a necessary step.

The detailed design was shown previously in Figure 32. Initially, a distance of 1 inch from the collimation aperture plate was left intentionally to the front of the detector due to the concern that tight spacing may cause dissipation of heat from the growth environment to the detector. After testing, it was found out this spacing caused a geometry shown in Figure 45 leads to a cut off of x-rays from the higher angle. In the schematic shown in Figure 45, x-rays coming through between the first blue line and the first red line is where the original design blocked off. The corresponding Si angular distribution curve shown in Figure 44 exhibit an obvious drop in Si intensity at ~1° angle. Mg intensity was less impacted which maybe due to the fact that Mg x-rays comes from the chamber surrounding accumulated depositories.

In order to more accurately study and confirm the angular distribution of x-rays in this system, the extra length was cut off so that the x-ray detector is right
behind the aperture plate with a distance of 0.05”. After the modification, the angular distribution was measured again, and it was observed that Si x-ray only started to drop off after the detection angle reaching 4° which is not of preference for critical angle measurement.

Figure 44: Angular dependence curve measured with the original design, where higher angle x-rays were blocked by the detector protection tube geometry, thus showing a cutoff around 1.5°.

Figure 45: Geometrical analysis of the cut off due to the unnecessary length of the detection tube.
This unique problem was caused by the fact that the detection system designed for this work is not in “line-of-sight” with the growth position of the sample or substrate. As described previously, the detector was moved linearly in the direction parallel to the substrate surface normal at a 24.6” distance (Figure 32). The detector movement of a maximum of 2” compared with the 24.6 distance satisfies the condition of small angle approximation (\(\sin \theta = 0\)). This small angle approximation is the basis for intensity-angle relationship measurement. However, the ideal situation is to position the detector at the sample surface and rotate it with the substrate as the center. If this scenario can be realized, the x-ray cutoff at higher angles will not occur. With the current setup, x-ray cutoff problem can be relieved for certain extent as shown in the comparison in Figure 46 (reducing the spacing and moving the cut off range to a higher angle for example), but cannot be completely solved unless rotational capability was introduced.

![Graph showing counts vs take-off angle for different apertures](image)

**Figure 46: Aperture plates with different aperture sizes exhibited different ranges of x-ray measurement window.**

The impact of the size of the aperture was also further investigated with the developed system to confirm the understanding from preliminary testings. Although
smaller aperture provides better blocking of “environment x-rays” that comes from sources other than the sample surface such as chamber wall, shutter and sample sample holder, it significantly cut the x-ray flux as well. By scaling up to the next size available, the intensity was significantly increased. Higher flux allow the usage of lower emission current thus reduce the potential impact on the growth process.

5.2.4 RHEED electron energy

The energies of RHEED electrons determine types of the characteristic X-rays excited. Because of the inevitable heat loss and other forms of energy loss during the scattering process, electrons with certain energy may not excite the X-rays of the same energy level. Electrons with a higher energy are necessary for the successful excitation of characteristic X-rays.

Germanium substrate was used during the preliminary characterization of the system. Shown in Figure 47 was the variation of Ge x-ray intensity with the increase of RHEED electron beam energy. The measurement started with electron beam energy of 12.5keV and different thresholds for different x-rays were observed. Before reaching the energy of 12.6keV, no significant signal from the Ge K lines can be observed; at around 12.6 keV, Kα line (9.89keV) was excited; at close to 13keV, Kβ (10.98keV) line was observed. The necessary RHEED energy required for Ge Kα line to be excited is about 1.27 times the energy of the x-ray itself, and for Ge Kβ line, this factor is 1.18.
Figure 47: Electron energy of the RHEED beam impacts the intensity of the excited x-rays. By varying only the kinetic energy of RHEED electrons, intensity of Ge K lines (Kα and Kβ) from a Ge substrate changes accordingly. When RHEED energy is lower than their K line energy, no x-rays can be excited.

Generally, the process of the excitation of a characteristic x-ray photon involves the ionization of the atom by removing the inner electron. In order to ionize the atom, the energy of the incident electron must exceed a critical excitation energy $E_c$. This critical energy varies approximately as a function of atomic number squared ($Z^2$) \(^{62}\). With these in mind, for element identification purposes, the incident electron energy used need to be sufficient and higher than $E_c$ in order to excite the x-ray of interest.

It is worth to point out that, at the same RHEED electron energies, Ge Kα line intensity is higher than Kβ line intensity. This is commonly the case for characteristic x-ray emissions \(^{63}\). If x-ray intensity is of high priority in a compositional analysis, it is recommended that Kα to be used because of its higher intensity. When peaks from
different elements but with similar energies overlaps, Kβ peak can be useful in helping to identify elements and be used as an alternative for composition analysis.

The energy of RHEED electron usually ranges from 8 to 20 keV for MBE systems; it also can be employed at electron energies as high as 50 to 100 keV. Operation in the range of 10keV to 20keV is optimal for electron diffraction. The RHEED system in the Interface Laboratory can provide an electron beam with energies up to 15keV. 12.5 keV is used for regular diffraction purposes and most RHEED-TRAXS system characterization studies. 12.5keV can excite all the elements involved in this work include Mg, Ba and Fe except that for Ba, only L lines can be excited. In order to improve the signal-to-noise ratio of Ba L lines, 13keV was used instead for growth mechanism studies. If necessary, the impact of the electron energy on the intensity of the x-rays can be calibrated with the element of interest and the linear trend can be used to convert the intensity at one energy level to another.

5.2.5 Impact of RHEED beam current

The RHEED heating current is the current applied to the filament that excites the electrons. The strength of this current determines the number of electrons excited. A greater heating current means more electrons in the e-beam and equivalently higher intensity of the X-rays excited. Since the intensity of the X-rays is the very fundamental factor that determines the setting of X-ray detection, it is important that the correlation between the current and the X-ray intensity be studied for quantitative analysis.

Different from heating current, another important factor in RHEED electron adjustment is beam emission current, which is a measure of the intensity of the
electron beam generated from the electron gun. Ideally, beam current is supposed to be constant during the operation when other parameters are fixed.

Data from Figure 48 was taken with both SiC substrate and a piece of Cu foil mounted in parallel on the sample holder. By varying only the emission current of RHEED electron beam, intensity of the Si K\(\alpha\) line (Red) and Cu K\(\alpha\) line (green) from a Si/Cu sample varied accordingly. The ratio of Cu/Si (blue), however, exhibited a lower slope over the range of 8-20 \(\mu\)A.

![Graph](image)

**Figure 48: Effect of RHEED emission current on absolute X-ray intensity and relative intensity ratio of x-rays with different energy.**

The sample stage was rotated to an angle such that the RHEED beam covered both samples over its path. As a result, both Cu characteristic x-ray and Si x-ray was observed. Then, with a constant RHEED gun energy, the emission current was adjusted in a range of 0-25 \(\mu\)A for data collection. X-ray spectrum at each tested emission current point was acquired for the same amount of time. Change in the
emission current of the electron beam determines the intensity of the characteristic x-rays, but the ratio of Cu/Si is relatively constant regardless of the change in emission current.

Once the relationship between the RHEED electron beam emission current and the excited characteristic x-ray intensity was established, it can be used to normalize the absolute intensity of spectra taken under different electron currents. In the RHEED-TRAXS system studied this work, emission current was varied between 3µA to 7µA for different applications. If the comparison between the absolute intensities of certain elements taken under different emission current is necessary, this linear slope shown in the plot can be used as a reference for the conversion.

The observation shown in Figure 48 suggested an emission current dependence of the relative intensity ratio. The reason for this is unclear. It could be due to several factors. First of all, at low emission current, copper peak has a lower count in peak intensity that results in lower signal/noise ratio. The peak intensity is more impacted by the noise as a result, will introduce fluctuation into the intensity ratio. Second, size of the electron beam is impacted by the emission current. The higher the emission current, the narrower the electron beam diameter. A lower emission current produces wider electron beams. Since the Si and Cu samples were mounted in parallel, it could be that when the beam size expanded with the decrease of emission current, proportion of electron beam on each sample was varied as well. To improve the understanding of the emission current impact on the intensity, it is recommended to use an alloy-like sample where all the elements are evenly distributed in the sample surface.
As previously mentioned, the emission currents used in this study varied according to different applications. During growth process such as pure metal deposition and Si x-ray critical angle measurement, no oxygen is used. The chamber pressure under this condition is usually in the range of $2 \times 10^{-9}$ to $1 \times 10^{-8}$ Torr depending on the operation status and temperature of the effusion cells. However, during oxide growth, oxygen gas is flowed into the system and the pressure is maintained at $5 \times 10^{-6}$ Torr. The increase in chamber pressure requires corresponding increase in the RHEED electron gun heating current to achieve the emission current used under low pressure conditions (i.e. $2 \times 10^{-9}$ Torr range).

The heating current is the current supplied to the electron gun filament and it sets the temperature of the filament, which decides the maximum emission current. The emission current is the current of the energized electron beam that come off the tip of the filament. During operation of RHEED gun, heating current is adjusted to achieve the desired emission current. Normally before operating the RHEED, it is left at a heating current of around 1.3-1.4 Amps for warm up. During the warm up process, emission current will slowly increase until about 30 minutes later, a relatively stable emission current is reached and maintained. After the emission current is stabilized, RHEED electron energy is set to desired level (12.5-13keV) for data collection. However, some irregularity from unknown sources was observed during film deposition that caused observable fluctuations in the corresponding elemental x-ray intensity (Figure 49). Under this situation, it was found that by taking the ratio between the elements (such as Fe/Si shown in Figure 50), the impact from the systematic fluctuation could be avoided. As the ratio between elemental x-ray intensities can also be related to relative stoichiometry in the excited sample volume, elemental ratios were used for all the growth studies that followed.
Figure 49: Absolute intensity of Si and Fe tracked with RHEED-TRAXS during deposition suggesting fluctuation observed at around 106min.

Figure 50: The relative intensity ratio taken from the absolute intensity normalized the impact by system fluctuation.
5.2.6 Beam width impact control

The impact of the RHEED beam is not as obvious as that of the RHEED energy and current but is of importance to the accuracy of the measurement. As can be seen from the chart, the size of the beam focus size can expand from 70 µm to up to 5mm. When using the electron beam for RHEED-TRAXS measurement, expansion of the beam means increased radiated area and thus less consistency. RHEED electron gun has the option of tuning the beam focus using the Grid and Focus control. The RHEED electron beam needs to be regularly tuned in order to achieve the best focus.

Table 2: RHEED RH 15 system electron beam parameter ranges.

<table>
<thead>
<tr>
<th></th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam energy</td>
<td>1.0 keV</td>
<td>15 keV</td>
</tr>
<tr>
<td>Beam intensity</td>
<td>0.01 µA</td>
<td>30 µA</td>
</tr>
<tr>
<td>Focus position</td>
<td>50 mm</td>
<td>500 mm</td>
</tr>
<tr>
<td>Focus size</td>
<td>70 µm</td>
<td>5 mm</td>
</tr>
</tbody>
</table>

Electron beam cross section on the sample surface is also an important factor. Although with a wide beam, radiated area on the sample surface will increase, a fine-tuned focused beam does not only radiate an area matching the beam size. Due to the glancing incidence geometry, the elongated cross-section of the electron beam can all radiate the surface of a sample. As shown in Figure 51, the footprint of the electron
was revealed by an illuminated path on two GaN samples (common candidate as a LED material) loaded in parallel with a SiC sample in between (dark part). It can be predicted that the electron beam will also pass the SiC sample in a line shape although no visible illumination is produced.

![Image](image.jpg)

**Figure 51: Image taken showing the footprint of electron beam on a series of samples: GaN substrate at the side with a SiC substrate in the center.**

The area radiated by the electron beam depends on several geometric variables such as size of the sample, orientation of the sample with respect to the e-beam (larger area if the beam runs diagonally) and the incident angle of the electron beam which decides the cross-section of the beam. The size of the irradiated area in turn will determine the number of excited atoms and hence the intensity of the characteristic x-ray lines.

Among the factors that impact the size of the radiated area, size of the sample can be resolved by using a larger sample, which exceeds the size of the electron footprint in any dimension. In the system in Interface Engineering Laboratory, sample size of $1 \times 1 \text{cm}^2$ is sufficient for this purpose.
The impact of the sample orientation comes from the need for RHEED crystal structure real-time control during deposition. Before the start of film deposition, the sample needs to be rotated to align the electron incidence with the preferred crystal structure orientations. Substrate cut from the same wafer should have the same orientation. As long as samples can be mounted with the same orientation, this factor can be excluded. This will become an issue when the sample is not cut into regular shapes, as the difference in orientation and the resulting actual size of electron footprint on the sample will impact the intensity of the excited x-rays.

The incident angle of the Staib RH-15 RHEED electron gun used in the Interface Engineering Laboratory is fixed at an incident angle of 2°. With the growth position fixed, this geometry should yield a fixed cross section of the electron beam on the sample surface. However, for systems with variable glancing angle control, the incident angle of the electron should be controlled to be constant in order to achieve comparable result from run to run.

5.2.7 Acquisition time

Acquisition time refers to the total time each spectrum was collected for. The x-ray detector counts and display x-ray at a rate of ~1Hz and can output the data as real-time spectra per second (Delta Mode) or as an accumulated spectra (MCA mode). For elements that are low in intensity due to factors such as low concentration, low transmission through the detector window or high ionization energy, the spectrum can be collected for longer time to provide a pronounced peak and higher counts under the peak and improve the signal-to-noise ratio. Generally, to achieve the same signal-to-noise ratio, shorter acquisition can be used for detection of x-rays of higher flux, while longer acquisition time is necessary for x-rays of lower flux.
In general, the accuracy of the measurement will benefit from a longer acquisition time. This is especially useful when elements with characteristic x-ray lines of significantly lower intensities need to be measured. The deposition study of barium hexaferrite using RHEED-TRAXS in the Interface Engineering Laboratory is a practical case where Fe Kα line and Ba Lα line were used for chemical analysis. The energy of Ba Kα line x-ray is 32.19keV. This requires electron guns with energy much higher than 32.19keV to excite the K line x-rays of the Ba atoms. However, an electron beam source of this much energy was not easily available. An alternative is to use the lower energy L line x-rays (4.47keV) for chemical analysis. The excitation of L line x-rays acquires a greater electron kinetic energy to ionize the atom, this result in lower intensity in the emitted characteristic x-rays.

The increase in control factors including the RHEED electron energy, emission current and the acquisition time will all impact the intensity of an x-ray spectrum. A set of experiments with RHEED electrons varying between 13keV and 15keV, emission current varying between 3.0 µA and 6.0 µA at acquisition time of 15s, 30s and 45s were conducted to compare the impact of these factors on the x-ray intensity. The sample used for all these measurements has a stoichiometry of Fe/Ba ratio equals 3.28. It was expected that, if sufficient signal-to-noise was achieved in the all the spectra for both Fe K line and Ba L line peaks, the Fe/Ba ratio from any of these combinations should be identical. And the purpose of the test was to find out what combination of the three control factors can meet this expectation (Figure 52).
Figure 52: Emission current, accelerating voltage and acquisition time combinations were tested to compare the consistency between different settings.

It was observed that when the 13keV energy and the 3.0 µA emission current were used, the excited Ba x-ray intensity was low which was more susceptible to noise and thus introduced fluctuations to the measurement. As the acquisition time increased from 15s to 45s, this fluctuation was counteracted by the longer acquisition time so the Fe/Ba was closer to the average (1.18) among all the data collected. When the emission current was increased to 6.0 µA, acquisition time does not impact the Fe/Ba as much, and is comparable to the data acquired at higher emission current and higher energy. According to the data, the ratios acquired at both 13keV/6.0 µA and 15keV/6.0µA settings were close, suggesting that 13keV is sufficient for achieving an accurate result. Hence, 6 µA emission current with 13keV electron beam energy with 15s acquisition time were employed as the operation conditions during real-time growth mechanism study.

5.3 Relative intensity study with Fe deposition on 6H-SiC

The primary purpose of developing RHEED-TRAXS in the Interface Engineering Laboratory is to establish an effective method for monitoring the surface
chemistry of complex oxides during growth in real-time. Before getting into the multi-element deposition process, deposition of single elements was attempted to prove this real-time ability.

Among all the elements used in this MBE system, Mg, Ba, Fe and Ti are the metal sources available for the study. Fe was the best element to study with because of several factors. First of all, the K\(\alpha\) line of Fe is 6.4keV, which does not interfere with the characteristic x-ray lines of other elements. Second of all, the intensity of Fe peak is relatively higher than the intensity of Ba and Ti peaks, and unlike Mg K\(\alpha\) line, its intensity is not impacted by the attenuation through detector elements. Besides, the Fe and SiC have different RHEED images. Hence, RHEED can be used in conjunction to enable the structural monitoring during the real-time tracking.

As can be observed (Figure 53), after Fe was deposited for 35s, the RHEED pattern slowly transitioned into a pattern that was later confirmed to be structure of the deposited Fe layer. Meanwhile, the peak intensity of the Fe slowly increased with the deposition time as more Fe atoms are deposited onto the SiC surface. Si x-ray signal, which came from the underlying SiC substrate, decreased with the increase of Fe. This process continued through the end of the deposition (around 1800s).
Figure 53: RHEED images of Fe deposited film observed during the deposition process.

Figure 54: Spectra captured at different times during Fe deposition onto 6H-SiC substrate.
The characteristic x-ray intensity measured from the spectra was plotted in accordance with the deposition time in Figure 55. Decreasing Si x-ray intensity and increasing Fe Kα line intensity suggests the building up of Fe layer above the substrate surface and the attenuation of substrate x-ray through the Fe overlayer. As described previously (section on X-ray escape depth, 2.3.3), attenuation of the substrate x-rays is a function of the energy and the material properties. At the given small angles under the RHEED-TRAXS geometry, the attenuation length also depends on the direction of x-ray propagation in the material. With the increasing Fe layer thickness during deposition, substrate Si x-ray need to propagate through the Fe layer before escaping into the vacuum and the x-ray detector. As a result, intensity of the detected Si x-ray gets lower when the Fe film grows thicker. When the Fe layer grows thicker than the escape depth of the Si substrate under the situation, no more x-ray can be detected. This happened at the end of the growth when the Fe film was thick enough to attenuate all the signals coming from the substrate.

During the deposition and data collection, the RHEED parameters were kept constant. Any shifting in the parameters below controllable levels that could impact the peak intensity and thus introduce error., should impact all peaks in the spectrum equally. With this consideration, the relative intensities were taken as an attempt to normalize any systematic fluctuation (Figure 56).
Figure 55: Absolute x-ray intensity changes during the deposition of Fe onto SiC substrate tracked by RHEED-TRAXS.

Figure 56: Relative ratios taken between Si and Fe x-ray intensity, and Fe Ka and Kβ peak intensity.
The ratio of the intensity of the Fe Kα x-ray to the intensity of the Si Kα x-ray in Figure 56 reduces the scattering of Figure 55, which suggests that the original fluctuation in the intensity data can indeed be attributed to systematic fluctuations. The Fe/Si trend is linear in the first 1000 seconds of deposition. The intensity of both Fe Kα and Kβ x-ray peak intensity are compared as a ratio (shown in green squares). As both Fe Kα and Fe Kβ both come from the same atoms, one would expect their ratio to be constant. The fluctuation in this ratio is about ± 0.5 from the medium of 5.5, suggesting an approximate error for the accuracy of chemical ratio data.

The study of Fe deposition on SiC substrates confirmed the effectiveness of normalizing the x-ray intensity by using relative intensities to help reduce the systematic impact from the RHEED parameters. It also has the potential to provide composition information if the ratios can be related to composition in the excited sample volume. If more than one element are deposited at the same time, the specific number of atoms for each of them could be reflected from the relative intensity of their characteristic x-rays. To make this relative intensity useful, initial calibration can be performed using established techniques with the similar sampling volume. However, with single element deposition, this calibration for composition is not feasible since only the metal atoms (in this case, Fe atoms) are on the surface.

5.4 Thickness approximation using RHEED-TRAXS

Due to its simplicity in elements and stoichiometry, MgO film deposition was used as a model material system for RHEED-TRAXS development in oxide growth environment to investigate its potential in assisting the deposition of oxides. A perspective in using Snell’s law in conjunction with the total external x-ray reflection was developed for heterogeneous film deposition in this study. It was learned from
the deposition of single element Fe on 6H-SiC substrate that, substrate signal attenuation could be tracked using RHEED-TRAXS. Given the energy of the x-ray and the properties of the material, if the optical path of the excited x-ray in the material can be tracked, the attenuation can lead to the total propagation path length in the material. Based on the following results, it is possible that if an effective and consistent geometry can be established, the substrate x-ray signal attenuation measured using RHEED-TRAXS can be used for real-time thickness analysis.

It will also be shown in this section that by positioning the detector at the substrate element x-ray critical angle, consistent measurement of characteristic x-ray intensity from the deposited elements can be acquired and related to the thickness of the film. Intensity increase of the elemental x-ray signal from the deposited film was observed to be proportional to the thickness of the film. If the intensity-thickness relationship can be related to the atoms in the film, in other words, if the intensity can be related directly to the absolute number of atoms excited, it might be used for thickness approximation of films with more complex structure and stoichiometry.

### 5.4.1 X-ray attenuation measured by RHEED-TRAXS

Intensity of x-rays gets attenuated during propagation in materials as explained in section 2.3.3. This attenuation process depends on the wavelength of the x-ray and the refractive index of the material. If the percentage of attenuation is known, total length of propagation can be approximated based on these two factors using Equation 9. In the situation of using RHEED-TRAXS to measure the electron induced x-rays, such attenuation happens when x-rays excited from the substrate material travel through the deposited layers. With RHEED-TRAXS, the percentage of
attenuation can be measured by comparing the decreased signal intensity $\bar{I}$ after deposition, to the substrate x-ray signal intensity $I_0$ before film is deposited\textsuperscript{28}.

$$\frac{\bar{I}}{I_0} = e^{-\mu l} = e^{-\alpha l} \quad (9)$$

The ratio of $\bar{I}/I_0$ is the amount of x-ray transmitted. The difference between $\bar{I}/I_0$ and one is the percentage of the x-ray attenuated. Given the energy of the x-ray and the physical properties of the material, $\bar{I}/I_0$ has an exponential relationship with the distance the x-ray travelled and the linear attenuation coefficient $\alpha$. Coefficient $\alpha$ is a material property that comes from the product of mass density $\rho$ and absorption coefficient $\mu$ (Eq. 9). $l$ in the equation is the distance of x-ray propagation.

### 5.4.2 Refraction in MgO//SiC heterostructures

When x-ray travels across the interfaces between the film and vacuum or the interfaces between different films in layered structures, refraction will occur and change the direction of the propagation. For x-rays, the refractive index in solid materials is slightly less than that in the vacuum and can be expressed in Eq.10. $\delta$ and $\beta$ are constants determined by the wavelength of the x-ray and they are both on the order of $<10^{-4}$\textsuperscript{[7]}. In solid films, imaginary term $\beta$ can be ignored which gives the final form of Equation 9.

$$n(\omega) = 1 - \delta + i\beta \approx 1 - \delta \quad (10)$$

Due to the less than unity refractive index, total external reflection can happen during the refraction of x-rays where critical angles on the vacuum side of the refraction interface can be observed. As in this case, vacuum is the more “dense” medium, all the x-rays will be refracted to angles greater than the critical angle $\theta_c$. Between the critical angle and the surface plane, no refracted x-ray will be observed.
\[ \theta_{\text{crit}} = \frac{1.65}{E} \sqrt{\frac{A}{Z}} \rho = \sqrt{2\delta} \]  
\[ (11) \]

where: \( \rho = \text{Density of the material (g/cm}^3\)\)

\( Z = \text{Atomic number} \)

\( A = \text{Atomic mass (g/mol)} \)

\( E = \text{Energy of x-ray (keV)} \)

\( \delta = \text{real part of refractive index} \)

**Table 3: Calculated critical angle of specific X-rays in different material systems.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Atomic Weight (g/mol)</th>
<th>Line Type</th>
<th>Characteristic Energy (keV)</th>
<th>Critical Angle in different Media (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>12</td>
<td>24.3</td>
<td>K(\alpha)</td>
<td>1.25</td>
<td>1.36</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>28.1</td>
<td>K(\alpha)</td>
<td>1.74</td>
<td>1.27, 1.54, 1.20</td>
</tr>
<tr>
<td>Ba</td>
<td>56</td>
<td>137.3</td>
<td>L(\alpha)</td>
<td>4.47</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>55.8</td>
<td>K(\alpha)</td>
<td>6.40</td>
<td>0.41</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>16.0</td>
<td>K(\alpha)</td>
<td>0.53</td>
<td>4.20, 3.98</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>12.0</td>
<td>K(\alpha)</td>
<td>0.28</td>
<td>7.83, 7.42</td>
</tr>
</tbody>
</table>

Using this equation, critical angles of the relevant situations in this work has been tabulated in Table. According to the different line types of various elements, their critical angles in different materials are listed in bright yellow.
5.4.3 Thickness approximation in MgO//SiC heterostructures

The x-rays from the substrate experience two refractions when propagating in the layered structure shown in Figure 57. The first is at the substrate/film interface, due to the slight difference in refractive indices of the two different material; the second at the film/vacuum interface due to the difference in refractive index between the film and vacuum.

![Diagram of x-ray refractions](image)

**Figure 57**: X-ray refractions at substrate/film interface and film/vacuum interface. Incident angle is defined as the angle between surface plane and the incident x-ray beam. Propagation distance is defined as l. Angles are not to scale.

Figure 57 described the geometry of total external refraction at a film/vacuum interface. The exiting angle of the x-rays on the vacuum side is defined as the take-off angle. According to Snell’s law, given the take-off angle, incident angle at the material side in each layer can be approximated (Eq. 12). \( n_{vac} \) is the refractive index in vacuum and is integer. \( \theta_{vac} \) and \( \theta_{film} \) are shown in Figure 57. \( 1-\sigma_1 \) is the refractive index of the x-ray in the film.

\[
\frac{\sin(90^\circ - \theta_{film})}{n_{vac}} = \frac{\sin(90^\circ - \theta_{vac})}{1-\sigma_1} \tag{12}
\]

The total distance \( l \) that the substrate x-ray travelled for in the film can be calculated based on the attenuation of the substrate signal and the geometry shown in
Figure 57. Assuming near-critical-angle detection on the vacuum side, the incident angle on the film side can be approximated using Snell’s law and the thickness of the layer follows the trigonometric functions and can be approximated as \( l \times \sin \theta \). Combining Snell’s law and equation for x-ray attenuation, Equation 13 can be used to approximate the thickness of the deposited film can be approximated with measured substrate x-ray attenuation in RHEED-TRAXS in real-time.

\[
\text{Thickness} \cong \frac{\ln \left( \frac{\text{Sub}_{\text{after}}}{\text{Sub}_{\text{before}}} \right)}{-\alpha_{1st}} \cdot \sin \left[ \cos^{-1} \left( \frac{\cos \theta_{\text{vac}}}{1-\delta_{1st}} \cdot n_{\text{vac}} \right) \right] \quad (13)
\]

where: \( \alpha_{1st} \) = linear attenuation coefficient (cm\(^{-1}\))

\( n_{\text{vac}} \) = refractive index of vacuum

In Equation 13, the calculation for thickness evolved from the basic equation \( l \times \sin \theta \) where \( l \) is the total distance travelled, and \( \theta \) is the incident angle of the substrate x-ray at the film side. Based on Equation 12, first term of Equation 13 \( \frac{\ln \left( \frac{\text{Sub}_{\text{after}}}{\text{Sub}_{\text{before}}} \right)}{-\alpha_{1st}} \) is \( l \). And \( \cos^{-1} \left( \frac{\cos \theta_{\text{vac}}}{1-\delta_{1st}} \cdot n_{\text{vac}} \right) \) is the calculation for the incident angle of substrate x-ray on the film side.

MgO film deposition on SiC substrates was used to test the validity of this thickness approximation. Based on several samples grown and monitored with x-ray detector positioned at the Si Ka line critical angle, Si intensity before and after the MgO films were deposited was measured for each of the samples using RHEED-TRAXS. The calculated thicknesses were then compared with the thickness measured from XPS using Si 2p3 photoelectron peak, and the comparison is shown in (Figure 59).

Effective Attenuation Length database was used to approximate the film thickness from XPS measurement. Attenuation of Si 2p3 photoelectron excited from
the substrate SiC is used to approximate the thickness of the overlayer thickness. Measurement of the thickness using Si 2p3 photoelectrons has ±10% error. The basic model based on Snell’s law and x-ray refraction was shown in the red curve (Figure 58). This model was modified by varying the take off angle θ\textsubscript{vac} in Figure 57 according to the detection spatial resolution to better fit the XPS data (shown in green).

Disparity can be observed for thickness around 35 to 50 Å of thickness (as much as 30% difference at ~52 Å). Since this is a comparison between the thickness based on XPS signals and thickness approximated with electron induced x-ray, error from both ends could contribute to this disparity, although the fluctuation in RHEED-TRAXS data may play a bigger role. Angular resolution of the detector aperture, changes in refractive index after MgO film deposition, non-line-of-sight detection of x-rays are all possible contributors to the deviation.

One of the tuning factors of the RHEED-TRAXS thickness model is the resolution of the x-ray detector setup. Attenuation was measured by comparing the Si x-ray intensity before and after the MgO deposition at the Si critical angle. The model shown in Equation 13 was based on the law assuming x-rays all come in parallel. However, when the x-rays are excited, they can travel in all directions (Figure 8). In this case, as the detector was protected with a beryllium foil supported by an aluminum plate with an aperture in the center, the resolution depends on the size of the aperture. In this work, an aperture size of 0.013” was used and this corresponded to an angular resolution of 0.04°. When measuring the critical angles of substrate x-ray Si Kα line, the detector was moved at an angular step of 0.06°. As a result, when measuring the angle dependence of the substrate x-ray, not the continuous angular range was covered. Some gaps were left out because of the difference in the angular
resolution and the steps of the linear movement. The relative comparison between the size of the aperture opening and the manipulator angular-step-resolution impacts the effectiveness in angular positioning of the detector and as a result needed to be considered into error analysis of the measured intensity.

**Figure 58:** Thicknesses approximated by Si 2p3 photoelectron attenuation compared with thicknesses approximated using RHEED-TRAXS substrate x-ray attenuation.

Two cases of incident θ were considered as references in the model shown in Figure 58, the “model” is the calculation based on the calculated incident angle, the “modified model” is the sum of the calculated incident angle plus half of the aperture size. The result from Equation 13 is sensitive to any variation in the take-off angle. For example, the take-off angles used for the model and the modified model are 0.734° and 0.802° respectively (calculated using Equation 12), the corresponding thickness may be different by ~10%. Besides, the fact that the detector is not line-of-
sight with the sample surface may also vary the composition of the incoming x-ray. To achieve a precise measurement, line-of-sight detector positioning are highly desired; continuous x-ray detection along the angular range will be optimum to map the intensity distribution of substrate x-rays.

Another factor that was considered to refine this model or take into account for the error analysis was the modified incident angle based on an extra refraction step. As the subject of comparison, the Si Kα line come from the substrate SiC, it needed to be noted that when no MgO was deposited, the exit angle of the Si x-ray can be approximated with Equation 12. However, after the MgO was deposited, Si x-rays excited from the substrate will propagate through the MgO film and change its direction at the MgO/vacuum interface. Since the refractive index for Si Kα line in SiC is less than that in MgO, Si Kα x-ray will experience total external reflection at the MgO side. This meant that at the MgO film near the MgO/SiC interface, no x-rays will be observed at below certain angle.

Moreover, calculations of critical angles of Si Kα x-ray in SiC substrate and MgO film respectively were 0.97° and 1.21°. As detector was positioned at the Si critical angle each time before the MgO deposition, after the deposition, the detection angle was relatively shifted to lower angles compared with the new Si critical angle. This could also contribute to the errors in using this model for the thickness approximation.

To improve the accuracy of the thickness approximation, the x-ray detection geometry needs to be improved, and a methodology to compensate the shifting of the substrate x-ray take-off is needed.
5.4.4 Intensity calibration based on film thickness

Elemental x-ray intensity during the film deposition can be followed using RHEED-TRAXS in real-time. With more atoms deposited onto film surface, RHEED-TRAXS can detect a corresponding increase in the x-ray intensity of these atoms. This increase in intensity could be related to the thickness of growing films if effective measurement strategies were available. Detection of the elemental x-rays at the substrate critical angle was shown in this work to be a viable approach for this purpose.

After MgO film was deposited onto SiC substrates, Mg x-ray intensity can be measured with the detector positioned at the critical angle of Si Kα line x-ray. Mg Kα line intensities measured from several MgO films of different thicknesses. The intensity of the Mg x-ray is proportional to the Mg layer thickness as indicated in Figure 59 suggesting that with a repeatable take-off angle for x-ray measurement, x-ray intensity gain of the deposited element can be directly related to the film thickness. Similar results were also obtained with the deposition of Ba onto MgO surfaces. However, data from several measurements were also taken at random angles showed random scatter and non-comparable results. This confirmed the conclusion that detection geometry calibration with the Si critical angle is key to consistent result and was proved to be an effective way to make the RHEED-TRAXS signals useful.

In addition, intensity of the Mg x-ray is proportional to the Mg layer thickness as indicated in Figure 60, which suggests that the film thickness has not yet exceeded the sampling depth of the RHEED-TRAXS sampling depth. If the sampling depth has been reached, a plateau of Mg intensity should be expected.
Figure 59: Absolute intensity of Mg K line from different samples grown for different thickness shown to increase linearly with the increasing thickness in the range of 20 to 80Å.

Another set of experiments with Ba deposition on SiC substrates were followed by RHEED-TRAXS at Si K critical angle. Increase in the Ba x-ray peak intensity is similar to the observation with MgO deposition. This further confirmed the consistency in RHEED-TRAXS measurement at the Si critical angle (Figure 60).

Higher intensity in the Ba Lα line peak corresponds to a greater thickness of deposited Ba film. This trend appears to be linear over the 5 to 40Å range. This linear pattern is followed by data from different runs, all of which are based on system calibration using Si Kα line critical angle, this suggests that with Si critical angle calibrated system geometry, data acquired at different runs can be directly compared.
Figure 60: Ba were deposited to MgO template layer at 40°C substrate temperature. The temperature of the Ba effusion cell was kept the same as that during BaM deposition (525°C). Ba x-ray was collected at different deposition times with RHEED-TRAXS, and the corresponding Ba film thickness was measured using in-situ XPS.

5.3.5 MgO initial growth stage tracked with RHEED-TRAXS

Mg Kα line x-ray intensity during MgO depositions were followed with x-ray detector positioned at Si Kα line critical angle. Figure 61 (a) are data collected during a 20min MgO deposition (approximately 20nm in thickness) at 2 minutes intervals. After every two minutes, growth was stopped by the shutter in front of the substrate to collect x-ray signal. Mg intensity was observed to be increasing with time. This suggested the increasing amount of Mg atoms deposited on the substrate. RHEED pattern also suggested the transition from SiC to MgO (110) crystal structure. A growth rate change at the first 4 minutes was observed, and RHEED also indicated a transition process. This might suggest a change in the growth mode of the MgO film. Separate short growth experiments were carried out focusing on the first four minutes of MgO growth (Figure 61 (b)). Regardless of the low intensity of Mg signal due to dominant Auger effect and the attenuation through beryllium foil attenuation,
RHEED-TRAXS was sensitive enough to pick up the Mg signal at the initial phase of MgO deposition when approximately only two monolayers (~5Å) of MgO was deposited.

Figure 61: Mg intensity tracked during (a) 20 minutes and (b) 4 minutes of MgO deposition onto SiC substrate.

With this more tightly monitored growth, which was stopped every 30s for RHEED-TRAXS signal acquisition, a more detailed initial deposition process can be observed. During the first 1 min of deposition, increase of the intensity was slower, indicating a slower growth rate. After 1min, growth rate increased sharply. This again slowed down after 2minutes of deposition and the rate slowly picked up after 3 minutes. The overall trend of this four-minute study was consistent with the trend observed for the first 4 minutes at the 20min growth. It is possible that between 2-3 minutes, although the total number of Mg is not changing significantly, the film is going through certain transition process.

Another set of experiments were done where five samples were grown each at a different periods of time and their thicknesses were measured with XPS. A transition phase between 60s and 90s can also be observed where the growth rate
decreased before a sharp increase between 90s and 120s (Figure 61). Although this plateau is similar to the trend observed in RHEED-TRAXS, the time period where the transition took place is slightly different. However, it was observed with RHEED-TRAXS measurement that, when the growth was interrupted for RHEED-TRAXS data acquisition, overall growth rate slows down as well. The mechanism behind this is not clear yet, but it explains why it took longer in the experiment shown in Figure 62 to reach the transition phase.

5.5 Process control during barium hexaferrite deposition

Barium hexaferrite (BaM) is a type of functional material that has a delicate balance of Ba and Fe and the oxidation state of Fe in a complex crystal structure that makes it ferri-magnetic. MBE processing of this material starts from a 6H-SiC substrate, a 10nm of MgO is then deposited as the template layer which is followed by the barium hexaferrite deposition. At about a minute after the BaM deposition starts, a RHEED pattern transition from MgO into what is typical of a spinel structure can be observed. Based on previous study, the corresponding XPS at this point also indicated a mixed oxidation states that resembles Fe$_3$O$_4$, which usually possesses a spinel structure $^{64}$. When the growth continues, the RHEED pattern again transit into what was later found out to be the BaM RHEED. Although through RHEED, it was determined that BaM has formed in the top few monolayers, the chemistry of the top 10 nm of the film at this point still shows a mixed oxidation state until the film is about 10nm thick. Only after the film thickness reaches above 10nm, when the Fe$^{3+}$ satellite peak, which is an indication of single Fe oxidation state, can be identified from XPS Fe 2p3 scans. This satellite peak becomes more pronounced at 20nm all the way to 200nm. With
these observations, it seemed that a transition layer of about 10nm thick in between the MgO and BaM film exists before the BaM structure was fully established. However, this result did not agree with the TEM findings where a spinel structure that is 20-30nm thick was observed.

Since XPS can only measure the chemistry of the top 10nm of a sample surface, and RHEED reflects the crystal structure of the top few monolayers of a growing film, it is possible that during deposition, reactions are not limited to the top 10nm of the growing BaM.

As RHEED-TRAXS can detect substrate x-ray at film thicknesses higher than 10nm when the detector is located at the Si critical angle, its sampling depth must be higher than XPS. As a result, RHEED-TRAXS was used to follow the BaM growth as an attempt to help explain the possible growth mechanism of the BaM.

5.5.1 Initial stage of BaM deposition

X-ray intensities of Mg Kα, Si Kα, Ba Lα and Fe Kα were tracked during the 20min deposition of BaM (Figure 62). From the peak intensity change of each element during the first 4 minutes of deposition, Mg and Si were observed to decrease in their respective x-ray intensity while Fe signal intensity increased corresponding to the expected increase in the number of atoms. Contradictory to expectations, absolute intensity of Ba Lα stayed relatively constant (standard deviation/average is 3.7%) during the first 4 minutes after the growth was initiated. It only started slowly picking up after about 5min.
Figure 62: Growth was interrupted at every time interval, each spectrum was collected for 30s, 3 spectra were collected for each time point for error bar.

Within the 20 minutes’ growth period, Ba x-ray intensity increased slower compared with that of the Fe intensity. This was not observed in a series of comparison experiments (Figure 63) where Ba deposition on to MgO template without oxygen environment was tracked with RHEED-TRAXS. Ba intensity was observed to show a steady increase with the increase in number of Ba atoms deposited to the sample surface, suggesting that the presence of Fe atoms, oxygen species and the elevated substrate temperature are the factors contributing to a different mechanism for Ba during BaM epitaxy.
Figure 63: Control experiment where Ba was deposited onto MgO film and monitored using RHEED-TRAXS set at Si critical angle.

Figure 64 shows the growth process of a BaM sample grown for 90min with RHEED-TRAXS data taken at a less dense rate (per 3min). Compared with previous study, where growth was stopped at everyone one minute, this growth exhibited similar trend of Ba intensity although slightly differences at the initial stage. The thickness of the grown film is 8 nm, and XPS suggest a mixed oxidation state of Fe, which suggest that this film is still at the spinel-BaM transition region.

As a 10nm thick MgO layer was deposited onto 6H-SiC as a template layer, before the deposition of BaM started, signals of only Si Kα peak and Mg Kα peak were observed in the spectra. After BaM deposition takes place, it is expected that as the amount of Ba and Fe atoms on the MgO surface increases respectively, intensity of the detected Ba and Fe characteristic x-rays will also increase accordingly. Meanwhile, x-rays excited from the MgO layer and the SiC substrate, i.e. Mg Kα and Si Kα lines will be attenuated through the deposited BaM layer, thus decrease in their intensity.
Figure 64: Growth stopped at every 2min intervals for RHEED-TRAXS data collection of 20s. Ba x-ray intensity increased during the first 4min (approx. 4.5 Å) then stayed relatively constant. Fe x-ray intensity showed a sharp increase during the first ~10-12min then slowed down.

From the elemental x-ray peak intensity change of each element during the first 6 minutes of deposition, Mg and Si were observed to decrease in their respective x-ray intensity while Fe and Ba signal intensity increased corresponding to the expected increase in the number of atoms. Contradictory to expectations, the increase of the absolute intensity of Ba Lα line x-ray slowed down after the first 6 minutes and appears to have plateaued. This unusual trend of the Ba atoms was not observed in a series of comparison experiments where Ba deposition on to MgO template without oxygen environment was tracked with RHEED-TRAXS (Figure 63). In these comparison experiments, Ba intensity was observed to show a steady increase with the increase in the number of Ba atoms deposited onto the sample surface, suggesting that the presence of Fe atoms, oxygen species and the elevated substrate temperature are the factors contributing to a different mechanism for Ba during BaM epitaxy.
As oxide systems are subject to electron fluctuations due to the non-conducting nature of the deposited oxide films and influenced by fluctuation in the RHEED electron beams, relative elemental x-ray intensities of Fe/Ba are used to normalize intensity fluctuations introduced by the system fluctuations (Figure 65). Although it is not yet known what sensitivity RHEED-TRAXS has with respect to each different element, Fe/Ba is expected to increase till they reach a saturated value representative of the BaM stoichiometry \((\text{BaFe}_{12}\text{O}_{19})\). As a result, it is expected that Fe/Ba in RHEED-TRAXS ratio will increase and reach a constant value. It was observed that, at the initial approximately 20 minutes of deposition (corresponds to a film thickness of \(~8-10\text{nm}\)), the slope of Fe/Ba is greater than the slope of after 20 min of growth, which could indicate two different growth modes that will be discussed later.

![Fe/Ba ratio graph](image)

**Figure 65**: Fe/Ba ratio of Figure 67. Transition of mechanism seems to happen during 15-24min.
It can be noticed that during the initial few minutes of the 20min growth, Ba intensity fluctuated during deposition with very slow increase (about 25% increase in intensity at the end of the growth). However, during the 90min growth, Ba intensity increased steadily during the first 6 minutes of deposition and then stayed relatively constant throughout the 90min deposition. The growth conditions of these two depositions are the same, except that the sampling is more frequent (every 1min) in the shorter growth compared with the longer growth (every 3min or more). It is possible that due to more interruptions in the first case, Ba incorporation into the film is much slower. Following this thought, growths with no interrupted growth were carried out and confirmed this possibility.

5.5.2 Extended BaM deposition in real-time

The deposition process of a ~20nm thick film was followed by RHEED-TRAXS (Figure 66). Based on the Fe/Ba ratio, two different growth modes are more pronounced which switched at around 20-30mins of the growth.

At the initial start of the growth, both Ba and Fe increased sharply. This increase gradually slowed down for Fe at around 20-30mins, and Ba intensity remained relatively constant around 10min. The Ba and Fe x-ray intensities continued to increase over the 200 minutes deposition process indicate that more Fe atoms are being added into the sampling depth of RHEED-TRAXS, suggesting a sampling depth of RHEED-TRAXS higher than the deposited film thickness. If sampling depth of TRAXS is greater than film thickness, Fe and Ba intensity will both increase; if the film thickness has exceeded the sampling depth, Fe and Ba intensity should stay relatively constant. In terms of the ratio of Fe/Ba, if the BaM formed is homogeneous and is thick enough (≥ sampling depth of RHEED-TRAXS), the technique only sees
the atoms on the top part within the sampling depth. As a result, after BaM has formed and its thickness reached the sampling depth, Ba, Fe intensity and Fe/Ba will all plateau. Before reaching the sampling depth of RHEED-TRAXS, the ratio will tend to slow down and eventually plateau (“saturate”) when film thickness equals the sampling depth.

Figure 66: 220min uninterrupted deposition (~20nm) were followed by RHEED-TRAXS at different time intervals.

Results in Figure 66 shows no plateau, which suggests two possible processes depending on the comparison between the film thickness and the sampling depth of RHEED-TRAXS. It can be observed that Fe x-ray intensity, Ba x-ray intensity and Fe/Ba are all showing an increasing trend towards the end of the deposition. Assuming that the sampling depths has not been reached, increase in Fe and Ba agrees with the assumption, while Fe/Ba increases suggests that the stable stoichiometry has not been reached yet, which means, the film is still in a mixed transition phase where BaM structure is only part of the whole thickness, a transition phase consisted of iron
oxides takes up the other part. Hence, RHEED-TRAXS is still looking at the transition phase formed before the formation of the BaM phase. If the sampling depth of RHEED-TRAXS has been reached, the intensity of Fe should slowly plateaus instead of keeping the upward mode. As a result, it is highly possible that the sampling depth is higher than the film thickness (approximated 20nm). The upper limit of RHEED-TRAXS would be the penetration depth of the RHEED electrons, which in this study is approximated to be 50nm for BaM films.

Previous study with BaM deposition reported a transition layer with a typical spinel structure forming between the hexagonal BaM phase and the MgO layer. In similar growth conditions with this study, a transition layer containing both Fe(II) and Fe(III) oxidation states were observed using RHEED and XPS and was determined to be approximately 10nm thick. However, cross-sectional TEM suggested that the spinel-structured transition layer spans over a thickness range of 20-30nm before finally turning into BaM unit cells. RHEED-TRAXS finding shown in Figure 67 suggested continuous increase in the amount of Fe and relatively low incorporation of Ba at the first few minutes, which in conjunction with the XPS study, confirms the formation of iron oxides during the first few nanometers of BaM deposition. In order to investigate the further growth of BaM into the 20-30nm regimes, growth of films thicker than 40-50nm needs to be carried out and investigated.

5.5.3 Plasma strength impact on growth mechanism

In oxide growth, oxygen source is a key component that plays an important role in determining the oxidation states of elements. By varying the plasma strength while keeping all the other factors the same, two experiments were followed by RHEED-TRAXS and the results are compared (Figure 67).
Ba and Fe increase of the growth under oxygen plasma with photomultiplier reading of 800mV is shown to be similar to the growth process with higher intensity plasma at 1500mV photomultiplier reading. This indicates no obvious impact of the plasma strength on the growth rate in terms of the number of atoms.

Meanwhile, when comparing the Fe/Ba ratio from these two growths, they also have very similar trend over the same time period (Figure 68). This suggests the possibility that the increase of plasma strength does not affect the growth rate of BaM and that the number of active atomic oxygen atoms did not impact the growth mechanism.
Figure 67: Absolute x-ray intensity gains are observed to be similar on both Fe (a) and Ba (b). Higher plasma strength (800mV) seems to show more fluctuation.
Figure 68: Fe/Ba ratios of two deposition processes under 800mV (orange) and 1500mV (green) plasma are very close regardless of the difference in number of active oxygen species.

5.5.4 Take-off angle impact on absolute and relative intensity

The idea of RHEED-TRAXS developed in literature is to detect x-ray intensity at total external reflection angles where the total x-ray intensity is the highest and more representative of the surface x-rays. However, critical angle varies based on the atomic number of the originating atom and the material properties of the medium. Besides, for heterogeneous deposition, critical angle of the deposited element cannot be measured prior to the deposition, which introduces complexity in determining the surface sensitivity of the technique. In this work, as the critical angle of Si x-ray that originated from the substrate material was measured and used for real-time measurement in order to achieve consistent measurement geometry, the sensitivity of the technique is believed to be compromised. Ba and Fe each has a critical angle much lower than that of Si, as a result, measurement made at the Si critical angle...
incorporated more signals from beneath the very surface. In another words, measurement made at Si critical angle can reflect the changes in the total number of Ba and Fe, but may not reflect the changes in the relative number of Fe and Ba at the very surface.

This raises concern of the legitimacy of the mechanism study shown previously using RHEED-TRAXS. And the following test was performed to find out if there is any significant change if the growth process was monitored at different critical angles. BaM deposition was carried out with regular conditions; RHEED-TRAXS data was collected at 2 minutes intervals, at three different angular locations. 1.16° was experimentally determined critical angle of Si Kα line; 0.52° was used as the lowest critical angle as it is close to the critical angles of Fe and Ba; 1.69° was the highest critical angles used which should represent more “bulk” x-rays (Figure 69 - 70).

![Ba intensity at different take off angle](image)

**Figure 69:** Ba intensity variation during the growth monitored at three different take-off angles.
As can be observed, the absolute intensity measured for both Fe and Ba share some similarities. First of all, data measured at the lowest critical angle turned out to be the lowest in intensity. Assuming 0.52° is closer to the critical angles of Ba and Fe, the intensities should be higher than those measured at higher angles according to the physics of total external reflection. Intensity measured at 1.16° and 1.69° are close in counts, which make sense because at off critical angle locations, detector is detecting signals from all the Fe or Ba atoms that was deposited (more bulk-like measurement). Second, the trend of two different phases can all be identified in the measurements taken all three angles. Sharp increases in the intensity can be observed between the start of the deposition and 4 minutes. After 4 minutes, growth rate significantly slows down, suggesting a different phase of growth.

Regardless of the differences in their absolute intensity at different angles, the relative intensity of Fe/Ba is shown to be quite close (Figure 71). Due to the low
intensity counts at 0.52° measurements, data point at this angle shows more scatter and fluctuation. However, the overall trend seemed to agree with the trend taken at higher angles. More studies need to be performed to explain the low intensity at 0.52°, however, the trend observed at different angles resemble each other did not invalidate the results of the growth mechanism studies carried out at the critical angle of Si.

![Fe/Ba at different take-off angles](image)

**Figure 71: Fe/Ba ratio at the three different take-off angles**

After the growth, Fe/Ba was measured over the take-off angle ranges of 0-3.5° (Figure 72). It can be observed that Fe/Ba reaches their maximum at ~0.6°. And 0.52° can be determined from the plot to be off the maxima of Fe/Ba ratio. If 0.52° is below the critical angles of Ba and Fe, measurement taken at this angle are expected to be lower in intensity. As a result, ideally, measurement should be taken at the Fe/Ba maxima angle, Si critical angle and a higher angle for comparison. However, the
Fe/Ba maxima angle cannot be accurately pre-determined before the deposition process.

![Fe/Ba over angle range](image)

**Figure 72:** Fe/Ba x-ray intensity ratio over the take-off angle range of 0-3.5°.

### 5.5.5 Ba cutoff test

It was consistently observed from tracking the BaM deposition process with RHEED-TRAXS that Ba intensity increases at the initial stage of deposition. The exact time length of the initial stage depends on the growth parameters and whether the growth was interrupted for x-ray data collection. After this stage, the increase in Ba slowed down, and the intensity kept relatively constant even for long growth. On the other hand, Fe x-ray intensity increased continuously throughout the entire deposition process (Figure 73).
Figure 73: Ba source was cut off at 90min of BaM deposition. RHEED-TRAXS signal showed a temporary drop in Ba intensity in response.

In this test, after the BaM deposition continued for 90 minutes, the shutter to the Ba effusion cell was closed, cutting off the source of Ba atoms. Fe source shutter remained open and the deposition of Fe under oxygen plasma environment was continued for another 40 minutes. Intensity of both Fe and Ba was tracked with RHEED-TRAXS at the critical angle of Si Kα line during the growth. Ratio of Fe/Ba was also plotted to show the relative changes.

At the beginning of the deposition, intensity of Ba did not start increasing until around 13 minutes of deposition. After 13 minutes of deposition, counts under the Ba Lα line peak fluctuated between 325 to 523. 7 minutes after the Ba shutter was closed, the intensity of Ba and Fe were measured again. It was found that Ba intensity fell out of the fluctuation range that it maintained previously, Fe continued to gain more intensity. Fe/Ba ratio was observed to pike due to the sudden decrease in Ba intensity. The drop in Ba after the cut off of Ba source was expected since the deposited Fe
atoms can bury the previously deposited Ba atoms and result in a decrease in Ba intensity. However, the Ba intensity did not continue decreasing as expected. Its intensity picked up again at 100 minutes and remained between 391 to 476. After the growth stopped, intensity of the Ba dropped again.

RHEED images taken during real-time suggested the forming of BaM (Figure 75). The XPS scans of Fe peak from the 90 minutes deposition suggested fully oxidized Fe atoms. XPS was also performed at the end of the 130 minutes deposition. XPS of the Fe peak for both samples showed single oxidation state (Figure 74). Overall composition of the final films confirmed the effect of Be cutoff (Table 4). Total thickness of the final film is about 4.5nm. It is still not clear why the intensity of Ba increased back up after the Ba source was blocked.

*Table 4: Composition of BaM films grown for 130 minutes (with Ba cutoff at 90 minutes) and for 90 minutes.*

<table>
<thead>
<tr>
<th></th>
<th>130min</th>
<th>90min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>Stoichiometry</td>
</tr>
<tr>
<td>O</td>
<td>65.0%</td>
<td>1.9</td>
</tr>
<tr>
<td>Fe</td>
<td>34.7%</td>
<td>1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>0.3%</td>
<td>NA</td>
</tr>
</tbody>
</table>
Figure 74: Comparison of Fe oxidation states in samples with (130min) and without (90min) impact from Ba cutoff.

Figure 75: RHEED suggest the MgO film transition into pattern typical of spinel structure.
5.6 Relative intensity for composition analysis

In quantitative x-ray analysis, the intensity of the excited x-rays depends on the number of atoms within the excited sample volume, thus can be related to the atomic composition within the excited volume. In RHEED-TRAXS setup, x-rays are excited by RHEED electrons and their intensity can be impacted by RHEED parameters, geometry factors as discussed previously, especially the take-off angles. With thorough characterization of the system, good understanding of the system can be acquired and these process parameters can be monitored and controlled. This ensures that the number of atoms in the excited sample volume is the primary factor directly impacting the x-ray intensity and therefore can be calculated using the intensity.

From the deposition of single element (Fe) onto the SiC substrate (section 5.2), it was learned that the relative intensity has the potential to represent the atomic composition if calibrated effectively. With the results from the MgO deposition onto SiC substrates, the geometry calibration approach with Si x-ray critical angle was shown to provide consistent results from independent experiments. Since the detector window absorbs oxygen, neither Fe nor MgO deposition is suitable for studying the relative intensity. BaM films has two metal elements at significantly different levels in terms of the atomic concentration (BaFe$_{12}$O$_{19}$), as a result, was suitable for relating the RHEED-TRAXS relative intensity with the film composition.

Fe/Ba ratio were acquired from the RHEED-TRAXS measurement at Si critical angles and compared against the composition measured using XPS (Figure 76). These films were deposited under various growth conditions (such as oxygen plasma strength, Fe effusion cell temperature, Ba effusion cell temperature and
substrate temperature) and for different period of time. As a result, they were not uniformly at the perfect BaM composition (Fe:Ba is 12:1) but were different from one another in both chemistry and thickness. It can be seen from Figure 76 that correlation between the composition and the RHEED-TRAXS relative intensity is weak. Scatter of the data can be observed over the Fe/Ba stoichiometry range from around 3.4 to 14. It can also be observed that, range of the Fe/Ba ratio in RHEED-TRAXS data ranges from 1.28 to around 3.5.

![Fe/Ba ratio: XPS vs. RHEED-TRAXS](image)

**Figure 76:** Fe/Ba ratios collected from RHEED-TRAXS measurements were compared with their composition measured using XPS.

The scatter of data could be due to several factors. First of all, and the most important of all, is that Ba is lower in intensity and thus is more subject to impact from noises. As discussed before, Ba Lα line peak was used for all the measurement. Ba L line requires a higher ionization energy and thus is lower in intensity. This give rise to another issue, which is the subtraction of background. Ideally, the difference in Fe and Ba intensity between the starting and the end of the deposition should be used and compared to represent the number of atoms in the deposited volume. However,
due to the low Ba intensity, this subtraction is not applicable because intensity from films grown for shorter times fluctuates so much that the intensity difference is too low or even negative in certain cases. The third factor is the non-line-of-sight detection of the x-rays. Ba and Fe signal from the chamber environment produces a background signal before the start of the deposition. Due to the limitation exerted by low Ba intensity, when the ratio was taken, the background signals had to be taken into account. When there is a relatively higher amount of Ba, although the background subtraction could be successful, the concern of different sampling depth of the RHEED-TRAXS and XPS need to be addressed.

Differences in the sampling depth of RHEED-TRAXS and XPS can also contribute to the low correlation. Compositions in Figure 76 measured using XPS were limited to the top 10nm of the sample surfaces. Sampling depth of RHEED-TRAXS, in comparison, is much higher as it can still “see” substrate Si signal through MgO films more than 10 nm thick. Thus the composition provided by XPS is only a fraction of the total sampling volume RHEED-TRAXS measured. To help understand the interface composition and the evolving process of the interface during film deposition, it’s important to identify the sampling depth of each technique and calibrate the relative intensity with the composition measured from a comparable technique.

Films with known thickness information were picked out of the data in Figure 76 above and compared separately (Figure 77). At thicknesses below 100 Å, TRAXS relative intensity appear to have a good correlation with the corresponding stoichiometry measured with XPS. Thickness of the third data point at about 230Å is approximated based on the growth rate. From the data points of 77Å to 230Å, the
increase in TRAXS Fe/Ba ratio appears to be less sensitive to the stoichiometry measured using XPS. Considering that XPS is always measuring the top 10 nm of the samples surface, the difference observed from the TRAXS ratio may come from the sampling depth difference. It is possible that, the RHEED-TRAXS ratio is an average of the Fe/Ba by atomic number throughout the total 23nm. The Fe/Ba ratio in the top 10nm need to be averaged with the Fe/Ba ratio in the rest of the 13nm of the deposited film. In this way, deviation from the stoichiometry measured in the top 10nm is introduced.

![Fe/Ba Ratio from XPS and TRAXS](image)

**Figure 77: Stoichiometry of samples measured using XPS and RHEED-TRAXS were compared and plotted with film thickness.**

In conclusion, to effectively calibrate the RHEED-TRAXS relative intensity to the stoichiometry of the sample, higher intensity in the elemental x-ray peaks are highly desirable. Longer acquisition time, higher RHEED electron beam energy and higher RHEED electron beam emission current are recommended to improve the intensity of elemental x-ray peaks for better calibration results. Line-of-sight design of the x-ray detection can also help reduce the background impact in the low intensity.
elemental peaks. If these conditions can be realized, increase in the elemental x-ray intensity can be used for calculating the relative intensity. Last but not least, preliminary calibration of RHEED-TRAXS should be done with techniques with comparable sampling depth. For this purpose, it is key to find a practical way to determine the sampling depth of RHEED-TRAXS.

5.7 Practical sensitivity at substrate x-ray critical angle

Sensitivity of RHEED-TRAXS is often discussed under the scenario where x-ray detection is carried out under the total critical angle $\theta_{\text{crit}}$ of the deposited elements. The reported sensitivities are all based on this measurement geometry. However, in practice, due to the transfer mechanism of MBE processing in UHV systems and complexity of the physics behind the critical angle involving a growing film, locating the critical angles of x-rays excited from the deposited elements before the initiation of the deposition is a complicated process that may introduce inconsistency and inaccuracy into the results.

In this work, the intensity of the substrate x-ray was used as a reference for most of the real-time measurement. The attenuation of the substrate x-ray due to the increasing thickness of the deposited overlayer film was used for thickness approximation of MgO films. As the thicknesses of most grown MgO films were controlled to be within 10nm for XPS analysis, Si Kα line x-ray intensity was observed throughout the deposition process.

In the study of BaM film depositions, MgO layers of about 10-20nm were deposited onto 6H-SiC substrates prior to the deposition of BaM films (Figure 78). As a result, Si x-ray intensity measured while depositing the BaM film experienced a
greater degree of attenuation, first through the MgO layer, then through the deposited BaM layer. The attenuation of Si x-ray is a sum of the attenuation in each layer of the multi-layer structure. When Si x-ray propagate through the MgO/BaM interface, before Si x-ray propagates into the BaM layer, its intensity is pre-determined by the thickness of the MgO layer. The thicker the MgO layer, the more attenuation will be exerted to the Si x-ray intensity. This scenario provides an opportunity to approximate the sampling depth of RHEED-TRAXS measurement in multi-layered structures conducted at substrate x-ray critical angle.

Figure 78: Heterostructure of BaM film deposited on MgO (111) film.

As can be seen from Figure 80 below, characteristic x-rays from Si, Mg, Ba and Fe in the BaM//MgO//SiC structure have observable different distributions of x-rays. Intensity of Fe increased sharply in the first 0.6°, whereas Si and Mg intensities reached their peak at around 1.9° and 2.4°, respectively. Ba intensity distribution is less defined, which could be attributed to its low atomic content in the sample surface and its low peak intensity relative to background. Theoretically, the critical angles for Ba and Fe in BaM are 0.5° and 0.4°, respectively. For Mg through BaM and Si through BaM, these numbers are 2.14° and 1.54°, respectively. A comparison between the theoretical critical angles and the measured angles are shown in Table 5. Both Fe and Mg critical angles shifted about 0.2° to higher angles, while Si critical angle shifted about 0.3-0.4° approximately. The greater shift in the Si suggests that
the Si x-ray experienced two refraction processes; one at the SiC/MgO interface, and the second one at MgO/BaM interface. This double refraction can change the geometry of the propagation path and thus alter the exit angle at the vacuum side. Surface roughness and surface structure are also factors that will impact the experimentally measured critical angles, which is beyond the scope of this work\textsuperscript{41}.

**Figure 79:** Angular distribution of characteristic x-rays excited from BaM//MgO//SiC heterostructure.

**Table 5:** Comparison of calculated and measured critical angles of Ba, Fe, Si and Mg in BaM films.

<table>
<thead>
<tr>
<th></th>
<th>Ba L(\alpha)</th>
<th>Fe K(\alpha)</th>
<th>Si K(\alpha)</th>
<th>Mg K(\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>0.5°</td>
<td>0.4°</td>
<td>1.54°</td>
<td>2.15°</td>
</tr>
<tr>
<td>Measured</td>
<td>NA</td>
<td>0.6°</td>
<td>1.9°</td>
<td>2.4°</td>
</tr>
</tbody>
</table>
The differences in the angular distribution and the dependence of the x-ray intensity with the corresponding take-off angle can be seen from Figure 82 above. This indicates that, at what angle to place the x-ray detector for x-ray collection will impact the corresponding x-ray intensities of different elements and consequently the relative intensity between elements. Determination of the substrate Si x-ray critical angle is practical during experiments and yields consistent result as described in previous sections. However, this means, the detector is placed away from the most surface sensitive angular regions of the heavier elements (in this case, Ba and Fe). In another word, the surface sensitivity of the measurement regarding these elements will be compromised.

On the other hand, detecting x-rays at Si x-ray critical angle also means more “bulk” instead of “surface” analysis. This is because Si Kα line has a much lower energy compared with that of Ba and Fe, and thus has critical angles further up from the surface plane. Instead of monitoring just the very surface (top few monolayers) of the growing surface, atomic composition of the top several nanometers are reflected in their relative x-ray intensities when detection are done at high critical angles. This turned out to be helpful in certain applications such as exploring the atomic dynamics during the BaM deposition. However, there was not a practical method to determine the effective sampling depth of the technique at this geometry. The experiment shown below will serve as an effective approach to solve the problem.

Intensities of the all the elements except oxygen were tracked during the growth of BaM film. RHEED images show the transition from a RHEED pattern typical of MgO (111) (3min) to the streaky features of BaM RHEED spinnel structure
The x-ray intensity of the deposited elements and substrate elements were tracked using RHEED-TRAXS and their changes were plotted in Figure 81.

Figure 80: RHEED image transition during the deposition of a 4.5nm thick BaM film on a 18nm thick MgO film.

Figure 81: Intensity variation tracked using RHEED-TRAXS during BaM deposition on MgO. Intensity variations of substrate signal Si Kα line x-rays, MgO layer signal Mg Kα x-ray and Ba, Fe x-rays were shown. Lines between data points are only to help guide the eye.
It can be observed from the Figure 81 that, intensity of both Mg and Si decreased with the increasing deposition time. As shown in Figure 81, intensity of Fe increased relatively rapidly during the first 15 minutes, and slowed down after 15 minutes. Ba intensity slowly picked up after about 5 minutes of growth, and increased significantly around 15 minutes, then fluctuated around the same intensity for the rest of the growth. These observations agreed well with the previously observed trend during BaM growths.

Meanwhile, intensity of both Mg and Si decreased with the increase in Fe and Ba atoms. The decrease in Mg and Si intensity can be understood as their intensities were attenuated through the deposited layers. The intensity of measured Si x-ray experienced a greater degree of attenuation, first through the MgO layer, then through the deposited BaM layer. The attenuation of Si x-ray is a sum of the attenuation in each layer of the multi-layer structure. The thicker the overlayer, the more attenuation will be exerted to the Si x-ray intensity. This scenario provides an opportunity to approximate the sampling depth of RHEED-TRAXS measurement in multi-layered structures conducted at substrate x-ray critical angle.

At the end of the deposition (130 minutes), the intensity of Si Kα line decreased to ~8% of the starting intensity. As discussed before in section 2.3.4, sensitivity of RHEED-TRAXS depends on both the x-ray escape depth and the electron penetration depth. In the material system discussed in this work, the electron penetration depth is within the top 50nm at 2° incidence. As electrons can penetrate 50nm into the surface and excite x-rays, it can be expected that the maximum probing depth of RHEED-TRAXS is 50nm. Although it was therefore expected that the electron penetration depth should be greater than the x-ray escape depth at the total
reflection critical angle, there is no direct evidence for this comparison. Given the fact that the MgO film and the BaM film were 18nm and 4.5nm in thicknesses respectively, it can be expected that RHEED electrons penetrated through both the MgO layer and the BaM layer and excited the Si characteristic x-rays in the SiC substrate. The observation of the attenuated Si intensity is an indication of that, in this measurement geometry, sensitivity of RHEED-TRAXS was approximately the sum of both layers, which is around 22-23nm and confirmed the thought that at higher take-off angles, the measurement is less surface sensitive.

Using the thickness of the MgO layer to probe the sampling depth of RHEED-TRAXS is an effective approach for the material systems used in the Interface Engineering Laboratory. However, the determination method of the RHEED-TRAXS sampling depth is not limited to tuning the thickness of the MgO.

In this work, thickness of the MgO layer was approximated with the growth rate of MgO film in the first 8-10 nm. Although it is also possible to approximate the growth rate of the BaM and predict the sampling depth with BaM, there are some advantages of using MgO for this purpose. First of all, MgO thickness approximation using XPS photoelectrons and EAL database are more straightforward and accurate compared with BaM thickness approximation. This is because of the simplicity of MgO stoichiometry and its layer structure. Stoichiometry is one of the input parameters when using the EAL database. BaM has a complex structure and has various possible Ba–Fe–O ternary compounds with different stoichiometry such as $\text{BaFe}_2\text{O}_4$ ($\text{BaO} \cdot \text{Fe}_2\text{O}_3$), $\text{Ba}_2\text{Fe}_2\text{O}_5$ ($2\text{BaO} \cdot \text{Fe}_2\text{O}_3$) and $\text{BaFe}_{12}\text{O}_{19}$ ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$). 65 66 67 Growth of the BaM film on the MgO is an evolving process that is still under research study. This complex process makes the stoichiometry a variable for the EAL.
approximation. BaM deposition also has a slow growth rate (~0.1Å min⁻¹), which requires a much longer time to deposit till the Si intensity is attenuated. In comparison, EAL approximation of the MgO thickness is less complicated. MgO has a simply stoichiometry of Mg:O equals 1:1. Growth rate of MgO is higher (~10Å min⁻¹) thus requires less deposition time. The approximation of MgO thickness using EAL in the Interface Engineering Laboratory was also proved to agree well with results of TEM measurements.

In different material systems however, substrate x-rays may not be the most convenient one to use especially if homogeneous deposition is involved. In that case, alternative methods should be developed based on the specific situation. For heterogeneous deposition, if the thickness of certain film can be accurately predicted and easily controlled, it can be considered as a candidate for sampling depths determination.
6. Conclusions

The goal of this work was to design and integrate a RHEED-TRAXS system in the existing oxide growth chamber for assisting the growth monitoring by providing real-time chemistry information. In order to reach this goal, a series of objectives needed to be achieved. First of all, an UHV compatible x-ray detection system needed to be designed and built. With a working system, the various influences on characteristic x-ray intensity needed to be understood and an effective methodology for data acquisition needed to be established. Meanwhile, the RHEED-TRAXS characteristic x-ray signal needed to be interpreted both qualitatively and quantitatively. With a comprehensive understanding of the system and the data collection, its application in assisting the development of functional oxides needed to be investigated.

An UHV compatible x-ray detection system was accomplished by modifying the existing oxide growth chamber and adding a side chamber where x-ray detector mounting and manipulation are both realized. Overwhelming x-ray intensity issue from the RHEED process was solved by a flexible aperture system. This custom designed aperture system not only helped reducing the incoming x-ray intensity, thus prevented x-ray detector overload, but also achieved line-of-sight x-ray detection with small angle approximation. This blocked out random x-rays excited in the chamber environment and allowed the detector to look at the x-rays coming from the sample surfaces only. The compact design of the aperture support also eliminated the need for additional shutter component and allowed broader detector movement space. This aperture design also acted as the support for beryllium foil protection that was essential for using the detector during real-time while the film was being deposited.
This designed system can provide a detection angle coverage of 0° to 4.7° from the sample surface during growth position, with the smallest step resolution of 0.04°.

With this system, various influences on characteristic x-ray intensity including RHEED electron kinetic energy, RHEED electron beam emission current, critical angle of various elements, data acquisition time and the chamber geometry factors were investigated. Critical angles in different material systems including bare 6H-SiC, MgO and BaM were measured and identified. Although it would be ideal to monitor elemental x-ray intensities at their specific critical angles in specific material systems, it was not practical with the current resources including the cost perspective and practicality of design. Substrate signal Si Kα line critical angle measured from hydrogen cleaned SiC substrate was used in this study as the reference to calibrate system geometry. It was found from various experiments that this geometry calibration method provided consistent and repeatable data. Data collected from independent measurements that were all calibrated with Si critical angle were consistent and comparable, and can be used to explain the expected physical process.

Absolute elemental x-ray intensity gains measured based on this calibration method from various independent film growths were compared with the XPS thickness analysis and their trend agreed with the XPS analysis. Thus, with proper calibration, absolute intensity gain can be used to approximate the film thickness for single element deposition and simple oxide deposition (such as MgO). Meanwhile, substrate x-ray attenuations were tracked with samples of different thicknesses. It was found that the corresponding film thicknesses could be modeled with the attenuation based on Snell’s law and x-ray total external reflection.
It was also demonstrated in the study of single element Fe deposition on SiC substrate that the relative ratio between elements was representative of the relative atomic numbers. If the probing depths can be defined, these ratios could be calibrated against the stoichiometry of the corresponding excited sample volume. It was found that, with x-ray detection angle at the measured Si critical angle, even when films were thicker than 10nm, substrate signal could still be detected. This suggested a much deeper probing depth due to the compromised surface sensitivity caused by detecting at Si critical angle. Unless a different geometry calibration method can be developed, XPS would not be sufficient to calibrate the relative elemental ratio in RHEED-TRAXS measurement into composition of the excited sample volume.

Real-time growth tracking using RHEED-TRAXS took advantage of the less surface sensitive aspect of the technique and this could help with the understanding of the growth mechanism of complex oxide such as barium hexaferrite. Different behavior of Fe and Ba atoms were observed during BaM growths. Continuous increase of Fe atom was in strong contrast with the flat profile of Ba atoms. Ba atoms were observed to increase at the initial 4-6minutes of growth and then stayed relatively constant for at least the first 20-30nm of film. Control experiments with Ba deposition onto MgO films were carried out and continuous increase in Ba intensity were repeatedly observed. This comparison suggested that with the presence of Fe, elevated substrate temperature and active oxygen species, the dynamics of Ba incorporation into a growing surface was essentially different.

This study demonstrated the potential of RHEED-TRAXS as a tool to provide real-time chemistry monitoring. The findings in this work presented a comprehensive study of the RHEED-TRAXS development in the oxide growth system. It also
identified the challenges that were involved in realizing RHEED-TRAXS is MBE systems for real-time analysis. The correlation between thickness with absolute and relative signal intensities based on calibrated geometry were a positive support for its potential in further quantitative development. The sensitivity response to deposited species at critical angle measurement conditions demonstrated its flexibility in assisting real-time monitoring of the deposited species. The understandings and results learned in this work can be extended to other material systems and other MBE systems to assist the development of functional materials.
7. Recommendations

7.1 Geometry Calibration and Challenges

The oxide chamber in the Interface Engineering laboratory has a manipulation system which provides two freedoms of movements for samples loading: forward and backward direction movement (Z direction movement) and 360° rotational movement. When transferring samples into the oxide chamber, RHEED beam equipped in the oxide chamber are often used as a reference to locate the sample in the Z direction. Rotational position depends on the orientation of the sample with respect to the incident and diffracted beam. Usually, the position which gives the corresponding diffraction pattern of the typical crystal orientation is used. Then by fine-tuning both the Z direction and the rotational dimension, the most crisp and brightest spot is found and used to be the growth position.

Geometry calibration in RHEED-TRAXS system is a process aimed at matching detection angle (take-off angle) with the Si critical angle and it needs to be done each time a new sample is loaded for growth. The variations in the geometry from run to run come from various possible sources. First of all, it is not likely to get an identical match between the crystal orientations of the samples with the orientation of the sample holder each and every time. The result of this is that the rotation of the sample stage needs to be adjusted each time to get the right crystal orientation. This is not unavoidable if all the samples were to be marked at a certain corner on the carbon face (“reverse” rough side) after dicing but before splitting. Second, z-directional position can be off due to the backlash of threads on the manipulator. A stopper can be attached to the thread to give approximately the same z coordinate, although it needs to be recalibrated after several runs to avoid the effect of backlash. Last but not
least, as the sample holder mounting mechanism is attached to the heater rod with three setscrews, repairs involve removing or altering the position of the sample holder on the rod may introduce variations in the absolute geometry in the z-direction.

Due to the above reasons, geometry of x-ray detection is not fixed but needs to be calibrated each time for a new sample. In most cases when no major alternation or repairmen is done on the system, consistent geometry calibration for RHEED-TRAXS measurement can be expected by maintaining the Z direction, rotation and RHEED beam positioning setting relatively constant from run to run. In this case, through a few repeated tests on different films, one can get a good feel about at what take-off angle, the critical angle of Si Kα line can be found. Meanwhile, for each sample or each run, once the geometry is calibrated, the sample can be removed for XPS measurements and remounted under previously calibrated locations and still maintain the calibrated geometry.

For the experiments done in this work, all of the x-ray angle dependence measurement was done by manually moving the detector. Ideally, motor controlled movement of the detector stage, synced with simultaneous acquisition of x-ray by the detector will make the process of finding the Si critical angle more efficient, provided that the emission current of the RHEED beam is stable over the acquisition period and that the sample does not charge under the electron bombardment. In reality, charging of the sample and the chamber environment, especially the sample side of the main shutter will disturb the path of the electron beam and induce inaccurate measurement of the x-ray intensity representative of the film stoichiometry. It had been observed that when the shutter is close enough to the sample surface, electrons bounced off the sample surface can hit the sample side of the shutter. As the shutter surface is covered
with deposited elements, charges build up much more quickly than does it conducted to ground. As a result, it can be observed that an electric field is build up on the shutter and it impacts the path of the electron beam.

7.2 Detector Limitations

Due to the fact that energy of the Mg Kα lines (~1.30 keV) fall into the category of soft x-rays, it gets absorbed when travelling through the beryllium foil (0.5mil) in the x-ray detector which is commonly used in X-ray detectors. Compared with its 56.0% transmission efficiency, more than 99% of Si K line x-rays (~1.8keV) is transmitted. Additional Beryllium foil (0.005mm) in the aperture design then again transmits 79.6% of the Mg x-rays coming through and leaves a 44.6% final transmission [8]. In addition, quantum efficiency of this x-ray excitation process is different. For lower atomic number atoms such as Mg, when interacting with high energy electrons, Auger effect is the dominant effect, whereas for Si, the x-ray emission process becomes dominant. As a result, low counts in low atomic number atoms such as the Mg signal is inevitable although undesired for accuracy concerns during real-time measurements. Higher RHEED electron energy and emission current or longer acquisition time may be adopted to improve similar situation with low atomic number elements, detectors with different filtering mechanism may also be considered to reduce the loss through detection elements. With better signal at any film thicknesses, RHEED-TRAXS should be of great potential in confirming the relationship between Mg intensity changes and the mechanism of MgO layer formation during initial phase.
7.3 RHEED electron emission current

RHEED electron emission current was stable after about an hour of warming up at the operation heating current. However, it was often observed that, emission current reading under stable conditions could fluctuate while the corresponding RHEED image brightness and the intensity of the excited x-rays stayed the same. To avoid this confusion of the data’s accuracy, emission current control methods will be highly desirable.
8. References


31. Vanmil, B. Gallium nitride growth by RF-plasma assisted molecular beam epitaxy: Determination of surface stoichiometry by RHEED-TRAXS, annealing


41. Chandril, S. In situ structural and compositional analysis using RHEED electrons induced x-rays. West Virginia University, 2009.


45. T. Yamanaka, S. I., Atomic depth distribution and effects of surfactants in growth of Ag and Au on Si(111)-?3\times?3-Ga(1ML) -?4\times?1-In and -2\sqrt{3}\times?2\sqrt{3}-Sn surfaces at room temperature. Physical Review B 2002, 66 (8), 7.


55. Goodrich, T. L. Atomistic investigation into the interface engineering and heteroepitaxy of functional oxides on hexagonal silicon carbide through the use of a magnesium oxide template layer for the development of a multifunctional heterostructure. Northeastern University, Boston, 2008.


