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450degree C Aln Thin Film Growth on Nitrided C-Plane Sapphire Substrates

Roger Eastman Feeley

University of Maine, roger.feeley@maine.edu

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450°C ALN THIN FILM GROWTH ON NITRIDED
C-PLANE SAPPHIRE SUBSTRATES

by

Roger Eastman Feeley

B.S. University of Maine, 1989
M.S. University of Maine, 2007
M.E. University of Maine, 2011

A DISSERTATION
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Advisory Committee
Nuri W. Emanteoglu, Associate Professor of Electrical and Computer Engineering, Advisor
Robert J. Lad, Professor of Physics and Astronomy & FIRST
David Frankel, Senior Research Scientist FIRST
Robert W. Meulenberg, Associate Professor of Physics and Astronomy & FIRST
James P. McClymer, Associate Professor of Physics and Astronomy
Low temperature (LT) growth of strongly textured AlN by molecular beam epitaxy (MBE) has not been extensively investigated. The low mobility of Al adatoms provides a challenge for growth of AlN at low temperatures (<600 °C). Consequently, AlN growth by MBE is typically at temperatures >700 °C. Growth at these temperatures can limit the selection of substrates and materials to grow with the AlN.

Highly oriented, LT AlN thin films (<50 nm) were grown on c-plane sapphire, using an interrupted growth procedure. Films were grown by periodically interrupting the Al flux with a nitridation. This two-step cycle was repeated until the AlN film reached the desired thickness. For comparison, two groups of AlN thin films were grown using an uninterrupted growth. One group was grown using an Al/N ratio >1, and the other grown with an Al/N<<1.

Prior to the AlN growth, the sapphire surface was pretreated with a radio-frequency nitrogen plasma to form an AlN template. As part of this work, a nitriding study investigated the
effects of plasma power, plasma ions, substrate temperature, and exposure time on the nitrided sapphire surface. The effect of plasma ions on the nitriding process, as well as the efficacy of nitriding pretreatment were evaluated using AlN film growth comparisons.

The sapphire nitridation investigation verified that nitriding is crucial to the growth of high quality LT AlN films. Additionally, concentration of high-energy N* has a role in the adequacy of the sapphire nitriding layer, and including plasma ions in the pretreatment improves the texture of AlN films grown atop the nitrided surface. Of the LT AlN film growth, the comparison films grown with an Al/N>1 were multiply oriented, with poor surface morphology. Comparison films grown with an Al/N<<1 had a nearly smooth surface and were close to being strongly textured. Using an Al/N>1, strongly textured films resulted from depositing 5-6 monolayers of AlN, and interrupting each growth with a 2–3 minute nitridation. The N* of a 600 W plasma produced a smooth surface. Using a 300W plasma increased surface roughness.
DEDICATION

This is dedicated to my family — my parents and siblings who have patiently supported and stood with me through every step of this journey.
ACKNOWLEDGEMENT

As I complete this work I must first acknowledge that my achievements are largely due to the kindness of others. I must thank my advisor, Dr. Nuri W. Emanetoglu and all other members of my committee who have been very patient with me. Had I been told two decades ago that I would still be on this path, I would have thought them crazy and asked them what they were smoking . . .

I especially need to thank Dr. George Bernhardt who, without him, I sincerely doubt I would be here right now.
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CHAPTER 1
INTRODUCTION

1.1 III-Nitrides

For the past three decades, interest in group III-nitride semiconductors has steadily grown due to their unique physical properties and promising potential for use in optoelectronic devices. As direct band gap semiconductors with strong polarization characteristics, ternary III-nitride alloys have the potential to be grown with tunable bandgaps, which can cover the Near IR (infrared) visible spectrum and into the Mid UV (ultraviolet). Figure 1.1 presents the bandgap energies and bowing parameters of AlN, GaN, and InN plotted against their lattice constants as well as the optical wavelengths associated with the bandgap energy.

Figure 1.1 Bandgap energy versus lattice constant of the AlGaN system.\(^1\)

Currently, III-nitride optoelectronic devices such as laser diodes (LD) and light emitting diodes (LED) have wide commercial use. In\(_x\)Ga\(_{1-x}\)N has been used extensively in producing high

\(^1\) Source: [Link to the figure source]
brightness green/blue LEDs and LDs, and is used in liquid crystal diode (LCD) displays and traffic lights.

For sensory and photovoltaic (PV) applications, high melting points (InN >1300 °C, GaN>2500 °C, AlN>3000 °C) and radiation hardness allows them to be used in harsh environments. III-nitride fabricated UV photo detectors are sensitive to UV radiation while blind to radiation of longer wavelengths. These devices can be used to detect UV light with a high visible or IR background. In,Ga, N alloys have been shown to have superior high-energy radiation resistance for space based PV applications. III-nitride based devices can work without optical filters due to their intrinsic solar blindness and low dark currents. For use in photovoltaic (PV) devices, the absorption coefficients of III-nitrides exhibit, (~10⁵ cm⁻¹) allow a large fraction of the incident light to be absorbed within 100 nm of material. This compares with the 10–100 µm of material needed in traditional Si photovoltaics. This reduces their size and launch weight significantly. The high performance PVs currently in use are based on Ge/GaAs/GaInP multijunctions. III-nitride based PV devices are more environmentally friendly since they do not contain toxic elements such arsenic.

Additional advantages III-nitrides hold are high electron mobility and high bulk saturation velocity, high breakdown field, and high thermal conductivity, all of which make them good for use in high-power, high-speed electronics. These properties have sparked research and the development of UV and IR detectors, chemical and biological sensors, terahertz radiation devices, neutron scintillation detection, spintronic applications, high electron mobility transistors, and thermoelectric devices.

The creation of III-nitride devices can only be achieved through the manufacture of high quality films. Film quality is influenced by all segments of the growth process. These include the
selection and pretreatment of the growth template, and the film growth method with its growth parameters. III-nitrides share similar substrate selection and pretreatment parameters. Similarly, growth techniques for AlN, GaN, and InN often differ only by temperature. This work will focus on the growth of AlN, but include background information on GaN and InN.

1.2 Substrate selection and pretreatment

As the foundation of a thin film, high quality native substrates for growth templates are required. Sapphire, Si, and SiC are the common choices. With its relatively low cost and high availability, sapphire is the dominant substrate choice for the LED (In$_x$Ga$_{1-x}$N) market.$^{17}$

A disadvantage of using sapphire is its large lattice mismatch with III-nitrides.$^{18,19}$ This mismatch can be allayed by pretreating the sapphire surface by nitridation, and has been shown to improve the epitaxy of III-nitride thin films grown atop sapphire.$^{20–23}$ For III-nitride films grown using chemical vapor deposition, nitridation is done by dissociating ammonia on the sapphire surface.$^{24,25}$ For films grown using physical vapor deposition, nitridation is typically done using ammonia gas,$^{26}$ from exposure to an electron cyclotron resonance (ECR) plasma,$^{27,28}$ or a radio-frequency (RF) nitrogen plasma.$^{29,30}$

Published studies have investigated the effects of substrate temperature,$^{19,31–33}$ nitriding time,$^{19,32,34}$ gas flow,$^{32}$ and plasma ions$^{19}$ on the nitridation layer grown by a RF plasma. The composition of the RF nitrogen plasma has also been investigated,$^{35,36}$ as well as its effects on nitriding$^{19}$ and on III-nitride growth.$^{36–44}$ Previous RF plasma studies have all nitrided using a constant RF power.

1.3 AlN as a buffer layer

For applications that require single crystal III-nitrides, the growth techniques best suited are molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD). One
technique used to improve the quality of III-nitrides, is the growth of a thin AlN layer, from <50
nm to 200 nm, prior to the start of the objective film growth. AlN nucleation layers or buffer
layers have improved the crystallinity and surface morphology of GaN, InN, AlN, and
III-nitride compounds. AlN buffer layers have also improved III-nitride device electrical
properties. When grown as a buffer or nucleation layer, the AlN layer has rarely been
independently characterized for crystallinity or surface morphology, but is only
evaluated by through the characterization of the final growth.

1.4 Epitaxial AlN

III-nitride films grown by plasma-assisted (PA) MBE are found to have better crystalline
quality and surface morphology when grown under metal-rich conditions. Metal-rich
conditions occur when the metal flux to N flux ratio is greater than 1 (metal/N>1). A
consequence of a metal-rich growth ratio is the potential formation of metal droplets on the
growth surface. For AlN, this is due to the low mobility of Al adatoms, and as a consequence,
droplet formation is temperature dependent. The energy needed to move the metal adatoms can
be provided by heating the substrate during growth. AlN is grown at temperatures up to 1300 °C
by MBE, and 1600 °C by MOCVD. For AlN growth by MBE at temperatures below 900 °C,
techniques have been developed to eliminate the formation of droplets. One such technique is to
periodically interrupt the metal flux, pausing the deposition to allow the N plasma to irradiate the
growth surface.

1.5 Low temperature AlN

III-nitride growth is often characterized in terms of high temperature (HT) or low
temperature (LT). LT is used as a label for temperatures below standard operating growth
temperatures. For MOCVD, temperatures as high as 1000 °C have been defined as LT. 48,49 For MBE, <600 °C58,67 is considered LT.

When used as a buffer layer, the role of LT AlN in reducing film stress and dislocations in III-nitrides is well documented.47,46,54,55 Recently, LT AlN passivation layers have been grown for device performance enhancement.58 However, the epitaxial growth of high quality LT AlN, not grown as a buffer layer, has not been extensively investigated. This lack of publications regarding a direct evaluation of the layers may suggest that direct characterization is not practicable or possible, due to the growth method, or due to the access or availability of characterization equipment. Another possibility is that since the purpose of the LT AlN layer is to improve the properties of the thicker III-nitride film grown on top, any unremarkable or inferior characteristics of the LT AlN layer go unreported. Thicker LT AlN films have been grown by MBE on Si (300 nm)67 and GaN (200 nm)58 using RF plasma and on Si (400 nm)68 using electron cyclotron resonance (ECR) plasma.

High quality LT AlN could lead to new semiconductor device possibilities, combining AlN with other LT materials. One example is the combination of AlN with InN. InN has a low dissociation temperature during MBE growth. InN begins to decompose at growth temperatures around 500 °C. As AlN is the semiconductor of the III-nitride family with the largest bandgap, and InN the narrowest gap, a material formed of In$_x$Al$_{1-x}$N would have a theoretical bandgap that encompasses the entire range of the available energies, covering the Near IR through the visible spectrum and into the Mid UV. Most III-nitride devices utilizing the properties of a wide bandgap involve GaN. In combination with InN, the (In$_x$Ga$_{1-x}$N) alloy bandgap spans from 0.7 eV to 3.4 eV.69,70 As the bandgap of AlN is 6.28 eV,71 this would more than double the energy range of the available bandgap from 2.7 eV to 5.6 eV. Multiple quantum well devices fabricated
with In\textsubscript{x}Al\textsubscript{1-x}N would allow intersubband photon transitions of the visible spectrum within the well.

1.6 Summary of this work

The objective of this thesis work was to develop a method for growing thin (<50 nm) LT AlN film that is both strongly textured (\textit{i.e.} comprised of grains with near to identical orientation of all principal axes), and has smooth surface morphology. The growth temperature (400-500 °C) was selected to correspond with the MBE growth temperature of InN. LT AlN thin films were synthesized by RF PA MBE, and categorized by an assortment of techniques. AlN films were grown on \textit{c}-plane sapphire, utilizing a variety of Al flux to N flux ratios, using a constant or interrupted Al flux, and with variations of the nitriding pretreatment.

The objective of this work was achieved by using an Al/N flux ratio greater than unity, and periodically interrupting the Al flux. Using this method, the film surface morphology was linked to variations of plasma power or interruption time. Film crystallinity was connected to pretreatment time as well as Al amount deposited each interruption cycle. Film crystallinity was verified by x-ray diffraction methods and surface morphology observed with scanning electron microscopy.

Leading up to the film grown by interruption, LT AlN films were grown without Al flux interruption using a flux ratio (i) greater than unity, (ii) slightly less than unity, and (iii) much less than unity. Two separate comparative growth studies verified the importance of substrate pretreatment and examined the effect of using plasma ions in the pretreatment. Through comparative analyses of select films, the effects of pretreatment time and temperature on LT AlN growth were examined.
In addition to the LT AlN growth, was a comparative examination of selected nitridation pretreatment parameters, and their effect on the nitridation layer. The layers were probed for chemical composition and physical formation using x-ray photoelectron spectroscopy (XPS), reflection high-energy electron diffraction (RHEED), and x-ray reflectivity (XRR).

An overview of III-nitride background, the RF plasma, nitriding, and AlN growth is presented in chapter 2. The experimental techniques and characterization equipment used in this work are included in chapter 3. Chapter 4 covers the sapphire nitridation examination as well as two comparative AlN growth studies regarding pretreatment effectiveness. The growth of LT AlN films is covered in chapter 5. Conclusions from this work and discussions of future work is contained in chapter 6.
CHAPTER 2
BACKGROUND

As a requisite for the growth of any thin film, a review of relevant information regarding the structural properties, growth parameters, and growth experience regarding the film is warranted. This chapter begins with a review of the III-nitride wurtzite crystal structure, identifying the standard planes with associated lattice dimensions of the AlN planes. As wurtzite is a polar molecule, it can be grown to take advantage of its polarization characteristics to affect the electronic properties of thin film devices. Since the AlN films in this work were grown using plasma-assisted physical vapor deposition, the characteristics of electron beam evaporation and radio-frequency plasma are discussed. Thin film growth orientation is largely determined by substrate selection. As sapphire was the substrate used, the four common sapphire orientations, c-, r-, m-, and a- are reviewed. Since nitriding the sapphire surface has been shown to improve III-nitride film quality, a discussion on sapphire pretreatment is included. The chapter ends with a review of prior relevant AlN growth.

2.1 III-Nitride properties

2.1.1 Semiconductor crystal structure

The unit cell of a crystal is defined by basis vectors a, b, and c. Angles α, β, and γ indicate the orientation of each basis vector. In the case where the basis vectors are also the interatomic distances of the lattice, the basis vectors are the lattice constants. Combinations of unit vector magnitudes and directions yield the Bravais lattices. The three cubic Bravais lattices, characterized by a = b = c and α = β = γ = 90°, include the simple cubic, body-centered cubic (BCC), and face-centered cubic (FCC).
Elemental semiconductors, such as Si and Ge, form into the diamond structure, which is composed of two interpenetrating FCC lattices. Each atom is at the center of a tetrahedron, surrounded by four nearest neighbors. Most III-V semiconductors can form into the zincblende structure, such as AlN shown in Figure 2.1, which is nearly identical to the diamond structure. The III-V semiconductors AlN, GaN and InN also form into the wurtzite structure. Wurtzite is composed of two interpenetrating hexagonal close-packed lattices. Similar to the zincblende structure, wurtzite has a tetrahedral arrangement; each atom is surrounded by four nearest neighbors. As presented in Figure 2.2, the basis dimensions of wurtzite are $a_1 = a_2 \neq c$, with separation angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. 

Figure 2.1 AlN Zincblende structure. Image created using CrystalMaker®. CrystalMaker Software Ltd (www.crystalmaker.com)

Figure 2.2 Al-polar AlN wurtzite structure. Al is blue, N is grey. a) Side view indicating separation angles $\alpha$, $\beta$, and $\gamma$, and lattice basis dimensions. b) Top view indicating c-plane basis dimensions and separation angle $\gamma$. Images created using CrystalMaker®, CrystalMaker Software Ltd (www.crystalmaker.com)
Group III-nitrides with their $c$-axis oriented up, *i.e.*, with the group III (metal) above the nitrogen in the hexagonal lattice) are labeled metal-polar (*e.g.*, Al polar, In-polar), and those grown with their $c$-axis oriented down, (the nitrogen above the metal) are called nitrogen polar, or N-polar. Figure 2.2 is an example of Al-polar AlN. In this figure, the bond lengths and atomic radii are drawn to the same scale. The side view, shown in Figure 2.2(a), denotes the 3 separation angles, as well as the lattice dimensions of AlN. Figure 2.2(b) shows a top view of the Al-polar structure, with c-plane dimensions and angles. III-nitrides grown in orientations other than the $+c$ or $-c$ directions are considered semi- or non-polar.

The polarity of III-nitride films is sensitive to the growth conditions and growth template. Polarity can influence growth behavior and III-nitride properties such as defect formation and doping efficiency. Consequently, polarity control is a critical aspect of III-nitride growth. The two factors that influence polarity of the III-N thin films are the stoichiometry of the growth template and the metal to nitrogen ratio. The polarity of GaN and InN are more influenced by the stoichiometry of the growth template rather than the ratio of metal to N during the thin film growth. Although the polarity of AlN is initially determined by the substrate, the metal/N ratio is the more important factor. AlN films grown using an Al/N $>1$ are Al-polar and those grown with an Al/N $<1$ are N-polar.

### 2.1.2 Mechanical properties

Wurtzite III-nitrides are chemically stable, mechanically strong, and have high melting points. They are less prone to degradation from the high current and radiation present in active regions of light emitting devices. III-nitrides also possess good thermal conductivity. Table 2.1 lists selected mechanical properties of III-nitrides,
Table 2.1 Selected mechanical properties of III-nitrides.\textsuperscript{2,3,4,71,73,79–82}

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td>$a$</td>
<td>3.111</td>
<td>3.180</td>
<td>3.533</td>
<td>Å</td>
</tr>
<tr>
<td></td>
<td>$c$</td>
<td>4.978</td>
<td>5.166</td>
<td>5.703</td>
<td>Å</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>$K$</td>
<td>210</td>
<td>210</td>
<td>140</td>
<td>GPa</td>
</tr>
<tr>
<td>Melting point</td>
<td></td>
<td>&gt;3000</td>
<td>&gt;2500</td>
<td>&gt;1300</td>
<td>°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>$\kappa$</td>
<td>2.85-3.2</td>
<td>1.3</td>
<td>0.8</td>
<td>Wcm(^{-1})K(^{-1})</td>
</tr>
</tbody>
</table>

Figure 2.3 is an illustration of a hexagonal unit cell denoting the orientation of 6 standard planes, indexed using Miller-Bravais indices ($hkil$). As noted above, the $c$-plane surface is polar. The $a$- and $m$-planes are non-polar surfaces. III-nitrides grown with these orientations are non-polar. The $r$-plane, ($10\overline{1}1$) plane, and ($10\overline{1}3$) plane are considered semi-polar.

Figure 2.4 shows the atom placement and dimensions of AlN for the 6 planes of Figure 2.3. Figure 2.4 planes are indexed using Miller indices ($hkl$), omitting the $i$ component of the Miller-Bravais indices ($hkil$) used in Figure 2.3.
2.1.3 Electrical properties

Wurtzite AlN InN and GaN are all direct bandgap semiconductors. AlN and GaN are wide bandgap semiconductors, with $E_g = 6.28$ eV and $E_g = 3.42$ eV at room temperature, respectively. Early studies of InN had indicated that its bandgap to be on the order of 2 eV, but later investigations have determined it to be 0.7-0.8 eV. The 0.7–6.2 eV energy range corresponds to a spectral range reaching from near IR to UV. III-nitride alloys can be designed for any bandgap within that range. A selection of electrical properties for AlN, GaN and InN is listed in Table 2.2.

The wide bandgaps of AlN and GaN make them excellent candidates for high power and high temperature electronic devices. The wide bandgaps of AlN and GaN cause them to reach the intrinsic temperature region at much higher temperatures than other semiconductors such as Si and GaAs. The dielectric breakdown fields of bulk III-nitrides are also an order of magnitude higher than Si and GaAs.
Table 2.2 Selected room-temperature electrical properties of III-nitrides.\textsuperscript{4,71,81,83–98}

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>$m_e$</td>
<td>0.40</td>
<td>0.20</td>
<td>0.11</td>
<td>$m_0$</td>
</tr>
<tr>
<td>Heavy Hole</td>
<td>$m_{hh}$</td>
<td>3.53</td>
<td>1.4</td>
<td>1.63</td>
<td>$m_0$</td>
</tr>
<tr>
<td>Effective density of states</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conduction band</td>
<td>$N_c$</td>
<td>$6.3 \times 10^{18}$</td>
<td>$2.3 \times 10^{18}$</td>
<td>$9.0 \times 10^{17}$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>Valence band</td>
<td>$N_v$</td>
<td>$4.8 \times 10^{20}$</td>
<td>$4.6 \times 10^{19}$</td>
<td>$5.3 \times 10^{19}$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>Intrinsic electron concentration</td>
<td>$n_i$</td>
<td>$9.4 \times 10^{-34}$</td>
<td>$1.9 \times 10^{-10}$</td>
<td>$9 \times 10^{10}$</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>Mobility</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>$\mu_e$</td>
<td>300</td>
<td>1400</td>
<td>3200</td>
<td>cm$^2$V$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Hole</td>
<td>$\mu_p$</td>
<td>14</td>
<td>$\sim 20$</td>
<td>220</td>
<td>cm$^2$V$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>Diffusion coefficient</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>$D_s$</td>
<td>7</td>
<td>36</td>
<td>80</td>
<td>cm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>Hole</td>
<td>$D_p$</td>
<td>0.3</td>
<td>0.5</td>
<td>5</td>
<td>cm$^2$s$^{-1}$</td>
</tr>
<tr>
<td>Peak drift velocity*</td>
<td>$v_d$</td>
<td>$1.7 \times 10^7$</td>
<td>$2.9 \times 10^7$</td>
<td>$4.2 \times 10^7$</td>
<td>cm$s^{-1}$</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>$\chi$</td>
<td>1.9</td>
<td>4.1</td>
<td>5.8</td>
<td>eV</td>
</tr>
</tbody>
</table>

*steady-state, with $10^{17}$ cm$^{-3}$ doping concentration

2.1.3.1 Carrier transport

III-nitrides have low electron effective masses and large effective density of states in the conduction and valence bands.\textsuperscript{71,81,84} The low electron effective mass also has the slight effect of raising the intrinsic Fermi level as temperature increases. Transport properties that influence the performance and efficiency of III-nitride devices are carrier concentration and mobility. The intrinsic carrier concentrations of AlN and GaN are small.\textsuperscript{4,71,81,84} InN has an intrinsic carrier concentration much larger, about the same magnitude as Ge.

Carrier mobility depends on temperature, electric field, doping concentration, and scattering within the material. Carriers can be scattered by other carriers, acoustic and optical phonons, impurities, dislocations, and at surfaces and interfaces. Under low-field conditions, the mobility and the diffusion coefficient are both material-dependent properties, related through the
Einstein relation, and independent of the field. Mobility due to scattering is determined through evaluating and combining the relaxation times of each scattering type.

Predicted mobility values for III-nitrides under these conditions have been derived using Monte Carlo and variational principle methods. In the presence of a high field, mobility and the diffusion coefficient become field-dependent properties. The bulk peak drift velocities for III-nitrides are high, as well as the saturation velocities and corresponding critical electric fields. Under high-field conditions, the drift velocity saturates to a constant value independent of the electric field.

GaN has been the favored material used for devices that require fast carrier transport and high breakdown voltage. GaN is used as the channel material in many field effect transistors (FETs), and the base material in AlGaN/GaN heterojunction bipolar transistors (HBTs). The transport properties of GaN have been studied extensively and are mostly understood. MC simulations of transient electron transport show high overshoot values. Calculations of GaN electron mobility at room temperature indicate that it is dominated by polar optical phonon (POP) scattering. Carrier-carrier scattering is also important with high carrier concentrations. Alloy scattering limits transport at GaN heterointerfaces.

Transport in AlN has not been studied as extensively as GaN, due to its large bandgap and high activation energy of donors. AlN has a very high critical field due to its large bandgap. The theoretical low-field mobility of AlN is limited by polar optical phonon (POP) scattering. Hole transport properties of AlN are not well understood. A measured value of the effective electron mass for AlN has been difficult to obtain. As with GaN, AlN transport has been studied by MC simulations.
InN has good electron transport properties such as high mobility and a large overshoot electron velocity\cite{85,100}. However, the high theoretical values of mobility calculated for InN have not been achieved experimentally. The observation of transient drift velocity oscillations make InN a promising material for high frequency devices operating in the THz range\cite{101}. THz emissions have been observed from InN thin films\cite{102,103}. However, most of the InN thin films grown to date have high electron concentrations, which inhibit the development of electronic or optoelectronic devices. Much of the literature regarding MC studies of electron transport in InN is based on the ~2 eV bandgap. Consequently, there is a need for a reevaluation of many prior MC studies and a call for new electron transport studies. Early studies of undoped InN indicated electron densities \(\sim10^{20}\ \text{cm}^{-3}\)\cite{104}. The development of MBE techniques for growing InN has achieved electron densities \(\sim10^{17}\ \text{cm}^{-3}\)\cite{105,106}, but InN layers <100 nm are often highly degenerate with electron concentrations \(\sim10^{19}\ \text{cm}^{-3}\). Due to the lack of proper p-doping, InN hole transport properties are not well understood.

### 2.1.3.2 Heterojunctions

Heterojunctions are formed at the interface of two semiconductors having different bandgaps. III-nitride heterostuctures allow for the formation of n-channels and intrinsically provide high carrier concentrations greater than or equal to \(10^{13}\ \text{cm}^{-2}\) through polar engineering without additional doping\cite{99}. Typically, the dissimilar semiconductors are also lattice mismatched. When the lattice mismatch is large, dislocations are formed at the heterojunction interface as the strained layer relaxes. These dislocations affect carrier mobility, but can be reduced or eliminated with the use of a buffer layer at the interface, or by making the strained layer thinner than its critical thickness. The critical thickness of the GaN/AlN interface is roughly 30 Å, and the critical thickness of the GaN/InN and AlN/InN interfaces are about 6 Å\cite{99}. 

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Band diagrams of junctions are drawn with reference to the vacuum level. Energy bands of each semiconductor are referenced to the vacuum level by its electron affinity. The Fermi level of doped semiconductors are referenced to the vacuum level by the work function. The discontinuities in the valence band ($\Delta E_v$) and the conduction band ($\Delta E_c$) are what accommodate the band gap difference. Ideally, $\Delta E_c$ would equal the difference in electron affinities, and $\Delta E_v$ would be the result of subtracting $\Delta E_c$ from the difference in bandgap energy ($\Delta E_g$). Band offsets for heterojunction have been found experimentally\textsuperscript{107–109} as well as through numerical methods.\textsuperscript{110} Consequently, there is a large range of values for band offsets. For example, the AlN/GaN valence band offset has experimentally measured values between 0.15 eV and 1.4 eV. The experimental offset values shown in Table 2.3 were determined by x-ray photoelectron spectroscopy (XPS) by Martin \textit{et al}\textsuperscript{107} and King \textit{et al}.\textsuperscript{108,109} Moses \textit{et al}\textsuperscript{110} calculated the theoretical values using the linearized augmented plane wave method. The understanding of InN interfaces has been limited due to the high-sheet charge concentrations present in InN. In III-nitrides, the bandgap offsets are also subject to a strain induced offset, dependent on polarization effects.

<table>
<thead>
<tr>
<th>Table 2.3 Valance band offsets of wurtzite III-nitrides.\textsuperscript{107–110}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{Experimental}</td>
</tr>
<tr>
<td>$\Delta E_v$</td>
</tr>
<tr>
<td>0.70±0.24</td>
</tr>
<tr>
<td>0.58±0.08</td>
</tr>
<tr>
<td>1.52±0.17</td>
</tr>
<tr>
<td>\textbf{Unit}</td>
</tr>
<tr>
<td>eV</td>
</tr>
<tr>
<td>$\Delta E_c$</td>
</tr>
<tr>
<td>2.3±0.1</td>
</tr>
<tr>
<td>2.22±0.10</td>
</tr>
<tr>
<td>4.0±0.2</td>
</tr>
<tr>
<td>eV</td>
</tr>
<tr>
<td>\textbf{Theoretical}</td>
</tr>
<tr>
<td>$\Delta E_v$</td>
</tr>
<tr>
<td>0.34</td>
</tr>
<tr>
<td>0.62</td>
</tr>
<tr>
<td>0.96</td>
</tr>
<tr>
<td>eV</td>
</tr>
</tbody>
</table>

\textbf{2.1.3.3 Quantum wells}

A quantum well (QW) is formed by two heterojunctions such that the material between the two junctions has the lowest $E_c$ for an electron well, and the highest $E_v$ for a hole well.
Within the well, energy becomes quantized into subbands, and carriers are confined on the subbands. The effective energy gap for interband transitions inside the QW becomes greater than the $E_g$ of the bulk material. When combining multiple quantum wells (MQW), separating each QW with a wide barrier layer will make the subbands of each QW independent of other QWs. When barrier layers between MQW are reduced such that the individual well wavefunctions begin to overlap, a superlattice is formed. The energy levels become continuous across the barrier space, and the discrete subbands widen into minibands. Making the wells thicker causes the band-to-band transitions to red-shift. Most QWs are grown with a c-axis orientation. QWs grown on $r$-plane substrates were shown to have smaller internal electric fields, and an increased radiative recombination probability. InAlN electron blocking layers (EBLs), lattice matched to GaN have been shown to improve the efficiency of QW light-emitting diodes.

2.1.4 Polarization

The wurtzite structure in III-nitrides is non-centrosymmetric. The arrangement of III-cations and V-anions produce a dipole moment parallel to the wurtzite $c$-axis. The growth of additional layers parallel to the $c$-axis cancel out the dipole moments of inner unit crystals and leads to the creation of an overall dipole moment along the $c$-axis with a fixed charge face at each end. The formation of the dipole moment is termed spontaneous polarization.\textsuperscript{111}

The spontaneous polarization vector points from the metal face to the N face. The spontaneous polarization can be determined experimentally, or by evaluating wurtzite structural parameters.\textsuperscript{112} Ideal wurtzite has a $c/a$ ratio of $\sqrt{8/3}$.\textsuperscript{113} The greater the $c/a$ ratio deviates from the ideal wurtzite, the stronger the spontaneous polarization. Using the $c$ and a lattice values from Table 2.1, AlN has the strongest spontaneous polarization, and GaN the weakest.
In the absence of an electric field, the polarization of a material is the sum of the spontaneous and piezoelectric polarizations. Piezoelectric polarization is a result of the displacement of charges due to physical strain within a crystal. Since the wurtzite crystal structure is non-centrosymmetric, it is also a piezoelectric material. As the lattice is physically deformed, the relative positions of nearest neighbors change, creating dipole moments. The piezoelectric polarization field can be calculated or determined experimentally.\textsuperscript{111,112,114}

Experimental and theoretical results indicate that (0001) oriented III-nitride films grown under compressive strain have piezoelectric polarization in the [0001] direction, and films grown under tensile strain have piezoelectric polarization in the opposite direction.\textsuperscript{115,116} Piezoelectric polarization is calculated by knowing the strain as well as the material’s piezoelectric ($e_{ij}$) and elastic ($c_{ij}$) constants. An example of a III-nitride grown with the (0001) orientation under a strain ($\varepsilon_j$), the piezoelectric polarization ($P_{pz}$) in the [0001] direction would utilize $e_{ij}$, $c_{ij}$ and $\varepsilon_j$ in the form:

$$P_{pz} = 2 \left( e_{31} - \frac{c_{13} c_{33}}{c_{33}} e_{33} \right) \varepsilon_1$$

(2.1)

Numerical values of spontaneous polarization, piezoelectric and elastic constants for AlN, GaN, and InN are shown in Table 2.4.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous polarization</td>
<td>$P_{sp}$</td>
<td>-0.09</td>
<td>-0.034</td>
<td>-0.042</td>
<td>C/m$^2$</td>
</tr>
<tr>
<td>Piezoelectric constant</td>
<td>$e_{33}$</td>
<td>1.5</td>
<td>0.67</td>
<td>0.81</td>
<td>C/m$^2$</td>
</tr>
<tr>
<td></td>
<td>$e_{31}$</td>
<td>-0.053</td>
<td>-0.34</td>
<td>-0.41</td>
<td>C/m$^2$</td>
</tr>
<tr>
<td>Elastic constant</td>
<td>$c_{33}$</td>
<td>377</td>
<td>354</td>
<td>205</td>
<td>GPa</td>
</tr>
<tr>
<td></td>
<td>$c_{31}$</td>
<td>94</td>
<td>68</td>
<td>70</td>
<td>GPa</td>
</tr>
</tbody>
</table>
Polarization has an influence on device physics and design. Polarization effects can influence the material properties of heterostructures and device operation. Since the polarization is along the c-axis, c-axis grown III-nitrides can be designed to take advantage of this polarization. The piezoelectric polarization of compressively strained GaN, AlN, and InN induces an electric field that opposes the field created from spontaneous polarization. When applied in heterojunctions, strain-induced piezoelectric polarization and the polarity-dependent interface potential have an effect on valence band discontinuities. The asymmetry of the discontinuities depend on the growth order of the binary layers. Strain-induced piezoelectric fields in III-nitrides always tend to decrease the apparent valance band discontinuities. Piezoelectric- and spontaneous- polarization fields cause tilting of the potential profile in quantum wells, resulting in the shift of the photoluminescence peak of multiple quantum wells (MQW). This tilting allows a MQW to be “tuned” over a range of wavelengths.

2.2 III-Nitride growth methods

Epitaxial growth can be classified into categories, depending on the medium through which the atoms travel to reach the growth interface. Transporting the material within a gaseous volatile compound is known as vapor-phase epitaxy (VPE). Liquid-phase epitaxy (LPE), moves the material within a saturated solution. VPE and LPE use chemical processes to grow epilayers. As such, VPE is considered a form of chemical vapor deposition (CVD). CVD techniques include hydride vapor-phase epitaxy (HVPE), and metal-organic vapor-phase epitaxy (MOVPE) – also known as metal-organic chemical vapor deposition (MOCVD). MOCVD is the most common form of CVD used in group-III nitride growth.

Depositing a film through a direct vacuum evaporation of the material is known as physical vapor deposition (PVD). PVD uses a physical method to create a thin film. It involves
vaporizing a film material and allowing it to condense onto a desired surface. This physical method can be mechanical, electromechanical, or thermodynamic. PVD methods include magnetron sputtering, laser ablation, MBE, and electron beam evaporation (EBE). In III-nitride film growth, the metal is supplied by PVD, and nitrogen is supplied by nitrogen plasma or ammonia.119

Electron beam evaporation (EBE) is a form of physical vapor deposition, similar to MBE. An accelerated beam of thermionic electrons, created by a heated filament, bombards the material to be evaporated. The kinetic energy of the electrons is transferred to the evaporation material, causing the material to melt or sublimate. The material vapor can then travel to the surface of a substrate.

A typical physical configuration of EBE involves an electromagnetic alignment of the electron beam. An ingot of the material to be evaporated is placed in a crucible or copper hearth, and is held at a positive potential with respect to the filament. For hearths with multiple pockets, a different material can be held in each pocket and moved into place when needed. To avoid cross-contamination of the filament and the film, the electron beam is directed onto a 270° arc by a magnetic field, resulting in no direct lines of sight between the filament and the evaporant. If desired, an electric field can be used to raster the electron beam over the evaporant’s surface for uniform heating. The crucible and hearth are water-cooled. The cooling helps prevent contamination of the evaporant by the crucible, since only the material at the evaporant’s surface is melted. The start and stop of the deposition is controlled by shuttering the effluent material. This control allows for atomically abrupt transitions between materials.

The mass deposition rate is a function of material temperature, material vapor pressure, and the source-substrate distance. The evaporated atoms have a Maxwellian energy distribution.
Since the vapor pressure of a material is a function of its temperature, the deposition rate of a material is controlled by varying its temperature. The higher the vapor pressure, the higher the material’s deposition rate. The electron beam can produce temperatures ~3000 °C, and is controlled by the filament current. The Al deposition rate can range from 10 to ~ 100 Å/s.\textsuperscript{120} The deposition atoms are of low (~0.1 eV) energy, and the lateral grain size of an EBE grown film ranges from 10 ~ 100 nm.

The mean free path of the evaporated particles exiting the e-beam determines the size and operational pressure of the deposition chamber. A general design criteria is that the mean free path of the particles should be larger than the geometrical size of the deposition chamber for pressures <10\textsuperscript{-5} Torr. The EBE beam is highly directional, which limits film uniformity for flat surfaces. This requires there be a minimum distance from the source to substrate, or minimum chamber size.

2.3 The RF nitrogen plasma

In PA PVD growth, the nitrogen plasma utilized for film growth can also be used to pretreat the substrate prior to the film growth. The plasma is typically generated by microwaves – electron cyclotron resonance (ECR) – or by a 13.56 MHz radio-frequency (RF) signal. These plasma sources produce excited neutral (N\textsubscript{2}*) and ionized molecules (N\textsubscript{2}+), excited atoms (N*) and ionized atoms (N\textsuperscript{+}).\textsuperscript{121–128} RF plasma contains a much larger concentration of N* than ECR plasma.\textsuperscript{129}

The states and transitions of activated molecular and atomic nitrogen are well documented.\textsuperscript{128,130–133} Four band systems associated with neutral molecular nitrogen are the triplet states, N\textsubscript{2}(A\textsuperscript{3}Σ\textsubscript{u}+), N\textsubscript{2}(B\textsuperscript{3}Π\textsubscript{g}), and N\textsubscript{2}(C\textsuperscript{3}Π\textsubscript{u}), and the singlet state, N\textsubscript{2}(a\textsuperscript{1}Π\textsubscript{g}).\textsuperscript{128,131–133} Molecular ion species include the ground state of the N\textsubscript{2}+ ion, N\textsubscript{2}+(X\textsuperscript{2}Σ\textsubscript{g}+), and the excited state,
Excited atomic nitrogen include the N(4S) ground state and the two metastable ground states of N(2D) and N(2P). The ground state of atomic ions is N⁺(2P).

Optical emission spectroscopy can provide real-time monitoring of a plasma and is commonly used to determine plasma composition. Figure 2.5 shows the 350-900 nm region of the nitrogen plasma emission spectrum produced by an Oxford Applied Research (OAR) HD25 RF atom source, at a RF power of 250 W, and gas flow of 1.0 standard cubic centimeters per minute (sccm). The first-positive molecular transitions (B²Π⁡_g⟩→A³Σ⁺_u⁺) of N₂ are the six multiple-peaked bands centered at wavelengths 540, 590, 655, 755, 820, and 880 nm located in the 500-900 nm region. The second-positive transitions (C³Π_u→B³Π_g) of N₂ are located within the 350-500 nm region and are much less intense. The first-negative transitions of N₂⁺, (B²Σ⁺_u⁺→X²Σ⁺_g⁺) occur within the 350-590 nm region. The dominant atomic N peaks located at 745, 821, and 869 nm are multiplets. The N peak at 745 nm is a triplet of the (3s⁴P→3p⁴S⁰) transitions. The 821 nm peak is a 7-line multiplet of the (3s⁴P→3p⁴P⁰) transitions. The 869 nm peak is the combination of a 4-line multiplet of the (3s²P→3p²P⁰) transitions and an 8-line multiplet of the (3s⁴P→3p⁴D⁰) transitions. At higher plasma powers emission line for the N⁺ (2s¹P⁰→3p¹P) transitions can be observed at 648 nm. At low RF power this line can be obscured by the more intense first-positive molecular transitions.
Figure 2.5 RF nitrogen-plasma optical emission spectrum. The 350–900 nm region of an Oxford Applied Research HD25 RF atom source, operating at 250 W RF power, and 1.0 sccm gas flow. Emission intensity is indicative of species concentration. The first-positive molecular transition series, an indicator of the N$_2^+$ concentration. The atomic N peaks located at 745, 821, and 869 nm are indicators of the N$^+$ concentration. Spectrum recorded with Ocean Optics Red Tide USB650 spectrometer, using SpectraSuite software.

Characterization of the plasma species is important for PA MBE growth since each species may have a different influence on the growth process. The species with lower energy are better suited for film growth, and the higher energy species are better suited for nitriding pretreatment.$^{35,38,40}$ Of the nitrogen species within the plasma, the excited N$_2$ species tend to have the lowest energies. The energy of an active nitrogen species is referred to as a potential energy since it represents an energy level above the ground state.$^{128,131}$ N$_2$(A$^3\Sigma_u^+$) is 6.17 eV above the X$^1\Sigma_g^+$ ground electronic state.$^{128,131}$ N$_2$(B$^3\Pi_g$) is 7.55 eV above X$^1\Sigma_g^+$, N$_2$(a$^1\Pi_g$) is 8.55 eV, and N$_2$(C$^3\Pi_u$) is 11.03 eV.$^{128,131}$ As for atomic N, the dissociation energy of molecular N$_2$ sets the N(4S) ground state energy of atomic nitrogen at 9.76 eV. The metastable ground states of N(2D) and N(2P) have energy of 12.14 eV and 13.33 eV.$^{128,131}$ For the ionized molecular and atomic nitrogen, the N$_2^+$ ground state, N$_2^+$(X$^2\Sigma_g^+$), is 15.58 eV above the X$^1\Sigma_g^+$ ground electronic state.$^{128,131}$ The N$^+$(2P) ground state of ionic nitrogen is 24.3 eV.$^{128,131}$

Of the excited N$_2$ states produced within the plasma, N$_2$(A$^3\Sigma_u^+$) has the longest lifetime, that being about 2 s.$^{125,128}$ The lifetime of the other excited N$_2$ states is much shorter. N$_2$(B$^3\Pi_g$) has a lifetime of about 1.3 μs.$^{125,128}$ N$_2$(a$^1\Pi_g$) has a lifetime of about 10$^{-4}$ s,$^{128}$ and N$_2$(C$^3\Pi_u$) has a
lifetime of about 40 ns. Consequently, N$_2$(A$^3\Sigma_u^+$) is the only excited molecular species that contributes to nitriding and growth. The lifetimes of metastable N are sufficiently long to contribute to nitriding and growth. N($^2$D) has a lifetime of 9×10$^4$ s and the lifetime of N($^2$P) is 12 s.

The relative density of plasma species created by a RF plasma source is dependent on RF power as well as nitrogen gas flow. Yao et al., using a SVT Associates RF-4.5 plasma source, operating between 200–500 W plasma power and 0.50–1.50 sccm gas flow, reported that the total amount of reactive nitrogen can be increased by increasing RF power or gas flow, and that the atomic/molecular nitrogen ratio is directly proportional to RF power and inversely proportional to gas flow. Observations of an OAR HD25 plasma source by Iliopoulos et al., and Carrère et al., corroborate this assessment. Iliopoulos, operating the plasma source between 100–500 W and 0.2–1.8 sccm, indicated that the N$_2^*$ increased with an increase in RF power or gas flow, and that N increased as RF power increased, but was unaffected by gas flow. Carrère operated the source between 90–400 W and 0.002–0.3 sccm, reporting that both N$_2^*$ and N increased as RF power increased, and as gas flow was increased N$_2^*$ increased, but N decreased.

Yao and Iliopoulos compared the integral intensities of the related atomic and molecular species peaks to estimate the N$^*/$N$_2^*$ ratio. Carrère estimated N$^*/$N$_2^*$ by comparing the 746.8 nm (N$^*$) and 775.3 nm (N$_2^*$ second-positive series) peak intensities. Khan et al., estimated the ratio by comparing the intensity of the 493.5 nm N peak with the intensity of the 380.4 nm peak of the N$_2$ second-positive series.

The amount of ionic species (molecular and atomic) produced by OAR RF plasma sources has been reported to be very small. Using an OAR CARS-25 plasma source, Ptak et al., reported a maximum ion content of 5% when operating at 600 W power and 6 sccm gas flow.
The ion content of the plasma exiting the aperture was reduced to <0.1% using a 255 hole aperture. A comparison of the OAR CARS-25 with the OAR HD25 plasma source by Blant et al. determined the ion content of the OAR HD25, used in this work, to be much smaller than the OAR CARS-25.

2.4 III-Nitride growth on sapphire

2.4.1 Sapphire selection criteria

Figure 2.6 shows illustrations of the sapphire unit cell and the orientations of the four most common sapphire planes used as substrates. Figure 2.6(a) shows the sapphire structure with dimensions, and Figure 2.6(b) denotes the c-, r-, m-, and a- sapphire planes. Not included in Figure 2.6(b) are the sapphire n- (1123) and s-planes (1011) due to their limited use as substrates for III-nitride growth. As a substrate, each plane brings a unique set of template dimensions. The spontaneous and piezoelectric fields present in wurtzite III-nitrides grown along the c-axis are not always desirable since they can impair device performance. Growth along a semi-polar or non-polar axis reduces or eliminates these fields, resulting in an increase in device efficiency.

Figure 2.6 Sapphire unit cell with basis dimensions. a) Unit cell with atomic radii drawn at 60% of bond length scale. Al is light blue and O is red. b) The unit cell denoting the c- (gray), r- (light blue), m- (pink), and a- (yellow) planes. Sapphire image created using CrystalMaker®, CrystalMaker Software Ltd (www.crystalmaker.com)
Table 2.5 presents the III-nitride plane orientations that have been reported on the four sapphire planes. Since the lattice dimensions of AlN, GaN, and InN are within 15% of each other, they align in similar orientations when grown on similar sapphire planes. Sapphire $c$- and $a$-planes have lattice dimensions favorable to grow $c$-axis polar III-nitrides. Non-polar III-nitrides have been grown on both $r$-plane and $m$-plane sapphire. The sapphire $m$-plane has been used to grow semi-polar films as well.

Table 2.5 Reported plane orientations of III-nitrides on sapphire planes.18,51,140–155

<table>
<thead>
<tr>
<th>Sapphire</th>
<th>III-Nitride</th>
<th></th>
<th></th>
<th>Polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$-plane (0001)</td>
<td>$c$-plane</td>
<td>$c$-plane</td>
<td>$c$-plane</td>
<td>polar</td>
</tr>
<tr>
<td>$a$-plane (1120)</td>
<td>$c$-plane</td>
<td>$c$-plane</td>
<td>$c$-plane</td>
<td></td>
</tr>
<tr>
<td>$r$-plane (1012)</td>
<td>$a$-plane</td>
<td>$a$-plane</td>
<td>$a$-plane</td>
<td>non-polar</td>
</tr>
<tr>
<td>$m$-plane (1010)</td>
<td>$m$-plane</td>
<td>$m$-plane</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$m$-plane (1010)</td>
<td>(1122)</td>
<td>(1122)</td>
<td>(1122)</td>
<td></td>
</tr>
<tr>
<td>$m$-plane (1010)</td>
<td>(1013)</td>
<td>-</td>
<td>-</td>
<td>semi-polar</td>
</tr>
</tbody>
</table>

2.4.1.1 $C$-plane sapphire

The (0001), $c$-plane of sapphire is the most commonly used sapphire substrate used in III-nitride growth. As indicated in Table 2.5, AlN, GaN and InN planes grow (0001)$_{III}$/ (0001)$_{Sapp}$. An advantage of this orientation on sapphire is the exploitation of III-nitride polarization, which is why $c$-plane sapphire was chosen as the growth substrate in this work. For AlN, the observed orientation is 30º rotated from the similar sapphire directions,18 i.e., the AlN [1010] direction is aligned with the sapphire [1120] direction. With the rotation, the hexagonal Al plane is matched to the closed-packed oxygen plane of sapphire, also rotated 30º with respect to the sapphire unit cell. With this arrangement, the 3.111 Å AlN and 2.748 Å sapphire dimensions have a mismatch of about 13%, with the AlN under compressive stress. Table 2.6 lists the effective lattice mismatch of AlN, GaN and InN with sapphire for 30º rotation and for no rotation.
Table 2.6 Effective c-plane lattice mismatch between III-nitrides and sapphire. Mismatch shown for 30° rotation nucleation and no rotation nucleation.19 (“+”: compressive, “-”: tensile, “*”: favored relation during heteroepitaxy)

<table>
<thead>
<tr>
<th>Top/Bottom layer</th>
<th>30° rotation</th>
<th>No rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[1010]_c//[1120]_sapp</td>
<td>[1010]_c//[1010]_sapp</td>
</tr>
<tr>
<td>AlN/sapphire</td>
<td>+13.3% *</td>
<td>-34.6%</td>
</tr>
<tr>
<td>GaN/sapphire</td>
<td>+16.1% *</td>
<td>-33.0%</td>
</tr>
<tr>
<td>InN/sapphire</td>
<td>+28.8%</td>
<td>-25.7%</td>
</tr>
<tr>
<td>InN/AlN</td>
<td>N/A</td>
<td>+13.7% *</td>
</tr>
<tr>
<td>GaN/AlN</td>
<td>N/A</td>
<td>+2.3% *</td>
</tr>
<tr>
<td>InN/GaN</td>
<td>N/A</td>
<td>+10.9% *</td>
</tr>
</tbody>
</table>

Two views of the (0001)_{AlN}/(0001)_{sapp} arrangement is shown in Figure 2.7. Figure 2.7(a) shows a three-dimensional askew view of Al-polar AlN aligned with the sapphire surface. The AlN unit cell c-plane is outlined with dotted lines, and indicates the unit cell’s footprint on the sapphire surface. The sapphire c-plane is outlined with solid black lines dotted line. Figure 2.7(b) shows a top view of the sapphire, showing AlN, GaN, and InN aligned with the close-packed oxygen, at a 30º rotation. This configuration determines the epitaxial orientation of AlN and GaN. The InN lattice parameters do not greatly favor a rotation. InN grown directly on c-plane sapphire will likely have both [10\overline{1}0]_{c}//[1\overline{1}2\overline{0}]_{sapp} and [10\overline{1}0]_{c}//[1\overline{0}1\overline{0}]_{sapp} orientations. By nitriding the sapphire prior to the InN growth, the InN will follow the orientation of the nitrided layer.19

Figure 2.7 Orientation of (0001) III-nitride on (0001) sapphire. a) Askew view of AlN on sapphire. b) Top view of AlN, GaN, and InN. Images created using CrystalMaker®, CrystalMaker Software Ltd (www.crystalmaker.com)
2.4.1.2 \(a\)-plane sapphire

The \((1\bar{1}20)\) sapphire \(a\)-plane, as indicated in Table 2.5, is also used to grow polar \(c\)-plane AlN,\(^{140-144}\) GaN,\(^{155}\) and InN.\(^{151}\) An advantage of using \(a\)-plane sapphire is the potential for fabrication of edge-emitters, since \(a\)-plane sapphire is easy for cleavage at the sapphire \(r\)-plane.\(^{141}\) Another advantage is that the AlN layer created by nitriding the \(a\)-plane sapphire surface does not contain the rotational domains that have been seen on nitrided \(c\)-plane sapphire.\(^{140}\) A distinguishing characteristic of AlN grown on \(a\)-plane sapphire from growth on \(c\)-plane sapphire is that more than one orientation is possible.

Two growth orientations of \((0001)_{\text{AlN}}//\(1\bar{1}20)_{\text{sapp}}\) were found in the literature: AlN oriented \([10\bar{1}0]_{\text{AlN}}//[0001]_{\text{sapp}}\) and (rotated 30° about the \(c\)-axis) \([11\bar{2}0]_{\text{AlN}}//[0001]_{\text{sapp}}\). Table 2.7 presents the reported planar orientations of AlN and the associated lattice mismatch along that direction. These orientations can depend on the growth method, the pretreatment temperature, and the growth temperature.\(^{137,141}\)

<table>
<thead>
<tr>
<th>AlN</th>
<th>In-plane orientation</th>
<th>Mismatch</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c)-plane (0001)</td>
<td>([10\bar{1}0]<em>{\text{AlN}}//[0001]</em>{\text{sapp}})</td>
<td>24.4%</td>
<td>[137,141,143]</td>
</tr>
<tr>
<td></td>
<td>([12\bar{1}0]<em>{\text{AlN}}//[\bar{1}100]</em>{\text{sapp}})</td>
<td>13.2%</td>
<td></td>
</tr>
<tr>
<td>(c)-plane (0001)</td>
<td>([11\bar{2}0]<em>{\text{AlN}}//[0001]</em>{\text{sapp}})</td>
<td>-28.1%</td>
<td>[141]</td>
</tr>
<tr>
<td></td>
<td>([1\bar{1}00]<em>{\text{AlN}}//[\bar{1}100]</em>{\text{sapp}})</td>
<td>-1.9%</td>
<td></td>
</tr>
</tbody>
</table>

An illustration of the \(a\)-plane plane is shown in Figure 2.8. Figure 2.8(a) shows the hexagonal unit cell, with the \(a\)-plane’s orientation within the sapphire unit cell. Figure 2.8(b) shows the arrangement of O and Al atoms on the \(a\)-plane. Figure 2.8(c) shows the planar dimensions of the unit cell as well as dimensions of a larger unit cell with equilateral sides. Figure 2.8(d) shows the reported \(c\)-plane orientations of the AlN on the \((1\bar{1}20)\) sapphire plane.
2.4.1.3 R-plane sapphire

The r-plane sapphire plane, as Table 2.5 indicates, results in a-plane AlN, GaN, and InN non-polar growth. As the growth is not along the c-axis, non-polar III-nitrides have no internal electric field along the normal. Internal fields obstruct radiative combination, decreasing the emission efficiency of emitters. In QW structures grown along the c-axis, this can lead to a redshift and broadening of the luminescence lines.

The two reported AlN growth orientations of (1120)_{AlN}//(10\overline{1}2)_{Sapp} are shown in Table 2.8. Although the orientation [0001]_{AlN}//[10\overline{1}0]_{Sapp} was grown using MOCVD and LPE, and the [1\overline{1}00]_{AlN}//[10\overline{1}1]_{Sapp} orientation was grown by laser ablation, there is no direct evidence that the deposition method was the cause of the difference. There was, however, no mention of sapphire pretreatment with the sample grown by laser ablation. These AlN orientations are at right angles to each other, rotated about the a-plane.
Table 2.8 Reported AlN orientations on r-plane sapphire with lattice mismatch.

<table>
<thead>
<tr>
<th>AlN</th>
<th>In-plane orientation</th>
<th>Mismatch</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-plane (1120)</td>
<td>[0001]<em>{AlN}/[1011]</em>{sapphire}</td>
<td>5.1%</td>
<td>[18,143,147]</td>
</tr>
<tr>
<td></td>
<td>[1100]<em>{AlN}/[1210]</em>{sapphire}</td>
<td>4.6%</td>
<td></td>
</tr>
<tr>
<td>a-plane (1120)</td>
<td>[1100]<em>{AlN}/[1011]</em>{sapphire}</td>
<td>-2.9%</td>
<td>[142]</td>
</tr>
<tr>
<td></td>
<td>[0001]<em>{AlN}/[1210]</em>{sapphire}</td>
<td>13.2%</td>
<td></td>
</tr>
</tbody>
</table>

An illustration of the sapphire r-plane is shown in Figure 2.9. Figure 2.9(a) shows the sapphire unit cell, with the r-plane’s orientation within the unit cell. Figure 2.9(b) shows the arrangement of O and Al atoms on the r-plane. Figure 2.9(c) shows the planar dimensions of the unit cell as well as dimensions of a larger unit cell with equilateral sides. Figure 2.9(d) shows the two reported a-plane orientations of the AlN on the (10\bar{1}2) sapphire plane.

2.4.1.4 M-plane sapphire

As indicated in Table 2.5, both non-polar and semi-polar III-nitrides have been grown on the m-plane sapphire plane. The advantages of semi-polar are the many of those of non-polar. The reduction of the internal electric fields increases the radiative recombination efficiency of III-nitride devices. The semi-polar (11\bar{2}2) orientation has been reported for AlN,\textsuperscript{148,149} GaN,\textsuperscript{153}
and InN. The semi-polar (10\overline{1}3) orientation has been grown on AlN, and non-polar m-plane AlN and GaN have also been observed.

Table 2.9 presents the reported AlN growth orientations on m-plane sapphire. The non-polar m-plane (10\overline{1}0) was the only orientation noted on the films Meinschien et al., grown by laser ablation. The (10\overline{1}0) was an additional orientation seen on the semi-polar (11\overline{2}2)AlN//(10\overline{1}0)Sapp films grown by Lahourcade et al. and Stellmach et al. The semi-polar (10\overline{1}3)AlN//(10\overline{1}0)Sapp was the only orientation observed on films grown by Kaltaev et al., but was an additional orientation seen on AlN(11\overline{2}2) grown by MBE. The creation of AlN(10\overline{1}0) and (10\overline{1}3) oriented domains appearing with AlN(11\overline{2}2) were controlled using the Al/N ratio. MBE AlN growth using an Al/N ratio ~0.85 appeared to prevent the creation of (10\overline{1}0) and (10\overline{1}3) AlN orientations.

Table 2.9 Reported AlN orientations on m-plane sapphire with lattice mismatch.

<table>
<thead>
<tr>
<th>AlN</th>
<th>In-plane orientation</th>
<th>Mismatch</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-plane (10\overline{1}0)</td>
<td>[\overline{1}2\overline{1}0]_//{(0001)}_sapp</td>
<td>-4.2%</td>
<td>[142,148,149]</td>
</tr>
<tr>
<td></td>
<td>[0001]_//{[\overline{1}2\overline{1}0]_sapp</td>
<td>4.6%</td>
<td></td>
</tr>
<tr>
<td>(11\overline{2}2)</td>
<td>[\overline{1}1\overline{2}3]_//{(0001)}_sapp</td>
<td>-9.6%</td>
<td>[148,149]</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}1\overline{1}00]_//{[\overline{1}2\overline{1}0]_sapp</td>
<td>13.2%</td>
<td>[148,149]</td>
</tr>
<tr>
<td>(10\overline{1}3)</td>
<td>[30\overline{3}2]_//{(0001)}_sapp</td>
<td>-9.6%</td>
<td>[143,148]</td>
</tr>
<tr>
<td></td>
<td>[\overline{1}2\overline{1}0]_//{[\overline{1}2\overline{1}0]_sapp</td>
<td>30.7%</td>
<td></td>
</tr>
</tbody>
</table>

An illustration of the sapphire m-plane is shown in Figure 2.10. Figure 2.10(a) shows the sapphire unit cell, with the m-plane’s orientation. Figure 2.10(b) shows the arrangement of O and Al atoms on the m-plane. Figure 2.10(c) shows the planar dimensions of the unit cell as well as dimensions of a larger unit cell with equilateral sides. Figure 2.10(d) shows the three reported orientations of the AlN on the (10\overline{1}0) sapphire plane.
2.4.2 Sapphire pre-treatment

The large lattice mismatch sapphire has with III-nitrides\textsuperscript{18,19} can be allayed by modifying the sapphire surface by nitridation. For III-nitride films grown using metalorganic chemical vapor deposition (MOCVD), nitriding is done by dissociating ammonia on the sapphire surface.\textsuperscript{24,25} When growing films using MBE, nitridation is typically done using ammonia gas,\textsuperscript{26} from exposure to an electron cyclotron resonance (ECR) plasma,\textsuperscript{27,28} or a radio-frequency (RF) nitrogen plasma.\textsuperscript{29,30} Nitriding the sapphire surface has been shown to improve the epitaxy of III-nitride thin films grown atop sapphire.\textsuperscript{20–23,156}

During nitridation, N atoms displace and replace O atoms at the interface, forming a thin layer of AlN\textsuperscript{28} or Al oxy-nitride ([AlN\textsubscript{1-x}O\textsubscript{x}]\textsuperscript{31} or [Al\textsubscript{x}O\textsubscript{y}N\textsubscript{z}]\textsuperscript{25}) on the sapphire surface. When formed, an Al\textsubscript{x}O\textsubscript{y}N\textsubscript{z} layer is unstable, and dissolves under high-temperature growth conditions.\textsuperscript{25} As with an MBE AlN film grown on (0001) Al\textsubscript{2}O\textsubscript{3}, the layer forms an epitaxial relationship of [10\textsubscript{1}0]\textsubscript{AlN}/[11\textsubscript{2}0]\textsubscript{sapp}. By utilizing RHEED patterns \textit{in situ}, previous researchers\textsuperscript{19,26,31,32} have verified the formation of this layer by measuring lattice-constant variations as the RHEED
pattern changes from a sapphire diffraction pattern to an AlN transmission pattern. High resolution imaging by transmission electron microscopy (TEM) has shown the Al$_2$O$_3$/AlN interface to be abrupt.$^{25,31,157,158}$

Previous RF plasma nitridation studies investigated the effects of substrate temperature,$^{19,31–33}$ nitriding time,$^{19,32,34}$ gas flow,$^{32}$ and plasma ions$^{19}$ on the growth of the nitridation layer. Prior studies indicate that temperature controls the kinetics of the nitriding process. Nitriding at temperatures above 700 °C resulted in quicker nitrogen diffusion, but also an increase in NO production.$^{31}$ This leads to faster formation of AlN, but also to non-homogenous coverage of the sapphire surface,$^{19,33}$ also called island growth. Nitriding at 200 °C leads to thin and well-ordered homogenous two dimensional (2-D) AlN layers.$^{31,33,159}$ Heinlein et al.$^{34}$ using X-ray photoelectron spectroscopy (XPS) of RF plasma nitridation, identified two regimes of nitridation: a linear regime, where the amount of N increases linearly with time; and a saturation regime, where the amount of N only slightly increases with time. Results of other groups$^{19,32}$ are in agreement with this. A nitriding study$^{32}$ using flow rates between 2 and 7 sccm (standard cubic centimeters per minute) indicated that the AlN nitridation layer formation is independent of nitrogen flow rate.

Nitriding at higher RF power is preferred due to the higher ratio of atomic to molecular nitrogen.$^{19}$ With ground state energies of 9.76 eV, 12.14 eV, and 13.33 eV, atomic nitrogen has more available energy to break Al-O bonds than the 6.17 eV of the N$_2$(A$^3\Sigma_u^+$) molecular nitrogen. The plasma power used in studies of sapphire surface nitridation with RF plasma has been in the range of 200-600 W$^{19,32,33,35,159,160}$ or not been reported.$^{31,34}$

The concentration of ionic species created by RF sources has been reported to be very small,$^{35,38,40}$ and can be deflected away using charged electrode plates. A nitriding study on the
influence of ionic nitrogen species on nitridation found that the inclusion of ions resulted in a much faster formation of the AlN nitridation layer, but a longer time to achieve complete coverage of the sapphire than with nitriding without ions.\textsuperscript{19} Studies using reactive ion (N\textsuperscript{+}, N\textsubscript{2} \textsuperscript{+}) beams in sapphire pretreatment found an improvement in the crystalline and optical properties of GaN grown by MOCVD.\textsuperscript{161,162}

\section*{2.4.3 LT AlN growth}

\subsection*{2.4.3.1 Prior relevant AlN growth}

As the objective of this work is the growth of thin (<50 nm) AlN films at a temperature within the 400-500 °C range, the search for relevant AlN film growth literature focused on (i) growth of AlN as a very thin film and (ii) growth of AlN as a film grown at temperatures lower than traditional AlN growth temperatures, and (iii) LT growth techniques. The aim of the thin film search, (i), was to find very thin AlN films for comparison with films grown in this work. The purpose of search (ii) was to find LT AlN films, also for comparison. Table 2.10 includes a number of representative AlN films selected from (i) and (ii).

Table 2.10 Prior growth of thin and/or LT AlN films.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>RC FWHM (°)</th>
<th>Substrate</th>
<th>Method</th>
<th>N source (Plasma)</th>
<th>Year</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room Temperature</td>
<td>15, 200</td>
<td>-</td>
<td>GaN on</td>
<td>MBE</td>
<td>(RF)</td>
<td>2015</td>
<td>[58]</td>
</tr>
<tr>
<td>250, 470, 660, 800</td>
<td>15</td>
<td>-</td>
<td>c-Al\textsubscript{2}O\textsubscript{3}</td>
<td>MBE</td>
<td>(RF)</td>
<td>2005</td>
<td>[53]</td>
</tr>
<tr>
<td>700</td>
<td>8, 13</td>
<td>-</td>
<td>c-Al\textsubscript{2}O\textsubscript{3}</td>
<td>MBE</td>
<td>(RF)</td>
<td>2015</td>
<td>[49]</td>
</tr>
<tr>
<td>930, 1130, 1100</td>
<td>15, 65, 200</td>
<td>0.86, 0.72, 0.53</td>
<td>c-Al\textsubscript{2}O\textsubscript{3}</td>
<td>MOCVD</td>
<td></td>
<td>2015</td>
<td>[49]</td>
</tr>
<tr>
<td>700, 800, 900, 1100</td>
<td>20</td>
<td>-</td>
<td>Si(111)</td>
<td>MOCVD</td>
<td></td>
<td>2018</td>
<td>[52]</td>
</tr>
<tr>
<td>400</td>
<td>20</td>
<td>-</td>
<td>Si(111)</td>
<td>MBE</td>
<td>(RF)</td>
<td>1999</td>
<td>[67]</td>
</tr>
<tr>
<td>400</td>
<td>300</td>
<td>5.7</td>
<td>Si(111)</td>
<td>MBE</td>
<td>(RF)</td>
<td>1999</td>
<td>[67]</td>
</tr>
<tr>
<td>600</td>
<td>100</td>
<td>4.4</td>
<td>Si(111)</td>
<td>MBE</td>
<td>(RF)</td>
<td>1999</td>
<td>[67]</td>
</tr>
<tr>
<td>550, 650</td>
<td>400</td>
<td>1.4, 1.2</td>
<td>Si(111)</td>
<td>MBE</td>
<td>(ECR)</td>
<td>1994</td>
<td>[68]</td>
</tr>
<tr>
<td>900-1200 [ten]</td>
<td>100</td>
<td>1.2-0.7</td>
<td>Si(111)</td>
<td>MBE</td>
<td>NH\textsubscript{3}</td>
<td>2017</td>
<td>[119]</td>
</tr>
<tr>
<td>1100</td>
<td>75</td>
<td>0.85</td>
<td>Si(111)</td>
<td>MBE</td>
<td>NH\textsubscript{3}</td>
<td>2017</td>
<td>[119]</td>
</tr>
</tbody>
</table>

AlN passivation layers are used in enhancing the performance of high-electron-mobility transistors (HEMTs).\textsuperscript{163} Faria, et al,\textsuperscript{58} grew a series of thin (15 nm) AlN films over a wide range of temperatures...
of temperatures on $c$-plane GaN by MBE. The films were evaluated for surface morphology and crystallinity. The XRD $\omega-2\theta$ scans indicated a (002) AlN peak for each of the samples, but no full width at half maximum (FWHM) data was published. As this study was the only one that grew thin AlN films at LT, it is included in Table 2.10.

The other representative thin films were selected from AlN layer growth. Including thin layers of AlN to some part of the growth sequence of a thicker III-nitride film is well documented within the literature. These layers include nucleation layers (NLs), buffer layers (BLs), and interlayers (ILs). As the name implies, NLs are an initial layer used to optimize nucleation, which directly influences the mechanical and electrical properties of thin films. NLs are generally thin ($\leq$30 nm),$^{52,53,164}$ but thicker films (160 nm) were also classified as NL.$^{165}$ BLs are layers inserted between two different materials to reduce the defects generated by their dissimilarity. Fälth $et al$, $^{53}$ identifies BLs as >100 nm, and some met that criteria.$^{45,50,51,57,166}$ The remainder of BLs found in the literature were thinner ($\leq$50 nm).$^{46–50,57}$ ILs are also thin ($\leq$25 nm). ILs are layers inserted within a thicker film growth, separating the growth into sections to disrupt the propagation of dislocations within the film growth, reducing stress. ILs are grown at a lower temperature than the film, and can be a different material (e.g., a LT AlN IL within a GaN film), or the same material as the film.$^{54–56,167–169}$

In growth studies that include AlN layers, the efficacy of the layers is evaluated through the characterization of the thicker III-nitride films. In some studies, the layer is characterized as well. There were three layers <50 nm that were characterized. They are included in Table 2.10. Fälth $et al$, $^{58}$ grew two NLs (8 nm, 13 nm) at 700 °C on $c$-plane sapphire by MBE. The two films were evaluated for surface morphology, but not for crystallinity. The Xiao-Hang Li $et al$, $^{49}$ group grew a series of AlN films, ending each at a different stage of the growth evolution. The films
were grown by MOCVD, and the first three stages are included here. The first stage (15 nm) was
grown at 930 °C. The next 50 nm was grown at 1130 °C and the next 135 nm was 1100 °C. Each
stage of growth was characterized for surface morphology and crystallinity. The FWHM rocking
curve of the 15 nm film was less than 0.9°. The Yuan Li et al. group grew a set of four 200 nm
films on Si(111) by MOCVD. Each film was grown with a 20 nm NL, using four different
temperatures. The NLs were characterized by surface morphology.

A search for LT AlN films, that spanned over two decades, did not garner more than a
handful of results. Auner et al., grew a selection of AlN films at 400 °C and 600 °C on Si(111)
by RF PA MBE. No pretreatment of the Si surface was noted. The N gas flow of 20 sccm and a
deposition rate of ~0.5 Å/s infer an Al/N ratio <<1. The relatively smooth surface morphology is
most likely a result of the ratio less than 1. The 600 °C, 100 nm film indicated a greater
crystallinity, with a rocking curve of 4.4° as compared to 5.7° for the 400 °C, 300 nm film. These
results are included in Table 2.10.

Stevens et al., deposited a selection of 400 nm AlN films at 550–900 °C on Si(111) by
ECR PA MBE. The Si substrate was heated to 900 °C prior to implant. Each deposition started
with opening the Al shutter before the nitrogen plasma was started. The gas flow rate was set at 2
sccm and the growth rate ~0.02 Å/s, inferring an Al/N<<1. It was difficult to construe any
information about the surface morphology from the SEM surface micrographs displayed in the
1994 paper, and no other surface data was reported. Rocking curves of the 550 °C and 650 °C
films were estimated to be 1.4 and 1.2 respectively. These two films were added to Table 2.10.

AlN films of two growth studies, considered representative of recent AlN growth, were
also included in Table 2.7. Tamariz et al., grew eleven AlN films (ten at 100nm, one 75 nm) on
Si(111) by MBE using NH₃ for the nitrogen source. One study grew films at 1100 °C while
varying the NH$_3$ flow. The other study grew films over a 900–1200 °C range at a constant ammonia flow. The surface morphology and crystallinity of all films were characterized. Rocking curve FWHMs for the 11 samples were 0.7–1.2°.

### 2.4.3.2 AlN growth diagram

Ideally, epitaxial growth occurs in a layer-by-layer manner, covering the entire growth surface in two-dimensional layers. Ideal epitaxial growth of III-nitrides by PA MBE can be difficult because of the limited migration distance of surface adatoms.$^{170}$ Surface mobility of the adatoms can be enhanced by using a metal/N flux ratio $>1$, which forms a thin adlayer on the nitride surface.$^{171}$ III-nitride films grown under metal-rich conditions displayed better crystalline quality and surface morphology.$^{37,59–62,172}$ However, growing III-nitrides by PA MBE with metal-rich conditions can be problematic. Large metal droplets (1-10 µm in diameter)$^{62–64}$ can form on the growth surface when growing within this metal-rich regime. Investigations of surface morphology as a function of metal/N and growth temperature have developed growth diagrams for GaN$^{173}$ and AlN,$^{64}$ defining specific growth regimes. An adapted version of the AlN growth diagram created by Koblmueller et al.$^{64}$ is presented in Figure 2.11.

![Figure 2.11 AlN growth diagram. Adapted from Koblmueller et al.$^{64}$ Al-rich droplet, Al-rich intermediate, and N-rich growth regimes are identified. Triangle F – AlN grown by Ferro et al.$^{63}$ Hexagon J – AlN grown by Jmerik et al.$^{62}$](image)

The boundaries of the N-rich, Al-rich droplet, and the Al-rich intermediate regimes were experimentally determined. AlN films were grown at temperatures ranging from 775 to 820 °C.
Films grown in the N-rich regime exhibited rough, three-dimensional surfaces, the result of threading dislocations (TD). When using an Al/N > 1, surface droplets formed when growth conditions were outside the window of optimal growth labeled the intermediate regime. An Arrhenius equation was fitted to the droplet and intermediate boundary data

\[
\phi_{Al} - \phi_N = 2.14 \times 10^{15} \text{ nm/min} \times \exp\left(\frac{-3.41 \pm 0.13 \text{ eV}}{kT}\right)
\]

(2.2)

where \(\phi_{Al}\) is the flux of the Al (in nm/min) and \(\phi_N\) is the N flux, set at 2.9 nm/min; \(k\) is the Boltzmann constant and \(T\) is the growth temperature in Kelvin. The activation energy was determined to be 3.41 ± 0.13 eV, which was determined to be in close agreement with the evaporation energy of Al over liquid Al. The observed boundary between two- and three-dimensional growth is explained by the excess of adatoms enhancing surface migration versus the deficiency of adatoms limiting surface migration.

Higher growth temperatures increase the intermediate growth window within the metal-rich regime that avoids droplet formation. As the growth temperature is decreased, the window disappears and droplet formation occurs at near stoichiometric conditions within the metal-rich regime. Koblmueller concludes that very high Al fluxes or low growth temperatures are responsible for Al droplet formation, referred to as the Al droplet regime (Al/N >> 1).

2.4.3.3 LT AlN growth techniques

When growing III-nitride films within the droplet regime, a number of growth techniques have been developed to reduce or eliminate droplets. Droplet density and size can be decreased with an increase in the \(N^*/N_2^*\) ratio. Other techniques involve an interruption of one or both growth material sources. Migration enhanced epitaxy (MEE), was proposed by Horikoshi et al. to achieve layer-by-layer growth of GaAs. Growth is accomplished by alternating between sources. The intent of depositing Al and N separately is to provide an Al adlayer to enhance the
surface mobility of Al adatoms. Short deposits of Al, of 1–4 seconds\textsuperscript{174,175} or up to 30 seconds\textsuperscript{164} are followed with a similarly short exposure to the N plasma. A time delay of 1–2 seconds is sometimes added within the cycle.\textsuperscript{175}

A second growth technique is to periodically interrupt the Al growth while maintaining a constant N flux irradiation of the growth surface.\textsuperscript{61–63} Droplets are eliminated through nitrogen radical beam irradiation, also known as DERI.\textsuperscript{61} Figure 2.11 also displays the temperature and approximate Al/N for AlN films grown by Ferro \textit{et al},\textsuperscript{63} and Jmerik \textit{et al},\textsuperscript{62} with markers F and J respectively. Figure 2.12 illustrates the Al interruption cycles used to grow the AlN films. Figure 2.12(a) displays the Al interrupted growth cycle used by Ferro \textit{et al},\textsuperscript{63} to grow an AlN film at 800 °C. The Al/N ratio is estimated to be \~1.5, from a reported Al flux rate of 3–4 Å/s and N flow of 1.7–2.3 sccm. Figure 2.12(b) illustrates the Al interruption cycle used by Jmerik \textit{et al},\textsuperscript{62} to grow a 720 °C AlN film using an Al/N\~1.3.

Surface formations of films growth within the Al droplet regime at lower growth temperatures are comprised of AlN rather than Al droplets. AlN layers grown at 650 °C by Kaneko \textit{et al}\textsuperscript{176} using an Al/N=1.67, exhibited surface hillocks originating from TDs, and formed large (50–100 nm), flat, triangular islands on the surface when using an Al/N=1.18. In reporting the growth of AlN at 650 °C, Kaneko also states that N\textsuperscript{+} is primarily responsible for AlN growth.
This would appear to counter a mutual conclusion of RF plasma investigations: that N$_2$* is the principal species responsible for III-nitride growth.\textsuperscript{19,36,38} The energy of N$_2$* (6.17 eV) is much closer to the cohesive bond energies of wurtzite nitrides (2.88 eV, 2.2 eV, and 1.93 eV for AlN, GaN, and InN, respectively).\textsuperscript{71,177} Using a minimal N*/N$_2$* ratio (i.e., plasma power), to facilitate III-nitride growth and minimize any detrimental effects from high-energy N* species, is supported by growth studies of III-nitrides grown within the intermediate regime.\textsuperscript{38,39,43,44,178,179} The AlN in this work is grown well outside that region, indicating that a high N*/N$_2$* ratio will be required for growth.
CHAPTER 3

EXPERIMENTAL METHODS

Integral to the fabrication of high quality AlN thin films by PA PVD are the deposition and characterization facilities, as well as the experimental methods used in their growth. This chapter introduces the deposition and monitoring equipment utilized in growing AlN.

Characterization of the film by reflection high-energy electron diffraction (RHEED), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and scanning electron microscopy (SEM) provide evidence in determining and verifying the films’ crystalline structure, stoichiometry, and surface morphology. Equally crucial is the documentation of the procedures used in substrate preparation and AlN growth.

3.1 Overview of the thin film synthesis, characterization and processing facility

The thin film synthesis, characterization and processing facility used at the University of Maine’s Frontier Institute for Research in Sensor Technologies (FIRST) is a unique ultra-high vacuum (UHV) system employing multiple elements all connected by a trolley system, allowing the transfer of samples through all stages of synthesis, processing, and characterization without leaving the UHV system. An overhead view of the facility is shown in Figure 3.1.

Figure 3.1 FIRST Thin film synthesis, characterization and processing facility. Adapted from Mozolf
All of the UHV chambers have the ability to operate at pressures ~ $10^{-10}$ Torr, and are gate valve isolated at their trolley connection. Access to the UHV system is through the entry chamber, which is pumped by a turbo pump. Before they are entered into UHV, samples are attached to holders allowing them to be manipulated within the UHV system. Sample holders are cut from tantalum (Ta) sheet stock. Each holder is 4.5 cm in diameter and has three tabs that extend out past the circumference, spaced 120° apart, allowing the holders to be manipulated and transferred. Samples are attached to holders using short (~10–15 cm) lengths of Ta wire. The wire lengths are spanned across a sample’s corner edges and the wire ends are welded to the holder. Once placed in UHV, samples can be moved from one system to another by the trolley carts. The trolley system maintains UHV using two ion pumps, and is capable of storing 28 samples on two carts. Samples are moved off the carts by lifting the sample off the cart with pick-up manipulators and placing them on transfer arms to be introduced into the respective chamber.

### 3.1.1 Deposition chamber

The deposition chamber shown in Figure 3.2 is a large cylindrical chamber housing deposition sources, process monitors and characterization equipment. The housing and attached equipment is designed to withstand a sustained temperature of ~150 °C for > 10 hrs. when “baking out” the chamber to establish the UHV environment. When the chamber is idle, vacuum is maintained at a base pressure ~$10^{-10}$ Torr with the turbo pump. Chamber pressure while nitriding or film growth can reach ~$10^{-6}$ Torr. Samples enter facedown from the trolley and are locked into a manipulator that rests on the top of the chamber and extends down with a 40 mm range of motion. The manipulator has an axis of rotation along its centerline, allowing for azimuthal rotation during deposition.
Figure 3.2 Side view of deposition chamber.

Figure 3.3 shows a top view of the deposition chamber, indicating the deposition, characterization and monitoring equipment of significant size. Locked into the manipulator facedown, the sample is situated at the center, above the deposition equipment. Included in the illustration: the back of the sample holder, two 6 kW Telemark model 568 linear UHV 4-pocket electron beam (e-beam) sources, an Oxford Applied Research model HD25 RF atom source, a Staib Instrumente model EK-2-35-R differentially pumped RHEED (reflection high-energy electron diffraction) gun, and two magnetrons manufactured by AJA International which can be configured for either DC or RF sputtering, and are both angled away when not in use. Separate sections on the e-beam (§3.1.2), RF source (§3.1.3), and RHEED (§3.2.1) are below.

Figure 3.3 Top view of deposition chamber. Sample and equipment are noted.
Other deposition chamber equipment not pictured in Figure 3.3 include: the Titanium sublimation pump (TSP), the residual gas analyzer (RGA), a boron nitride (BN) heater, quartz crystal oscillators (QCO), and deposition shutters.

The TSP is a Varian Vacion Plus 300 StarCell. It is operated just before bringing a sample into the deposition chamber to remove reactive gases. Normal operating pressure ranges from $10^{-2}$ Torr to $10^{-11}$ Torr. The maximum starting pressure allowed when starting the StarCell is as high as $5 \times 10^{-2}$ Torr.

The mass spectrometer RGA is installed within the deposition chamber to monitor vacuum quality and trace gases. It can operate when chamber pressures are $<10^{-6}$ Torr, and can measure gas partial pressure concentrations in the $10^{-13}$ Torr range. During nitriding and thin film growth, the RGA is used to monitor oxygen and other contaminant gas levels. When preparing the deposition chamber for a bake-out, the RGA can also be used as a helium leak detector.

A BN heater is located above the sample to radiantly heat the back of the holder. Since the sample is loaded with the sample facing the chamber bottom, the sample is heated through its contact with the holder. The heater is designed to reach $\sim 1500$ °C before the BN dissociates. The sample temperature is determined using an S-type thermocouple, calibrated to the surface temperature of the sample holder, and located between the heater and the sample holder. Since the surface temperature of the sample can vary from the sample holder by as much as 100 °C, sample temperatures are verified with a pyrometer targeting the sample through a bottom access window.

Deposition rates of films as well as film thickness are measured in real-time by strategically placed QCOs. The chamber contains three oscillators. One QCO is located at the sample, and one QCO is located at the output of each e-beam evaporator. QCO deposition rates
were determined through tooling factors, which were obtained through profilometry calibrations. The QCO at the output of e-beam 1 (used in this work) has a six-crystal oscillator. With six crystals, the oscillator allows for any one crystal to be exclusive to a designated material. This insures that the measured thickness is not influenced by multiple materials deposited on that crystal.

Deposition shutters are located at the output of each e-beam, the output of the RF plasma source, and at the sample. The sample shutter is located directly below the sample. Its primary purpose is to start and stop growth depositions. It is manually operated and can be held partially open, allowing one sample to be partially exposed, or isolating separate samples on a holder. Because the shutter is situated directly below the sample, it must be fully opened to allow the sample to be lowered for RHEED analysis. The plasma source shutter\textsuperscript{182} is manually operated and used to shield the source when not in use, not used to control or isolate plasma flux. The shutter of each e-beam is located directly above the material pocket exposed to the e-beam. Each e-beam shutter can be operated while that e-beam is in use, and is used to block the effluent material at the source. The e-beam shutter can interrupt material flux to the sample without interrupting the plasma flux irradiating the sample. The shutter on e-beam 1 can be operated remotely by solenoid.

3.1.2 Electron beam source

The films in this work were grown using one of the Telemark 4-pocket electron beam sources. Each pocket can hold 7 cc of material and can be translated to be in line with the electron beam for evaporation. The pockets of both sources are water-cooled. As Figure 3.4 illustrates, an accelerated beam of thermionic electrons, created by a heated filament, is directed into a 270° arc by a magnetic field, and bombards the material within the pocket, causing the
surface of the material to sublime or evaporate. The vaporized material then travels outward from the pocket. Enclosing the pocket is a shield that blocks the effluent material, and an opening in the shield provides an unobstructed path toward the sample. The shield enclosing the pockets of e-beam 1 (used in this work) is water-cooled.

Increasing or decreasing the e-beam current controls the evaporation rate. The beam can also be rastered – rapidly sweeping the e-beam across the surface of the material – to heat the material more uniformly. Rastering was utilized when initially heating the material from ambient temperature, but not used during film deposition. It was found that when the beam is rastered, the metal flux rate can be inconsistent and the operator loses fine control of the evaporation rate.

3.1.3 Radio-frequency plasma source

The HD25 RF plasma source by Oxford Applied Research (OAR) is used for substrate cleaning, nitridation, and nitride thin film growth. A simplified illustration of the plasma source is presented in Figure 3.5. The HD25 creates a plasma within a ceramic cavity through the inductive coupling of an RF excitation coil. Reflected power is minimized by impedance.
matching the resonant cavity to the RF generator. The HD25 operates at 13.56 MHz with a power range of 100 W to 600 W and is equipped with an auto-tuning device. The optical emission spectrum of the nitrogen plasma was observed through the window of the RF cell and monitored using an Ocean Optics Red Tide USB650 spectrometer. When equipped with an alumina discharge tube and aperture plate the RF source may be used with reactive gases. A pyrolytic boron nitride (PBN) discharge tube and 276-hole alumina aperture was used in this work.

The HD25 is designed to operate at chamber pressures $< 7.5 \times 10^{-5}$ Torr. The plasma within the cavity contains ions and neutral reactive atoms. Most of the charged particles are retained within the plasma, and the reactive atoms effuse into the deposition chamber through the aperture plate. Dissociated atoms of the plasma that collide with the inside surface of the discharge tube exhibit a low recombination coefficient and may contribute to the total beam flux. During optimal operation, the flux of ions or electrons that escape the plasma is $< 20$ nA cm$^{-2}$. The HD25 is configured with ion deflection plates, which deflect any ions that have passed through the aperture away from the sample.

![Figure 3.5 RF plasma source. Illustration includes cut-away view of RF coil and discharge tube. RF impedance matching unit and RF generator are electrically connected to the coil at the water exit, generating plasma within a PBN discharge tube. Plasma flux exits through a 276-hole alumina aperture. A spectrometer can observe the plasma through the window. Deflection plates can be charged to deflect plasma ions.](image-url)
3.2 Film characterization

3.2.1 Reflection high-energy electron diffraction

An advantage of UHV deposition systems is the ability of \textit{in situ} monitoring. Reflection High-Energy Electron Diffraction (RHEED) is a powerful tool for monitoring crystal quality and surface morphology. Electrons are emitted from a heated filament and accelerated with an energy from 10 –35 keV. The electron beam hits the sample at a grazing incidence, between 1° and 5°. Since the apparatus does not obstruct the surface, analysis of the thin film growth may take place in real-time.

With the low incidence angle the electron wave vector does not penetrate more than a few atomic layers, making the RHEED technique very surface sensitive. The bulk of the material below the surface can be neglected, and the sample volume can be approximated by a two-dimensional layer. For a flat, smooth, two-dimensional surface of a single crystal, the reciprocal lattice constructed is an array of one-dimensional rods perpendicular to the surface. In scattering theory, the difference between the incident ($k_0$) and diffracted ($k'$) wave vectors is the reciprocal lattice vector ($G$).

$$k' - k_0 = G$$  \hspace{1cm} (3.1)

For elastic scattering, the magnitudes of the incident and diffracted wave are equal. This diffraction condition allows the construction of an Ewald sphere in reciprocal space. The sphere is centered at the point of incidence on the sample, and has a radius of $|k_0|$. Reflections are allowed for all points the reciprocal lattice rods intersect the Ewald sphere surface and project onto a phosphor screen on Laue circles as presented in Figure 3.6.
Figure 3.6 Ewald sphere construction and diffraction geometry of RHEED. (a) Side view. Intersections of reciprocal lattice rods with Ewald sphere correspond to illuminated spots \((L_n)\) on screen. (b) Top view. The parallel and perpendicular lattice vectors of the reciprocal lattice rods are labeled \(g_{\parallel}\) and \(g_{\perp}\). Horizontal spot separation on screen is \(t\). (c) Laue circles as projected on screen. Adapted from Hernández-Calderón and Höchst 183.

Figure 3.6 displays a side (a) and top (b) view of the Ewald sphere construction and diffraction geometry in reciprocal space. Figure 3.6(c) indicates the screen view in real space. The sample is positioned so that part of the incident electron beam misses the sample and directly hits the phosphor screen at \(I\). This spot created by the transmitted beam is labeled the \((000)\) point, and locates the origin of reciprocal space. Specular spot \(S\) is the result of the \((00)\) rod intersection with the Ewald sphere, and is labeled point \((00)\). The rod/sphere intersection points are projected upon the screen in the form of Laue circles, centered at point \(C\). Spots on the circles have a horizontal screen spacing of \(t\). Measured vertically on the screen, halfway between the \((00)\) and \((000)\) points is the shadow edge. The reciprocal lattice vectors \(g_{\parallel}\) (parallel to the incident beam) and \(g_{\perp}\) (perpendicular to the incident beam) indicate the spacing dimensions of the reciprocal lattice rods. Using geometry, equations can be formulated:
\[ n_{g\parallel} = k_0 \left[ \cos \theta - \frac{1}{\sqrt{(L_{\parallel}/L)^2+1}} \right] \]  
Equation (3.2)

where \( n_{g\parallel} \) is measured from the (00) rod, and

\[ n_{g\perp} = \frac{k_0}{\sqrt{(L/nt)^2 + 1}} \]  
Equation (3.3)

which for small angles (\( nt \ll L \)) can be reduced to

\[ n_{g\perp} = \frac{nt}{L} k_0 \]  
Equation (3.4)

which is also measured from the (00) rod.

In addition to the lattice parameters, RHEED can be used to identify other characteristics of films. Real films are not necessarily single crystal with flawless, flat surfaces. Actual growth may be polycrystalline with some surface irregularity. Figure 3.7 illustrates the real space, reciprocal space and RHEED pattern for some surfaces. For an atomically flat and single crystalline surface, as in Figure 3.7(a), the reciprocal rods are sharp and narrow, and the RHEED pattern shows spots arranged in Laue circles, similar to the ideal case presented in Figure 3.7(c). However, in practice, the electron beam does not just interact with the top layer, but penetrates several layers below the surface. The reflection off multiple layers creates interference, varying the intensity of diffraction spots. For a flat surface that is not single-crystal, but composed of small individual domains, as presented in Figure 3.7(b), the reciprocal rods are thicker. This is because reciprocal rod width is inversely proportional to the average domain size. The thickening of the rods appears as streaks in the RHEED pattern.
Surface roughness has the affect of widening the reciprocal lattice rods. If the surface is rough, with multilevel terraces of different widths as presented in Figure 3.7(c), the reciprocal rods vary in thickness. This is due to the electron beam reflecting off upper and lower terraces, generating constructive and destructive interference. A surface may be so rough that it consists of three-dimensional formations as in Figure 3.7(d). With a small incident angle, the electron beam no longer reflects off the surface, but is transmitted through the bulk, creating a transmission pattern. Transmission diffraction patterns are distinguishable from reflection diffraction patterns. They do not lie on Laue arcs or circles, and can be thought of a continuation of the incident electron beam. RHEED becomes less of a surface sensitive tool. The internal quality of the film shows itself in the quality of the diffraction pattern. Wide transmission beams indicate that internally, the film contains grain boundaries, voids, defects, or other limitations to long-range order.\textsuperscript{185}
To quantitatively analyze the RHEED projection, it needs to be calibrated for absolute lattice spacing determination. The calibration is from diffracting off a known substrate in a known crystallographic direction. A calibration equation can be derived using Equation (3.4) with \( g_\perp = \frac{2\pi}{d_\parallel} \), where \( d_\parallel \) is the in-plane atomic spacing between atomic rows parallel to the incident electron beam, and \( k_0 = \frac{2\pi}{\lambda_0} \). For absolute in-plane atomic spacing, the KSA user’s manual provides a calibration method using the following equation:

\[
d_\parallel \times t = L \times \lambda_0 \tag{3.5}
\]

Where \( t \) is the horizontal spacing of vertical streaks or points as measured in pixels by the KSA 400 software on the phosphor screen, \( L \) is the distance between the center of the sample and the phosphor screen, and \( \lambda_0 \) is the electron wavelength. The units are pixel-Angstroms. The right-hand side of the equation is a product of the electron beam energy, and the position of the sample within the chamber. The right side of Equation (3.5) can be difficult to accurately determine. The electron wavelength is calculated from the electron beam energy. The process of positioning the sample within the chamber may alter the distance between the center of the sample and the phosphor screen, and a precise measurement may be difficult to determine. However, once the sample is in place and electron excitation energy has been set, the right-hand side of the equation becomes a constant.

With the right-hand side a constant, the product of the in-plane atomic spacing \( (d) \) and the horizontal pixel spacing \( (t) \) for a given bulk terminated surface is also constant. Equation (3.5) can be modified to correlate the atomic row spacing of a substrate with the atomic row spacing of a grown film, and is presented as Equation 3.6.

\[
d_f = d_s \frac{t_s}{t_f} \tag{3.6}
\]
The variable $d_f$ is the grown film in-plane atomic row spacing, $d_s$ is the substrate in-plane atomic row spacing, $t_s$ is the pixel distance between substrate points, and $t_f$ is the number of pixels measured between film points. For $c$-plane sapphire, with a lattice constant of 4.759 Å, the interplanar distances are 4.1213 Å for \{10\bar{1}0\} and 2.3795 Å for \{11\bar{2}0\}.\(^{19}\) A RHEED pattern and associated line plot of a nitrided sapphire substrate is presented in Figure 3.8. The six equally spaced peaks were identified as sapphire \{10\bar{1}0\} planes. Figure 3.8(a) shows a total pixel count encompassing the six peaks of 229, resulting in an average pixel count between the sapphire peaks of 45.8. The two remaining peaks were 249 pixels apart, making each 124.5 pixels from the center peak. Using Equation (3.8), the peaks spaced 124.5 pixels apart correspond to a lattice plane distance of 1.516 Å, approximately 97.5% of 1.555 Å, identifying the peaks as the AlN \{11\bar{2}0\} planes.

![Figure 3.8 RHEED pattern and associated line plot of nitrided sapphire \{10\bar{1}0\} planes. a) Sapphire and AlN peaks are identified, along with measured pixel distances. b) RHEED pattern of nitrided sapphire \{10\bar{1}0\} planes. Red horizontal line indicates where line plot was taken.](image)

### 3.2.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a useful tool in element identification and the chemical analysis. The technique involves irradiating a material with x-rays to eject...
photoelectrons from core levels of the material. The ejected electrons are counted, along with their respective kinetic energy. The binding energy ($BE$) of an electron in a material is

$$BE = h\nu - KE - \phi$$  

(3.7)

where $h\nu$ is the energy of the incident X-rays, $KE$ is the kinetic energy of the ejected photoelectron, and $\phi$ is the work function. The electron energy levels of an atom are quantized with a distinct set of energy levels giving each a unique spectrum. The position of the peaks can change as elements undergo chemical changes in state, and can also be shifted by charging effects.

The surface sensitivity of XPS is typically described in terms of inelastic mean free path (IMFP). As a basic material parameter ($\lambda$), every material has a specific IMFP, and from the “Universal curve” of IMFP,\textsuperscript{186} for photoelectron kinetic energies seen with XPS (~10 to ~1 keV), the IMFP is generally less than 30 monolayers. The IMFP is used to determine the sampling depth, $d$, defined as the depth from which 95% of the photoelectrons are scattered by the time they reach the surface. Equation 3.8 can be used to calculate the sampling depth:

$$I(E) = e^{-d/\lambda_{m}(E)}$$  

(3.8)

where $I$ is the percentage of electrons that leave the sample without scattering, and $\lambda_{m}$ is the IMFP. The sampling depth, $d = 3\lambda$. This is about 10 nm for most materials. For extremely thin films, the sampling depth can exceed the film thickness. This can prove problematic if the surface film and substrate both contain the same element in similar chemical forms. It may be difficult to distinguish between the substrate and film. This can also be beneficial if the underlying substrate is being used for calibration or normalizing the data. For thicker films, with the sampling depth less than the film thickness, modifying the incident angle can reduce the
effective sampling depth. The finite sampling depth makes angle-resolved (AR)XPS more surface sensitive.

Other means of describing surface sensitivity by XPS include, effective attenuation length (EAL), mean escape depth (MED or ED), and information depth (ID). The EAL is used for overlayer-film thickness measurements and quantitative analyses, and the MED and ID are used as different measures of surface sensitivity.\textsuperscript{187} The numerical values of the terms for a given material and electron energy will be different due to elastic scattering of the signal electrons. Each material has a specific value for IMFP, but the EAL, MED, and ID values also depend on the elastic scattering properties of the sample as well as the particular experimental setup.

When wide bandgap materials such as sapphire undergo XPS, charging effects occur from electrons leaving the surface. The surface becomes positively charged, giving it a higher potential with respect to the detector, and reduces the energy of the electrons. When this occurs, all peaks from material on the insulator are shifted to a higher \(BE\) and need to be calibrated to a standard energy reference. Typically, the C 1s (284.5 eV)\textsuperscript{188} peak or the O 1s (531.0 eV) peak is used. For very thin films where the grown film was less than the sampling depth, the sapphire O 1s peak was used. For films thicker than the sampling depth, the O 1s of surface oxygen was corroborated with the C 1s peak if available. Graphite was used on the samples and sample holders. Both charged and uncharged carbon peaks were usually apparent.

XPS peak analysis can yield information regarding the elemental composition as well as the chemical state of the surface. The electron energy levels of an atom include core levels and valence levels. The core levels are tightly bound to the nucleus, whereas the valence levels are weakly bound. Valence levels are involved with chemical bonding, and change as they interact with the valence levels of other atoms. The energies of core level electrons are not involved in
the bonding process, which makes them less affected by the bonding with other elements. A quantitative analysis of the surface composition can be determined by measuring relative peak intensities. The area of select level energy peaks are integrated and combined with a calibrated sensitivity factor to determine the elemental composition of the surface in terms of atomic percent. Relative sensitivity factors (RSFs) are normalized to the C 1s peak.

A chemical shift occurs when there is a change in the \(BE\) of a core electron due to a change in chemical bonding of that element. Core binding energies are determined by their electrostatic interaction with the nucleus and other electrons. The charge of the nucleus shields each electron from all other electrons in the atom. This shielding changes with the addition or subtraction of a valence electron. Withdrawing a valence electron (oxidation) will increase the \(BE\), and adding a valence electron will decrease the \(BE\). The binding energy of a metal in an oxide compound is higher than the \(BE\) of the metal with itself. Combined with the oxygen, the metal’s valence electron density of the metal is less because of the oxygen. Materials that include more than one chemical state can exhibit peaks with greater FWHM due to the difference in \(BE\) of the multiple states. For certain cases, it may be possible to separate an imbedded peak using certain types of analytical software.

The XPS characterization equipment is housed in the surface characterization chamber. This chamber is connected to the deposition chamber through the trolley system, allowing the sample to be moved and characterized without breaking UHV. This chamber includes a sample heater, microwave-powered electron cyclotron resonance (ECR) plasma source, and RGA. As for the XPS, an achromatic aluminum source (VG Microtech LTD.) was operated at 300 W, which emits Al K\(\alpha\) radiation with \(h\nu = 1486.6\) eV. The photoelectron energy spectra were collected using a SPECS PCU300 Detection Unit with a SPECS PHOIBOS/HSA 3000 Plus
hemispherical energy analyzer, and analyzed using CasaXPS software. Spectra were measured using SpecsLab data acquisition software using a pass energy of 100 eV for all initial survey scans and 20 eV for all high-resolution, narrow scans.

3.2.3 X-ray diffraction

X-ray diffraction (XRD) is a very sensitive analytical tool for structural analysis. XRD can reveal the lattice spacing, orientation, thickness, density, defects, and the mosaicity of textured films. “Texture,” is used as a general term to describe the preferred orientation in a polycrystalline material. Textured films can be classified into one of three defining categories: 1) textured polycrystalline, 2) strongly textured polycrystalline, or 3) textured epitaxial.189 A textured polycrystalline film can be defined as one with grains preferentially orientated normal to the surface, but randomly orientated in the plane, and a distributed grain size. A strongly textured polycrystalline film consists of grains with nearly perfect preferential orientation of all principle axes. The orientation is usually strongly correlated to the substrate. A textured epitaxial film is composed of mosaic blocks in near perfect registry with the underlying substrate, both normal and parallel to the surface.

A model used to understand XRD is Bragg’s Law. As Figure 3.9 illustrates, incident x-rays on a family of lattice planes are specularly reflected from those planes. As the wave-front of x-rays reflect off a plane the waves will constructively interfere if the difference in path length is an integral number of wavelengths. The mathematical condition for constructive interference is Bragg’s Law,

\[ \lambda = 2d_{hkl} \sin \theta \]  

(3.9)

where \( \lambda \) is the wavelength of the x-rays, \( d_{hkl} \) is the spacing between the lattice planes, and \( \theta \) is the angle between the plane and the incident x-rays. When Bragg’s Law is satisfied and the x-rays
are elastically scattered and constructively interfere, the difference between the incident and reflected beams – the scattering vector, \( \Delta k = k_f - k_i \), is parallel to the normal of the crystal plane. If \( \lambda \) is known, the \( d_{hkl} \) spacing can be identified for a given angle \( \theta \). Bragg’s Law is x-ray diffraction in real space.

\[
\Delta k = k_f - k_i
\]

Figure 3.9 Illustration of Bragg’s Law. Incident x-rays (\( k_i \)) specularly reflect (\( k_f \)) off of lattice planes with spacing \( d_{hkl} \), and interfere constructively. The scattering vector (\( \Delta k = k_f - k_i \)) is parallel to the lattice plane

X-ray analysis was accomplished using a PANalytical X’Pert Pro materials research diffractometer (MRD). A photograph of the diffractometer with defined measurement angles and optics is presented in Figure 3.10(a). A simplified schematic diagram of the measurement angles as related to the sample film is presented in Figure 3.10(b).

Figure 3.10 PANalytical Pro MRD diffractometer. a) Photograph with measurement angles \( 2\theta, \omega, \chi, \) and \( \phi \) identified. The x-ray source and incident optics are shown on the right, the goniometer with the sample in the center, and the detector with receiving optics on the left. b) Simplified schematic diagram of the same diffractometer angles as pertaining to the sample being investigated.
3.2.3.1 $\theta$-2$\theta$ scan

The $\theta$-2$\theta$ scan, (also known as a Gonio scan when using $\omega = \theta$) is often the initial scan performed in thin-film characterization. Presented in Figure 3.11, this scan detects crystal planes that are parallel to the substrate and is used in identifying the crystalline structure of a thin film. The result of the $\theta$-2$\theta$ scan also determines what other characterization techniques are called for, as well as the necessary instrument settings. As Figure 3.11(a) illustrates, incident ($k_i$) x-rays are reflected off the sample ($k_f$) to a detector. As the incident angle $\omega$ is swept, 2$\theta$ is also changed so to maintain $\Delta k$ fixed and parallel to the surface. An example $\theta$-2$\theta$ scan of a 31 nm AlN film grown on c-plane sapphire is presented in Figure 3.11(b). Constructive interference creates peaks in x-ray intensity, and the corresponding lattice plane is identified from the 2$\theta$ angle. A drawback to the $\theta$-2$\theta$ scan is that it only probes the planes that are parallel to the surface, meaning it can only identify the planes with that orientation. For a textured polycrystalline material, oriented with the surface plane, but randomly oriented in all other planes, a $\theta$-2$\theta$ scan would not detect the lack of orientation of the other planes.

![Figure 3.11 XRD geometry for $\theta$-2$\theta$ scan. a) Angles $\omega$ and 2$\theta$ are changed while keeping the scattering vector ($\Delta k$) orientation fixed. b) $\theta$-2$\theta$ scan (25°-85°) of a 31 nm AlN film grown on c-plane sapphire identifying the AlN (002) and (004) peaks, and the sapphire (006) peak.](image-url)
The \( \theta-2\theta \) scan can provide information about the lateral grain size of the film plane. The mean grain size, \( D \), can be determined using the Scherrer equation,

\[
D = \frac{K\lambda}{\beta_D \cos \theta}
\] (3.10)

where \( K \) is a constant related to crystallite shape, normally 0.9, \( \lambda \) is the X-ray wavelength in nm, \( \beta_D \) is the \( \theta-2\theta \) peak FWHM in radians, and \( \theta \) is the \( \theta-2\theta \) peak position. The equation indicates that for a given plane, a sharper \( \theta-2\theta \) peak indicates a thicker lateral grain, or crystallite size. Equation (3.10) does not account for microstrain \( \varepsilon \). The effect of microstrain on peak broadening can be derived by differentiating Bragg’s Law, Equation (3.9), with respect to \( \theta \) (in radians), indicating that microstrain FWHM is proportional to \( \tan \theta \), or more specifically,

\[
\beta_\varepsilon = 2\xi \tan \theta
\] (3.11)

where \( \xi \) is the strain distribution. Williamson and Hall\(^{191} \) introduced the approximation that the total FWHM, \( \beta \), was the sum of the crystallite size FWHM \( \beta_D \) and the microstrain FWHM \( \beta_\varepsilon \). Combining Equations (3.10) and (3.11) (along with some algebra) yields,

\[
\beta \cos \theta = C\varepsilon \sin \theta + \frac{K\lambda}{D}
\] (3.12)

where \( C \) is a proportionality constant converting \( \xi \) to \( \varepsilon \). This equation can be plotted as a straight line, plotting \( y = \beta \cos \theta \) against \( x = \sin \theta \), known as the Williamson and Hall plot. Other information that can be obtained from the \( \theta-2\theta \) scan is the macroscopic strain. A film under macroscopic strain results in a peak shift.

With the x-ray source in line focus, the incident optics used for the \( \theta-2\theta \) scan were: x-ray mirror, Ni filter, \( \frac{1}{2}^\circ \) divergence slit, and 10 mm mask. The diffracted beam optics: the 0.18 parallel plate collimator and a 0.02 rad Soller slit. Data was taken using the proportional Xe detector for all scans.
3.2.3.2 X-ray reflectivity scan

X-ray reflectivity (XRR) uses properties similar to thin film interference of visible light, and can be used to determine density,\textsuperscript{192} film thickness\textsuperscript{193} and surface roughness.\textsuperscript{194} XRR scans use the same geometry and optics as the $\theta$-2$\theta$ scan (Figure 3.11(a)), but with the addition of a receiving slit on the refractive optics. An example XRR scan of a 25 nm AlN film is presented in Figure 3.12. In thin-film interference, reflected light waves constructively and destructively interfere based on the film thickness and the material’s index of refraction. X-rays interact weakly with matter, and the index of refraction of x-rays in media is <1. As a consequence, the beam can be totally reflected as it travels from a less dense material into a more dense material. When the incident angle $\omega$ is less than the critical angle, x-rays undergo total external reflection. The reflectance, $R$, from the Fresnel Equations is 1 for all $\omega$ less than the critical angle. The critical angle, $\theta_c \approx \sqrt{2\delta}$, can be shown to be directly related to the density of the material, and is a function of the real dispersive term ($\delta$) of the refractive index, and is usually in the range of 0.1-0.4 degrees for Cu K$_a$ radiation.\textsuperscript{195} As $\omega$ increases above the critical angle, the intensity of $R$ decreases as per the reflectance Fresnel Equation, and can be approximated as $R \approx \omega^{-4}$. As the x-rays penetrate the film, the reflected x-rays undergo constructive and destructive interference. This presents itself as an intensity oscillation, with the period directly related to the film thickness. Information that can be accessed directly from the XRR plot includes film thickness and the critical angle. Further information on thickness and interface roughness can come from modeling the plot with non-linear regression models. Top surface roughness will dampen the XRR curve as a whole, and interface roughness will dampen the oscillations.
3.2.3.3 Rocking curve scan

Rocking curve (RC) scans are used in the analysis of stronger textured films. It is used to indicate the quality of the lattice planes. As Figure 3.13(a) shows, RC scans involve setting the scan geometry for a specific Bragg angle and “rocking” the sample about the ω axis. That specific Bragg angle is determined from the $d_{hkl}$-spacing obtained from the initial $θ-2θ$ scan of the sample. An example RC of a 29 nm AlN thin film is shown in Figure 3.13(b). The RC FWHM in this example is 1.2°. For a perfect crystal, the RC peak will only be present when the crystal is tilted so that the normal of the lattice plane is parallel to the scattering vector. The peak will have some width due to broadening by the instrument and the intrinsic width for that crystalline material. Defects like mosaicity, dislocations, and curvature, disrupt the perfect parallelism of lattice planes. These disruptions further broaden the peak.
Figure 3.13 XRD geometry for rocking curve (RC) scan. a) The scattering vector ($\Delta k$) is fixed and the sample is rocked about the $\omega$ axis. b) RC of a 29 nm AlN film grown on c-plane sapphire with a FWHM of 1.2°.

Using a line focus, the hybrid monochromator, and a $\frac{1}{2}$° divergence slit were the incident optics. The hybrid monochromator combines a graded parabolic x-ray mirror with a Ge crystal to produce an intense, parallel, single monochromatic x-ray beam. The triple-axis RC cradle was used for the diffracted beam optics. In using the triple-axis, the detector can be blocked from observing more than one $\theta$-$2\theta$ angle by a slit on the cradle.

3.2.3.4 Grazing incidence scan

The grazing incidence scan, illustrated in Figure 3.14, is done using a very small (grazing) fixed incident angle. As Figure 3.14(a) illustrates, while holding $\omega$ constant, the detector is swept through $2\theta$ changing both the direction and magnitude of $\Delta k$. Due to the shallow incident angle, grazing incidence is very surface sensitive, and can be used to identify certain plane orientations outside of the surface plane. When wurtzite AlN is grown on c-axis sapphire, the favored lattice orientation is $[10\bar{1}0]_{\text{AlN}}//[11\bar{2}0]_{\text{sapphire}}$, meaning the AlN $[10\bar{1}0]$ direction is azimuthally rotated 30° from the sapphire $[10\bar{1}0]$ direction. The graphical plot of Figure 3.14 includes two grazing incidence scans of a c-axis oriented, 28 nm thick, AlN film. The peak present in Figure 3.14(b) is identified as the (103) AlN plane. When the sample is rotated 30° about the $\phi$ axis, there is no (103) peak, as indicated in Figure 3.14(c). This indicates
that the AlN film in this example is strongly textured. The optics used with the grazing incidence scan were the same optics used with the $\theta$-2$\theta$ scan: incident – x-ray source in line focus, x-ray mirror, Ni filter, $\frac{1}{2}^\circ$ divergence slit, and 10 mm mask – and diffracted – 0.18 parallel plate collimator, 0.02 rad Soller slit, and proportional Xe detector.

**Figure 3.14 XRD grazing incidence scan geometry.**
a) The $\omega$ remains fixed with 2$\theta$ and the scattering vector ($\Delta k$) varied.
b) Grazing incidence scan of a 28 nm AlN film along the [10\bar{1}0] direction indicating the (103) plane.
c) Grazing incidence scan of same AlN after rotating 30$^\circ$ about the $\phi$ axis indicating no (103) plane.

### 3.2.3.5 Pole figure scan

The pole figure (PF) is a stereographic projection showing directional orientation of the material in question. It is an XRD technique to determine the preferred orientation of the grains in a polycrystalline. It is also known as a texture map. Inferring texture and orientation from scans such as $\theta$-2$\theta$ and RC scans could provide misleading information since the scans are limited to show the orientation of the plane parallel to the substrate plane. Figure 3.15(a) illustrates the geometry of a PF scan. While set to look for a specific $d_{hkl}$ spacing, the angular direction of crystal plane normals are mapped out by rotating about the $\chi$ and $\phi$ axis. The map is a hemisphere containing points that represent the poles for the $(h k l)$ planes of the individual grains. Points of films with stronger texture will be more tightly grouped. The hemisphere is then projected onto a plane, creating the pole figure. Figure 3.15(b) is the AlN (002) plane PF of a 28
nm AlN film grown on c-plane sapphire. The center peak is narrow and intense, indicating the film is strongly (002) textured. Three additional peaks are present, spaced 120° apart, and located at about 38.2° χ are identified as the sapphire (104) plane using the International Centre for Diffraction Data (ICDD) database. Using CrystalMaker® software, the sapphire (104) plane is oriented 38.2° from the c-plane surface. The sapphire peaks appear because the dhkl spacing of the (104) sapphire plane is within 1° of the AlN (002) plane. Figure 3.15(c) is the AlN (101) plane PF of the same 28 nm AlN film on c-plane sapphire. The lack of an intense peak at the center indicates that there are not a significant number of grains with (101) oriented parallel to the surface. The six peaks are narrow and intense, and arranged in a hexagonal pattern, indicating that most grains in this AlN film are similarly oriented and that this film is a strongly textured polycrystalline.

With the x-ray source in point focus, the incident optics was the 8 mm polycapillary x-ray lens, with the x-y adjustable mask set to 10×10 mm. The diffracted beam optics was the 0.27 parallel plate collimator and a 0.04 rad Soller slit.

Figure 3.15 XRD geometry for pole figure (PF) scan. a) The scattering vector (Δk), ω and 2θ are set to a specific dhkl spacing. The sample is rotated about the χ and ϕ axis. b) AlN (002) plane PF of an AlN film grown on c-plane sapphire. The center peak indicates the film is (002) textured. Located 38.2° χ from the center peak, the three additional peaks are identified as the sapphire (104) plane. c) AlN (101) plane PF of an AlN film grown on c-plane sapphire. The six narrow peaks set in a hexagonal pattern indicates the film is a strongly textured polycrystalline.
3.2.4 Scanning electron microscopy

In scanning electron microscopy (SEM), a high-energy (0.5-50 keV) electron beam is focused on the surface of a sample. The electrons penetrate the surface and interact with the material, resulting in an emission of electrons and photons from the surface. As the e-beam is rastered, every point the beam strikes on the sample is mapped onto a corresponding coordinate on the operator’s monitor, presenting the operator with a magnified image of the surface very similar to what one would expect to “see” visually. The image brightness is related to the intensity of the detected electrons providing, composition and topographical information.

As the incident electrons interact with the sample, they inelastically scatter with atomic electrons to produce Auger and secondary electrons, and elastically scatter with atomic nuclei to produce backscattered electrons. Most secondary electrons are produced within the first few nm of the surface. Since they are produced through inelastic collisions, the energy of secondary electrons is less than 100 eV. Secondary electrons with energy less than the material work function will not exit the surface. Those that do, exit the surface in all directions. Backscattered electrons, created through elastic scattering with atomic nuclei, come from much deeper within the sample, and have energies comparable to the incident beam. Backscattered electrons are useful for material analysis. Since backscattered electrons come from elastic scattering with atomic nuclei, materials with higher Z numbers (heavier elements) will likely have more backscatter, making their imaging brighter.

The secondary electrons are what make SEM a good tool for surface morphology analysis. The secondary electron detector of the Zeiss NVision 40 SEM is located near the surface beside the sample. Since the detector is not along the axis of the incident beam, it can be shadowed from secondary electrons by surface features, increasing the image contrast.
3.3 Growth of low-temperature AlN

3.3.1 Sample preparation

C-plane sapphire substrates were initially cleaned in an ultrasonic cleaner using a regimen of detergent, acetone, isopropanol, methanol, and deionized water. Substrates were then annealed in air at 800 °C for 12 hours. Before attaching the substrates to the Ta holders, the face of the holders and the backside of the substrates were coated with graphite. Graphite was applied to aid the thermal conductivity between the substrate and the holder as well as provide a surface on the sapphire that the pyrometer could detect. The substrates were held to the holders by placing short strips of Ta wire across the substrate corners, and tack welding the wire ends to the holder. Unless noted, each holder held one sapphire substrate. After attaching the substrates to the holders, they were loaded into UHV onto a cart on the trolley.

After entry into UHV, substrates were transferred to the surface characterization chamber for an initial XPS characterization. Following this, substrates were transferred to the deposition chamber and annealed at 800 °C in O₂ at a chamber pressure of 1.6±0.3×10⁻⁵ Torr for a minimum of 30 minutes to remove any remaining surface hydrocarbons. After annealing, substrates were again characterized by XPS. This second XPS characterization was to assess the effectiveness of the surface hydrocarbon removal. After the second XPS characterization, the samples were returned to the deposition chamber for initial RHEED characterization.

3.3.2 Surface nitridation

During RHEED characterization, the substrate temperature was set and a chamber pressure ~10⁻⁹ Torr was verified. Nitriding did not begin until after the substrate reached the set temperature and the RHEED characterization was complete. The gas flow was set to 1 sccm, and the nitrogen plasma was struck at 100 W.
In most cases, (a) the sample shutter was open when the nitrogen plasma was struck, and as plasma power was increased in 50W increments (ramping) every 5 minutes to the desired maximum RF power (usually 600 W), the sample was exposed to the plasma throughout the entire power transition. Once maximum RF power was reached, the nitriding continued at that RF power for a prescribed time, at which the sample was shuttered, completing the nitriding. One modification of this procedure (b) was to decrease RF power before ending the nitriding, rather than ending it at the maximum power, as in the instance of growing an AlN film with a 300 W plasma after nitriding the sapphire with a 600 W plasma. A third modification of this procedure was to (c) ramp the plasma up to the desired RF power before opening the sample shutter, and carry out the nitriding at a constant power.

Use of the ion deflection plates is noted in the results. Unless noted, the gas flow was maintained at 1 sccm. Chamber pressure was maintained at $1.0 \pm 0.3 \times 10^{-5}$ Torr. RHEED and plasma optical emission spectrum data were recorded in situ. Unless noted, at the end of the nitridation, additional RHEED patterns were recorded for all sapphire substrates.

For those substrates only being nitried, once nitriding was complete, the nitried substrates were returned to the surface characterization chamber for a post nitriding XPS characterization. After XPS characterization the samples were removed from UHV for characterization by XRD.

Those substrates selected for AlN growth as part of the nitridation verification study were attached to holders in pairs, i.e., two substrates on a holder. These substrates were blocked from RHEED monitoring by a shutter temporarily installed in the chamber for another project. Each substrate was nitried separately by shuttering the other substrate on the holder. These were also returned to the surface characterization chamber for a post nitriding XPS characterization. After
characterization, these samples were returned to the deposition chamber for AlN film growth. Once in the chamber, nitrided samples were shuttered as the plasma and e-beam were prepared for deposition. Once prepared, AlN thin films were grown on the substrates by EBE (e-beam 1) using an uninterrupted Al flux as outlined in the low-temperature AlN film growth study described in §3.3.3.

Those substrates selected for AlN growth as part of the AlN growth study were not removed from the chamber after nitridation. Once nitriding was complete, the sample was shuttered until the e-beam was energized, brought up to operational power, and an Al flux rate was established. The shutter was opened, and AlN thin films were grown by EBE (e-beam 1) as part of the low-temperature AlN film growth study described in §3.3.3.

3.3.3 LT growth of AlN

Substrates were nitrided in preparation for the low-temperature AlN growth study using the experimental procedures noted in §3.3.2 above. For samples not removed from the chamber after nitriding, between nitriding and growth the substrate was shuttered at the sample as e-beam 1 was energized and an Al flux rate was established. For pre-nitrided samples placed in the chamber for AlN growth, the sample was shuttered until all growth conditions were met. The ion deflector plates were energized prior to AlN growth. The plasma was set, and monitored by spectrometer. The Al flux rate was constantly monitored, and e-beam 1 was not rastered during deposition to ensure a steady flux rate. Growth thickness was measured by the crystal 6 QCO.

Two methods of AlN film growth were used to grow LT AlN by EBE using e-beam 1. One method grew AlN films using an uninterrupted Al flux. For films grown using an uninterrupted flux, once the desired growth temperature, Al rate, and gas flow were established the sample shutter was opened to start the deposition and closed to end it. The AlN films grown
by this method include the nitridation verification study films, and group A and B films of the low-temperature AlN film growth study.

The other method involved interrupting the Al flux periodically. Group C films of the low-temperature AlN film growth study were grown using this method. The deposition began once the desired growth temperature, Al rate, and gas flow were established, by opening the sample shutter. The Al flux was periodically interrupted by closing the shutter located at e-beam 1, which blocked Al flux to the sample without affecting the sample’s exposure to the plasma. At the completion of the deposition, the sample shutter was closed.

With the exception of the AlN films grown as part of the nitridation verification study, the grown AlN films were characterized by RHEED before removing them from the deposition chamber. Nitridation verification study films were blocked from RHEED monitoring by a shutter temporarily installed in the chamber for another project. After the films were characterized by XPS, they were removed from UHV for characterization by XRD and SEM.
CHAPTER 4

NITRIDING STUDY WITH AlN GROWTH ASSESSMENT

In introducing this chapter, it must be noted that chronologically, the nitriding described in this chapter took place after the growth study, the subject of §5. After successfully growing LT AlN films, the impetus placed on further improving AlN thin films led to this nitriding study. This chapter is placed before the growth chapter because nitriding is a pretreatment, taking place before the growth.

The parameters selected for pretreatment for the samples grown in §5 were based upon a review of nitriding studies. These studies concluded that superior pretreatment occurs when nitriding at low temperatures. Longer nitriding times improve surface morphologies, and nitriding is more effective when using a high N/N₂ ratio.

The scope of this study was to investigate nitriding parameters to optimize the nitriding template, including nitriding temperature and time, plasma power and plasma composition. There are few plasma characterization studies regarding the role of atomic N in nitriding. Most are focused on the role of atomic N in film growth. There are few studies regarding the use of plasma ions in nitriding.

There are no studies that attempt to determine a minimum RF power or N/N₂ ratio necessary for adequate nitriding. The choice of RF power settings is rarely explained. All nitriding studies prior to this work have used a constant RF power when nitriding. No publications have been found investigating the effects of varying the plasma power over the progression of the nitriding.
4.1 The RF plasma

The plasma species generated by the HD25 RF plasma source varies with power. The plasma emission spectrum for five RF powers 200–600 W is illustrated in Figure 4.1. Over the 350–900 nm range, the plasma contains the first- and second-positive N₂ series, the first-negative N₂⁺ series, and the 3 dominant atomic N multiplet peaks at 745, 821, and 859 nm. In addition to the 3 dominant atomic N peaks, 4 other peaks are also labeled. Three of the peaks pertain to the nitrogen plasma, and one peak indicates contamination of the plasma source. The N₂ peak at 380.4 nm and the N⁺ peak at 493.5 nm were used in estimating the ratio of excited species, N/N₂. Using the resolution of the spectrometer, the N/N₂ ratio was estimated by comparing the intensities of the peaks at 493 nm (N⁺) and 380 nm (N₂). The third peak of nitrogen is the N⁺ peak at 648 nm. It is visible above the background of the first-positive series, at lower RF powers, and becomes dominant at higher RF powers.

![Image of the OAR HD25 RF nitrogen-plasma optical emission spectra. The 350–900 nm region of five plasma powers 200–600 W is shown. The N peak at 493.5 nm and N₂ peak at 380.4 nm were used to estimate the N/N₂ ratio. The dominant N⁺ peaks at 745, 821, and 869 nm and the N⁺ peak at 648 nm are noted. The Na contamination peak at 589 nm can be resolved above the background of the first-positive series at 300 W, and increases as RF powers increases.](image)

The fourth peak noted in Figure 4.1 is from the sodium contamination of the alumina aperture. The Na peak observed at 589 nm is a doublet known as the sodium D-lines. The Na doublet can be distinguished above the first-positive N₂ series emissions at 300 W RF power, and
increases for powers above 400 W. Although a number of films grown using this HD25 were
discovered to have small amounts of Na (<1% by XPS), no nitrided samples in this study were
found with Na contamination. A nitridation study\textsuperscript{35} of sapphire using an Oxford CARS-25 and
EPI Unibulb RF plasma source found boron contamination on the sapphire from the PBN
discharge tube. HD25 plasma source used in this study has a PBN discharge tube. No boron
contamination has been found on samples in this study.

![Figure 4.2 OAR HD25 RF nitrogen-plasma optical emissions spectrum. a) Operating at 250 W and 1 sccm gas flow. b) Emissions added when increasing plasma power by 150 W from 250 W to 400 W. c) Emissions added when increasing power by 200 W from 400 W to 600 W.](image)

Figure 4.2 illustrates the intensity added as plasma power is increased from an initial
power of 250 W. This peak Figure 4.2(a) shows the plasma emission spectrum at 250 W, with a
gas flow of 1 sccm. Figure 4.2(b) indicates the intensity added to the spectrum as the plasma
power is increased from 250 W to 400 W. Figure 4.2(c) indicates the intensity added as RF
power is increased from 400 W to 600 W. At lower plasma powers, as in Figure 4.2(a), the
plasma contains 3 to 4 more times N\textsubscript{2} than N. As (b) and (c) in Figure 4.2 indicate, the increase
in power produces much more N than N\textsubscript{2}. 

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At 1.0 sccm and 300 W, the HD25 used in this study produced a N/N₂ ~ 0.3–0.4. Figure 4.3 is a plot of the N/N₂ ratio as a function RF plasma power for sample B of the nitriding study, which is representative of the plasmas used in this work. At 600 W, the value of N/N₂ was usually ~ 0.5–0.6. Observations of nitriding c-plane sapphire with the HD25 using a range of RF powers found that no AlN nitridation layers formed when using a plasma power less than 300 W. Typically, when nitriding at high temperatures (>600° C), the formation of AlN was observed when N/N₂ ~ 0.5, at powers greater than 500 W. The N₂ with a lifetime long enough to interact with the sapphire has potential¹²⁸,¹³¹ energy of 6.17 eV.¹²⁸ This compares with the 9.76 eV to 13.33 eV of the N*.¹²⁸ As plasma power increases, more N⁺ is produced, with more energy to effect sapphire nitriding. Published density function theory (DFT) formation energies of neutral oxygen vacancies include 5.83 eV, 7.08 eV, 10.14 eV, 12.93 eV, and 13.3 eV.¹⁹⁹ With the ion plates on, and at low RF power, most of the species interacting with the sapphire surface are molecular species with a maximum kinetic energy of 6.17 eV. This energy is less than most of the formation energies to create oxygen vacancies in the sapphire.

The ion content exiting the HD25 aperture is estimated to be to <0.1%.³⁵ The presence of ions has been reported to have some effect on nitriding using other RF plasma sources.¹⁹ As RF power is increased above 250 W, the N⁺ peak at 648 nm intensifies, appearing within the first-positive N₂ series. With the ion plates off, N₂⁺ and N⁺ ions exiting the aperture can interact with
the sapphire surface. The minimum energy of N$_2^+$ (15.58 eV) and N$^+$ (24.3 eV) are much higher than neutral species.$^{128}$

### 4.2 Nitriding study

The nitriding study involved investigating the dependence of the nitriding process on RF power, ions, time, and temperature. Table 4.1 shows six representative samples. With the exception of samples C and D, all samples in the study were nitrided using procedure (a) of §3.3.2. Sample D was nitrided as per (b) in §3.3.2, and sample C nitrided as (c) in §3.3.2. Nitriding time took effect when plasma power was ≥300 W. Sample A was used as the representative standard for comparison with other samples in the study. This sample was nitrided at high temperature for a total of 140 min (120 min at RF power ≥300 W) and no efforts were taken to prevent plasma ions from reaching the substrate. Sample B was nitrided using the same conditions as A, except B was nitrided an extra 90 min longer at 600 W. Sample C’s difference from A was that the entire nitridation was at 600 W RF power. Sample D had two nitriding differences, 1) D was nitrided using the (b) procedure of §3.3.2, and 2) for D, the HD25 ion deflection plates were on, deflecting ions away from the sample. The maximum RF power used for nitriding sample E was 400 W. Sample F, nitrided at 450$^\circ$C for a total of 230 min (210 min at RF power ≥300 W) was used as a representative of the nitriding parameters utilized in growing AlN films of §5. As it was nitrided for a longer time, it was compared with sample B.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp $^\circ$C</th>
<th>RF Power $W$</th>
<th>Nitriding time $min$</th>
<th>Ion Plates</th>
<th>AlN onset $min$</th>
<th>XRR Thickness nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>775</td>
<td>100-550</td>
<td>50 600 90 n/a n/a</td>
<td>120 off</td>
<td>38</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>775</td>
<td>100-550</td>
<td>50 600 180 n/a n/a</td>
<td>210 off</td>
<td>40</td>
<td>4.9</td>
</tr>
<tr>
<td>C</td>
<td>775</td>
<td>n/a</td>
<td>600 120 n/a n/a</td>
<td>120 off</td>
<td>10</td>
<td>1.9</td>
</tr>
<tr>
<td>D</td>
<td>775</td>
<td>100-550</td>
<td>50 600 60 550-100 50</td>
<td>120 on</td>
<td>35</td>
<td>1.3</td>
</tr>
<tr>
<td>E</td>
<td>775</td>
<td>100-350</td>
<td>30 400 100 n/a n/a</td>
<td>120 off</td>
<td>38</td>
<td>1.5</td>
</tr>
<tr>
<td>F</td>
<td>450</td>
<td>100-550</td>
<td>50 600 180 n/a n/a</td>
<td>210 off</td>
<td>20</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Included in Table 4.1 is the AlN onset time, measured from initial exposure to the plasma. The AlN onset time should be construed as the time the nitriding layer forms, not that the layer is necessarily pure AlN. The onset of AlN was determined \textit{in situ} through periodic monitoring of the sapphire RHEED pattern during nitridation. Since the RHEED monitoring was not continuous, the onset time was estimated to have a precision of \( \pm 2 \) min. Sample F, nitrided at 450° C, and RF power ramped using procedure (a) in §3.3.2, and Sample C, nitrided at 775° C, and at a constant 600 W as per (c) in §3.3.2 had the shortest onset times. The onset time of the remaining 4 samples nitrided at 775° C and RF power ramped occurred \( \sim 15-20 \) min later.

\textbf{4.2.1 Nitriding study results and discussion}

Samples in the nitridation study were observed with RHEED, analyzed using XPS, and thickness measured with XRR. RHEED line plots are presented in Figure 4.4, and XPS spectra in Figure 4.5. In the analysis of the nitrided samples by XPS, measurements were calibrated to an oxygen 1s binding energy of 531.5 eV, the generally accepted value for O1s in pure sapphire,\textsuperscript{160,200} to compensate for surface charging effects. The XPS spectra of the N 1s photoemission for the six nitriding study samples is shown in Figure 4.5. Lines are drawn at 397.0 eV for AlN and 399.1 eV for the N-O bond of aluminum oxynitride.\textsuperscript{33} The peaks shifted to higher binding energies contain more oxide bonds. For reference, Figure 4.4 includes the RHEED line plots of an AlN film (C-4 of §5.1.3) and a sapphire substrate. Figure 4.5 includes the XPS spectra of an AlN film (C-4 of §5.1.3). The surface charging effects of the 30 nm AlN film was calibrated to a surface O1s binding energy of 532 eV.\textsuperscript{201} This is because the oxygen identified with the AlN film is not sapphire, but surface oxygen.
Samples A and B, both nitrided at high temperature (775°C), nitrided while ramping power, and nitrided for 90 minutes (sample A) and 3 hours (sample B) at 600 W, show relatively narrow peaks centered at the reciprocal spacing corresponding to AlN dimensions from the RHEED line plot of Figure 4.4(A) & Figure 4.4(B). The reciprocal space RHEED pattern of sample B indicated a flat surface with small domains (Figure 3.7(b) of §3.2.1) as well as some modulated transmission streaks (Figure 3.7(c) of §3.2.1). This gives some indication that the surface becomes a stepped, multilevel surface with the extended nitriding time. As for the composition of A and B, the XPS binding energy peaks of Figure 4.5(A) and Figure 4.5(B), are centered about 396.7 eV, just below the 397.0 eV AlN line. The XPS results indicate a minimum number of O bonds within the material. As indicated in Table 4.1, the XRR measured thickness of samples A and B were 1.9 nm and 4.9 nm, respectively.
Sample C, nitrided at high temperature at a constant 600 W for two hours, was grown to a XRR measured thickness of 1.9 nm. The RHEED line plot peaks of C, shown in Figure 4.4(C), appear wider than peaks of samples A and B, and have the highest intensity at the AlN dimension. The XPS binding energy peak of sample C (Figure 4.5(C)) is shifted towards the “N-O” line, with the center of the peak located at roughly 398.6 eV, indicating the presence of N-O bonds within the material. The shape of the binding energy peak indicates that it contains subpeaks of different energies. Subpeaks can be attributed to particular bonds. A XPS analysis of AlN films conducted by Rosenberger et al.,202 identifying N 1s subpeaks, proposed a binding energy of 398.0 eV for AlO$_x$N$_y$ grain boundaries.

Sample D was nitrided at high temperature, while ramping power to 600 W, and with the HD25 ion plates energized. Of the 2 hours D was nitrided with power $\geq$300 W, only one hour was at 600 W. Figure 4.4(D) shows the sample D peak with the greatest intensity at the sapphire reciprocal space dimension, but also some peak broadening located at the AlN spacing,
indicating the presence of an AlN layer. The higher intensity at the sapphire rather than the AlN supports the indication that the AlN film is very thin. The XRR measured thickness was 1.3 nm. The shape of sample D’s binding energy plot (Figure 4.5(D)) showed no distinguishable peaks in the binding energy range 390–405 eV. This made an accurate determination of binding energy for the sample difficult. Additional analysis of the data inferred there may be a peak centered ~398–400 eV, but there was not enough corroborating evidence to confirm this. These results also support the indication of the sample having a very thin nitriding layer.

Sample E, was nitrided at high temperature, was nitrided as power was ramped, was nitrided for 100 minutes using a maximum plasma power of 400 W. The RHEED pattern of sample E showed vertically elongated transmission spots, having traits appearing in the RHEED patterns presented in Figure 3.7(c) and Figure 3.7(d) of §3.2.1. The spots were separate, as in Figure 3.7(d), but also elongated as in Figure 3.7(c). This points to sample E being a multileveled surface of 3-D islands. The RHEED plot presented in Figure 4.5(E) was taken from a horizontal line through a row of transmission spots. The RHEED line plot through the spots appears similar in shape to the reference AlN film sample, with the addition of some peak broadening at the sapphire spacing. Within the vertical spacing between transmission spot rows, were intensities located at the sapphire reciprocal space dimensions, indicating areas between the islands of little, if any, AlN growth. The XRR measured thickness was 1.5 nm. The XPS binding energy plot (Figure 4.5(E)) of sample E did not have a definitively strong peak that could be used to determine a binding energy within the energy range 390–405 eV. An analysis of the data inferred that a peak was centered ~397.2–397.4 eV, but the available evidence was insufficient to verify this. The peak broadening on the RHEED line plot indicates that where the 3-D islands exist, the
nitriding layer covers the sapphire. The lack of a strong binding energy peak indicates that the average thickness of the nitriding layer is very thin.

Sample F was nitrided at low temperature (450° C), ramped while nitriding, and nitrided for 3 hours at 600 W. As indicated earlier, the nitriding parameters used for F are similar to those used in the nitriding pretreatment of the LT AlN films of §5. Other than the nitriding time, the sole difference is that the HD25 ion plates were off when nitriding sample F. The XRR measured thickness was 2.6 nm. The RHEED pattern of sample F was streaky (Figure 3.7(b) of §3.2.1), indicating a 2-D layer surface with small domains. The RHEED line plot peaks (Figure 4.4(F)) are similar in shape to the reference AlN sample, with a slight peak broadening asymmetry similar to that seen with sample E. The binding energy peak (Figure 4.5(F)) of sample F is centered at a binding energy about 397.3 eV, and encompasses both the AlN and “N-O” lines, suggesting that pure AlN is not forming on the surface, but rather a form of AlO_xN_y. The shape of the binding energy peak indicates that it contains subpeaks of different energies. Losurdo et al. has reported that at nitriding temperatures greater than 200° C, N-O formation competes with AlN formation, and that N-O can be incorporated into the nitried sapphire surface.

4.2.2 Effect of ramping RF power on nitriding

Comparing the RHEED and XPS results of samples A and B, which were ramped, to sample C, the only sample nitrided at constant power, indicates that ramping the plasma lowers the oxide content of the layer for high temperatures. The lower initial power would limit the amount of N* at the start of the nitriding. When starting the nitriding when the plasma is struck, the low power plasma may be initially cleaning the sapphire surface and removing surface oxygen rather than growing a nitriding layer from the sapphire corundum. As plasma power is gradually increased, and the concentration of N* increases, the nitriding layer would begin to
form. Also, since the production of $N^*$ is gradually increased, rather than produced at a constant maximum, interactions of the $N^*$ with the interface are slowly increased, allowing time for AlO$_x$Ny to dissolve$^{25}$ over the course of the nitriding. This also appears to be the case at lower temperatures as well, since sample F appears to have a lower oxide content than sample C.

In a comprehensive nitriding study by Yao et al.$^{19}$ sapphire substrates were nitrided with a RF plasma source, using RHEED patterns to chronicle the onset time and time of complete coverage of the nitriding layer. A RF power of 300 W, and gas flow of 0.5 sccm were used for all nitriding. A comparison of high and low temperature nitriding found that the AlN onset when nitriding at 800°C occurred 20 min sooner than when nitriding at 300°C. Yao attributed the later onset to a lower chemical reaction rate at low temperature. The onset time of AlN for sample C, nitrided at high temperature and constant power, appears to follow the Yao’s results. The later onset time of the 4 ramped samples in this study, nitrided at 775°C, also appears to agree with Yao’s findings since the initial $N^*$ concentration of the samples was lower and increases as power was increased, causing the onset delay. The RF power for all the ramped samples was <600 W when AlN onset occurred.

The AlN onset time of sample F, nitrided at 450°C, does not follow Yao’s results. The sample F onset of AlN occurred ~15–20 min sooner than the onset time for the 4 other ramped samples, and only ~10 min later than the sample C AlN onset time, all of which were nitrided at 775°C. The sample F onset occurred at a RF power of 300–350 W. The AlN onset may be sooner at 450°C because the Al-N bonds at the sapphire surface are more stable at low temperature, and at lower RF power there is a smaller influx of $N^*$ atoms, resulting in fewer high-energy species available to disrupt the Al-N bonds.
In comparing the thickness of sample A with C (Table 4.1), the plasma power increase experienced by A over the first 50 min of nitriding does not appear to have an observable effect on nitriding layer thickness. The reduction in RF power over the last 50 min of nitriding sample D may have been a contributing factor in the nitriding layer thickness of sample D.

### 4.2.3 Effect of plasma ions on nitriding

Although the ion content leaving the plasma source aperture was expected to be minimal, the presence of ions was still expected to have an effect on nitriding. Sample D was nitrided with the ion plates energized, thus deflecting the ions away from the sample. The XRR measured thickness of 1.3 nm was the thinnest of all nitriding samples. The RHEED line plot in Figure 4.4(D) show the maximum intensity located at, or closer to, the sapphire dimensions. As noted earlier, it was difficult to identify a peak of any magnitude from the binding energy spectra in Figure 4.5(D). The presence of ions did not appear to have an affect on the onset of AlN.

The nitriding study by Yao et al\textsuperscript{19} included an investigation into the influence of plasma ions on nitriding. As sapphire substrates were nitrided, the amount of ionic species reaching the sapphire surface was controlled with the ion deflection plates. For high temperature (800 °C) sapphire nitriding, the onset of the nitriding layer occurred sooner when plasma ions were allowed to interact with the surface. When plasma ions were deflected away, although the nitriding layer formed later, it took less time for an ion-free layer to completely cover the sapphire. It was suggested that this phenomenon might be the related to the mechanism that N\textsuperscript{+} can be adsorbed on the sapphire in a weakly bound state, and easily removed from the surface through interactions with N\textsuperscript{+}, reducing the coverage, as well as the homogeneity of the nitriding layer.\textsuperscript{35} The study included a GaN film growth comparison, concluding that nitridation without ions improves crystalline quality.
The result of sample D appears to counter Yao’s results, that when nitriding at high temperatures, ions in the plasma lead to thinner and less homogeneous nitriding layers. Plasma ions were not involved in the sample D nitriding layer, which would infer that D should have formed later and been the thickest of the 120 min nitriding layers. Referring to Table 4.1, of the 120 min sample D was nitried, only 60 min were spent at maximum RF power, the shortest time of any sample in the study. From this, it could not be concluded that sample D’s result contradicted Yao’s results, and prompted an investigation into the effect of plasma ions when nitriding at lower temperatures. The result of this investigation is the growth assessment study on the effect of ions in the pretreatment, which is presented in section §4.3.2.

4.2.4 Nitriding at 400 W plasma power

Sample E was nitrided using a lower atomic/molecular nitrogen ratio than other nitrided samples in this study. The N/N₂~0.4 for sample E at 400 W was ~0.1 less than sample A, nitrided at 600 W. The XRR measured thickness of sample E (nitrided for 100 minutes at 400 W) was less than sample A (nitrided for 90 minutes at 600 W). The lower plasma power yielded a lower atomic/molecular nitrogen ratio, meaning less N⁺ and N⁺ to interact with the sapphire surface. Although the minimum concentration of N⁺ that is necessary for nitriding to occur was met with sample E, a greater concentration of N⁺ appears to avoid the formation of island growth on the sapphire surface. More N⁺ available to create vacancies in the sapphire increases the amount of available Al and leads to a higher effective Al/N ratio, promoting layered growth. The adage, “more is better,” applies to the amount of available N⁺ for optimal nitriding.

4.2.5 Nitriding at 450° C

Given the original nitriding for the AlN films grown in §5 was 450° C, sample F was added to the investigation for comparison to the samples nitrided at high temperatures. A direct
comparison of sample F to B (nitrided at 775°C) was possible due to all parameters except temperature being similar. As stated earlier, the extended nitriding time of sample B resulted in a surface with a stepped, multilevel growth. Nitriding sample F at 450°C for the same amount of time as nitriding sample B resulted in a 2-D surface on F as observed by RHEED. Both samples were ramped, and it was shown that for high temperature nitriding, ramping the plasma results in a lower oxide content of the layer. Nitriding at high temperature dissolves the unstable AlOₓNᵧ bonds, lessening the amount of AlOₓNᵧ.²⁵ For nitriding at lower temperatures, this does not appear to be the case. The binding energy location and spectral peak width of sample F indicates the presence of N-O bonds.

Yao also reported that after AlN onset, complete coverage of the sapphire surface occurred much sooner when nitriding at low temperature (300°C). Complete coverage was considered quicker at low temperature because the Al-N bonds at the sapphire surface are more stable. At high temperature, the topmost N atoms on the surface have a greater probability to be removed by incoming N atoms, forming N₂, and reducing the homogeneity of the AlN layer.¹⁹ Nitriding at low temperatures promotes a flatter, more homogeneous surface.³¹,³⁶ The RHEED observations over the nitriding of sample F were consistent with these results.

4.3 Nitriding pretreatment evaluation through AlN film growth

In addition to the 6 nitrided samples in the nitriding study, four AlN thin films – two sets of two – were grown to assess the effect of sapphire surface nitridation in subsequent thin film growth. One set of AlN thin films (i) were grown to verify the effectiveness of nitriding pretreatment. An AlN film was grown on pretreated sapphire and compared with an AlN film grown on sapphire that was not pretreated by nitriding. The second set of AlN films (ii) was grown to assess the utility of plasma ions in the pretreatment plasma. For this set, the ion
deflection plates of the HD25RF plasma source (§3.13) were turned off during the nitriding pretreatment of one of the sapphire substrates. The other substrate was nitrided with the ion plates on. AlN films were grown on both pretreated substrates and compared.

4.3.1 Effect of nitriding pretreatment on LT AlN thin film growth

The verification that nitriding pretreatment is beneficial to AlN growth was performed by comparing an AlN film (sample W) grown on pretreated sapphire with an AlN film (sample X) grown on sapphire that was not pretreated by nitriding. Prior to entering UHV, samples W and X were chemically cleaned using the procedure of §3.3.1, and attached to the same holder. Table 4.2 shows the nitriding and growth parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion Plates</th>
<th>Nitriding Temp. °C</th>
<th>Time at plasma power min</th>
<th>Maximum N Flow sccm</th>
<th>Growth Plasma Temp. °C</th>
<th>Power W</th>
<th>Al Rate (ave.) Å/s</th>
<th>Ion Plates</th>
<th>XRR Thickness nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>off</td>
<td>600</td>
<td>600</td>
<td>65</td>
<td>90</td>
<td>1</td>
<td>450</td>
<td>550</td>
<td>1.8</td>
</tr>
<tr>
<td>X</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1</td>
<td>450</td>
<td>550</td>
<td>1.8</td>
</tr>
</tbody>
</table>

W was nitrided at a temperature of 600° C for 90 min at plasma power ≥300 W, with 65 min at 600 W using procedure (a) of §3.3.2. Plasma ions were not deflected away, as the HD25 plasma source ion plates were off. During the nitriding pretreatment of W, the sample shutter was positioned to block sample X from the plasma output flux. After both were nitrided, both samples were characterized by XPS. Sample W indicated a N 1s binding energy peak centered at ~397.3 eV, the N 1s binding energy observed on sample F. There were no N 1s peaks found on sample X. After post-nitriding XPS characterization, a 94 nm (measured by XRR) AlN film was grown by EBE on both films at the same time as per §3.3.3 using an uninterrupted Al flux rate of ~1.8 Å/s, with gas flow of 1 sccm. Growth temperature was 450° C. The plasma power during growth was 550 W due to intermittent power fluctuations of the RF generator output when
operated at 600 W. The HD25 plasma source ion plates were on for the AlN growth, deflecting plasma ions out of the plasma flux.

Figure 4.6 Nitriding assessment a) growth cycle, b) θ-2θ plots, and c) SEM images.

The Al and N rates corresponded to an Al/N ratio ~1.5 >1, i.e., AlN growth was within the metal-rich regime, as described in §2.4.3. Figure 4.6(a) shows a graphic of the growth cycle, illustrating the relative Al/N flux ratio. The XRD θ-2θ scan presented in Figure 4.6(b), using a log intensity scale to augment low intensity peaks, indicated both (002) and (101) AlN orientations on each film. Results of the XRD scans are also displayed in Table 4.3. The (002) peak on sample W, the pretreated sample, was more intense than the (101) peak, with a FWHM of 0.53°. The lateral grain size, calculated from the Scherrer equation is 13.3 nm. The (101) peak was not intense enough above background intensity to determine a FWHM. Both θ-2θ peaks on sample X were close to background, with the (101) peak slightly more intense than the (002) peak, and neither peaks intense enough to determine a FWHM. Rocking curve measurements of the two films did not contain peaks intense enough above background to determine a FWHM.
Table 4.3 Nitriding assessment XRD FWHM values. Corresponding $\theta$-$2\theta$ lateral grain sizes are calculated from the Scherrer equation. Intensities of all peaks except the W (002) AlN peak were too close to background intensity to determine a FWHM value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$-$2\theta$ FWHM ($^\circ$)</th>
<th>Lateral Grain Size (nm)</th>
<th>$\theta$-$2\theta$ FWHM ($^\circ$)</th>
<th>Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>0.53</td>
<td>13.3</td>
<td>undetermined</td>
<td>undetermined</td>
</tr>
<tr>
<td>X</td>
<td>undetermined</td>
<td>undetermined</td>
<td>undetermined</td>
<td>undetermined</td>
</tr>
</tbody>
</table>

The formation of the two predominant (002) and (101) planes, shown in Figure 4.6(b) is supported with an examination of the lattice planes involved. A cross-section of the (002) and (101) AlN planes (blue), and c-plane sapphire growth surface (red) are presented in Figure 4.7. Figure 4.7(a) shows a cross-section of the (002) AlN surface aside and atop the c-plane sapphire surface. The hexagonal pattern of the Al (blue) follows a similar orientation as of the sapphire (red). The (002) plane has the lowest surface energy of the AlN planes, making it thermodynamically favorable.\textsuperscript{205,206} Figure 4.7(b) compares the (101) AlN surface to the same sapphire surface. Portions of the (101) pattern align with the sapphire surface. Either (002) or (101) orientation appears as likely to initially form, but the lattice parameters of sapphire would discourage the continual formation of a uniform (101) oriented surface AlN. Any (101) textured AlN grown from the sapphire would likely have no other common orientation. A sapphire surface that is pretreated by nitriding, forming an oriented AlO$_x$N$_y$ layer atop the sapphire surface, would more closely match the dimensions of (002) AlN, favoring the growth of that orientation over the (101). With no pretreatment, the $\theta$-2$\theta$ results of sample X in Figure 4.6(a) indicate that neither orientation is favored since the film appears polycrystalline.
Figure 4.7 Comparison of c-plane sapphire and AlN surface dimensions. a) Comparison of sapphire to (002) AlN plane. b) comparison of sapphire to (101) AlN plane. Bonds shown are Al–N and extend out from the surface. Images created using CrystalMaker®, CrystalMaker Software Ltd (www.crystalmaker.com)

SEM images of samples W and X, presented in Figure 4.6(c), show a visibly rough surface, attributed to growth in the Al-rich regime. SEM analysis, utilizing backscattering electrons, indicated no Al droplets on the surface. Rather than producing Al droplets,62,63 as observed with Al-rich growth at high temperature, the growth conditions resulted in AlN hillocks, similar to those described by Kaneko et al176 on AlN grown at 650°C. Both surfaces included a number of large surface features measuring at least 200 nm across. A significant difference in the two samples was the shape and size of these features. All the large features on the pretreated sample (W) were triangular in nature, with the largest measuring over 2 µm across. Triangular features have been observed on LT AlN films, grown by sputtering at high deposition rates,207,208 and are indicative of the (101) orientation. The largest surface feature observed on X, the sample not pretreated, was nearly 900 nm across, and 5-sided. Most large surface features on sample X tended to have no common shape.

Since θ-2θ scans only identify parallel planes, and rocking curve scans are limited to the orientation of one plane type for a fixed θ, the θ-2θ and rocking curve scans can only indicate that texture is present in these AlN thin films. A more complete determination of the preferred orientation was conducted with pole figures. Since a PF is a two-dimensional projection of a three-dimensional film, each grain of material contributes to the pattern. Films with stronger
texture show a tighter grouping of the pattern from the contributions since more material within the film is oriented. Films with weaker texture are less oriented, and indicate this with pole figures that display a broader distribution pattern since fewer grains are similarly oriented.

The texture of both films was investigated with pole figures. Figure 4.8 & Figure 4.9 compare the (002) plane of samples W and X. Figure 4.8 are full pole figures plotted on a square-root scale with similar intensity color scales. Figure 4.9 presents the projections using a linear scale with the intensities greater than 250 and less than 90 removed to highlight low intensity features. Much of the “hour-glass” type image seen on many pole figures presented in this work is an artifact of the equipment, and is not related to the sample. The 3 sharp peaks on Figure 4.8 (holes on Figure 4.9) spaced 120° apart along φ and located at a χ angle of 38.2°, are identified as the sapphire (104) plane using ICDD database powder diffraction files.197

![Figure 4.8 Nitriding assessment (002) plane pole figures. The (002) plane is parallel to the surface as indicated by the center peak. The 3 additional peaks at 38.2° χ indicate the sapphire (104) plane.197](image)

The center peak of the pretreated sample (W) shown on Figure 4.8(a), confirms the θ-2θ scan that the sample has (002) texture. The PF for an ideal c-axis oriented wurtzite film would have an intense center peak with no other peaks. The circular ridge on Figure 4.8(a) & Figure 4.9(a), located at 61.6° χ is evidence that W has some (101) texture. The circular ridge indicates that the grains with the (101) plane parallel to the surface are otherwise randomly oriented. Sample X, not pretreated, shows some (002) texture as evidenced from the center intensity on
Figure 4.8(b) and Figure 4.9(b). The low intensity of the center peak confirms that the sample has very little (002) texture, a confirmation of the sample X $\theta$-$2\theta$ scan in Figure 4.6(b). Since the $\theta$-$2\theta$ scan of X in Figure 4.6(b) also indicated some (101) texture, the lack of a perceptible intensity ring at $61.6^\circ\chi$ on Figures 4.8(b) and 4.9(b) suggests that X is nearly polycrystalline.

Figure 4.9 Nitriding assessment (002) pole figures without high and low intensities. A center hole and three surrounding holes indicate an intensity greater than 250. Intensity scale is the same for both plots.

Figure 4.10 illustrates the $61.6^\circ$ separation between the AlN (002) and (101) planes in red and green, respectively. With the AlN (002) plane parallel to the surface, as in Figure 4.10(a), the (101) plane is angled $61.6^\circ$ from the surface plane. As the (002) grains become randomly oriented in the plane, the (002) PF would still observe a peak at $0^\circ\chi$, but the 6 peaks seen with a (101) PF will begin to appear as a ring of intensity encompassing $360^\circ\phi$ at $61.6^\circ\chi$. A film with the (101) plane parallel to the surface, as in Figure 4.10(b), a PF scan of the (002) planes will observe the (002) plane at $61.6^\circ\chi$. If the (101) plane grains are randomly oriented, the (002) plane will be observed as a ring at $61.6^\circ\chi$, as in Figures 4.8(a) & 4.9(a).

Figure 4.10 Relative orientation of the (002) and (101) AlN planes. a) The (002) AlN plane orientation (red line) parallel to the surface with $61.6^\circ$ offset (101) plane orientation (green lines). b) The (101) AlN plane orientation (green line) parallel to the surface with $61.6^\circ$ offset (002) plane orientation (red lines). Images created using CrystalMaker\textsuperscript{®}, CrystalMaker Software Ltd (www.crystalmaker.com)
Figure 4.11 presents the (101) pole figures of the W and X samples. Both have similar maximum intensities and are plotted on a linear scale. The (101) plane PF for an ideal c-axis oriented wurtzite film would have a hexagonal distribution of 6 intense peaks, each spaced 60° φ apart, located radially from the center at 61.6° χ. There would be no other peaks. Here, a center peak is visible on both plots, indicating the (101) orientation parallel to the surface.

Sample W (Figure 4.11(a)) show some hexagonal symmetry of wurtzite, as well as parts of a circular ridge connecting the (101) peaks. The center peak of W is the most intense peak, corroborating the presence of (101) planes parallel to the surface as indicated on the W θ-2θ scan of Figure 4.6(b). The line at 61.6° χ that encircles the center, includes peaks and less intense ring. As noted earlier, the ring indicates that most of the grains with their (002) plane parallel to the surface are randomly oriented about their c-axis. Below the PF of Figure 4.11 is an intensity vs. φ plot of the circumscribed line at 61.6° χ. It allows for a direct side-by-side comparison of the peak intensities and FWHM of the (101) peaks. The average FWHM of the W (101) peaks along the 0–360° φ line is 10.8°.

The center peak of the X (101) plane PF is the most intense peak of Figure 4.11(b). This confirms the (101) texture indicated on the sample X θ-2θ scan of Figure 4.6(b). There are no
discernable peaks or ring at 61.6°χ on Figure 4.11(b), as indicated by the intensity vs. φ plot of X and the dotted line drawn at 61.6°χ on the PF. Since the (002) pole figures of X (Figures 4.8(b) and 4.9(b)) had indicated some c-axis orientation, the lack of a ring of higher intensity at 61.6°χ suggests that X is nearly polycrystalline.

An interesting feature of the X (101) PF are the 3 intensities located at 38.2°χ, spaced 120° apart along φ, and identified as the sapphire (104) plane. These peaks are present on other AlN (101) plane pole figures, but are only noticeable on the X (101) PF due to the low AlN (101) intensities of sample X. Although W, the pretreated sample, can be considered a very poor quality film, it is significantly more textured than X, the sample that was not pretreated. The XRD analysis indicates that W contained more oriented c-axis AlN than (101) oriented AlN, and much more c-axis oriented AlN than X. From this, it can be concluded that the nitriding pretreatment improves film crystallinity, and promotes c-axis AlN growth on c-plane sapphire.

4.3.2 Effect of ions in the pretreatment on LT AlN thin film growth

The second assessment regarding the usefulness of plasma ions in the pretreatment, was done by comparing an AlN film (sample P) grown on sapphire pretreated with the ion plates of the HD25 plasma source off (not deflecting the plasma ions within the N flux), with an AlN film (sample Q) grown on sapphire with the ion plates on (deflecting aside the plasma ions within the N flux). As with the nitriding verification study, prior to entering UHV, samples P and Q were prepared as per §3.3.1, and attached to the same holder. Table 4.4 shows the nitriding and growth parameters of the growth set.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion Plates</th>
<th>Nitriding Temp °C</th>
<th>Time at plasma power W min</th>
<th>≤ 300W W min</th>
<th>N Flow sccm</th>
<th>Growth Plasma Temp. °C</th>
<th>Power W</th>
<th>Al Rate (ave.) Å/s</th>
<th>Ion Plates</th>
<th>XRR Thickness nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>off</td>
<td>600</td>
<td>600</td>
<td>120</td>
<td>150</td>
<td>1</td>
<td>450</td>
<td>600</td>
<td>1.1</td>
<td>on</td>
</tr>
<tr>
<td>Q</td>
<td>on</td>
<td>600</td>
<td>600</td>
<td>120</td>
<td>150</td>
<td>1</td>
<td>450</td>
<td>600</td>
<td>1.1</td>
<td>on</td>
</tr>
</tbody>
</table>
Since sample P was nitrided with the ion deflection plates off, and sample Q was nitrided with the ion plates on, they were nitrided at different times. Each was nitrided at a temperature of 600° C for 150 min at plasma power ≥300 W, with 120 min at 600 W using procedure (a) of §3.3.2. As either sample was pretreated, the sample shutter blocked the other sample from the plasma flux. The in situ monitoring by RHEED was not possible as the samples were located behind the shutter at an elevation above and out of the RHEED electron beam path range. The samples were blocked from a post nitriding RHEED by an additional shutter temporarily installed in the chamber for another project. After pretreatment, the samples were removed to the characterization chamber for XPS and then returned to the chamber for growth.

![Figure 4.12 XPS N 1s photoemission spectra of nitrided sapphire samples P and Q. Vertical lines are drawn at binding energy 399.1 eV, corresponding to the N-O bond, and 397 eV, corresponding to the Al-N bond. Material that contains more oxide bonds is shifted left. Sample peak heights are normalized to Al 1s.]

The XPS characterization of samples P and Q provided additional information into nitriding time, temperature, as well as the influence of ions in the nitriding. As shown in Figure 4.12, XPS spectra of the nitrided surface prior to AlN film growth indicated that both nitrided layers contained AlOxNy compounds. The peak shapes indicated that both peaks contained subpeaks. The N 1s binding energy peak of P was about 397.3 eV, nearly the same as samples F and W. When the N 1s peaks were normalized to the Al 1s peak, the intensities of P and F were found to be nearly identical, and the W peak intensity was not significantly higher than sample E.
Samples W and P were nitrided under the same conditions of temperature, plasma power, gas flow, and use of plasma ions. As Table 4.2 presents, sample W was nitrided at 600° C for 90 min with RF power $\geq$ 300 W, including nitriding ~1 hour at 600 W. As Table 4.4 shows, P was nitrided an additional hour at 600W, for a time of 120 min at 600 W, and a total nitriding time with RF power $\geq$ 300 W of 150 min. Samples F and P were nitrided under different temperatures and times. As presented in Table 4.1, F was nitrided at a temperature 150° C lower than sample P, but was nitrided an additional hour at 600W, with a total nitriding time of 210 min with RF power $\geq$ 300 W.

The thickness of the nitridation layers on W, P, and Q were not measured by XRR. An attempt to determine thickness by angle resolved XPS\textsuperscript{209–211} was inconclusive. Using the normalized N 1s binding energy peak intensity to infer thickness, in comparing sample P to sample W, it appears that the additional hour sample P spent nitriding at 600 W noticeably increased the nitriding layer thickness. This result concurs with studies of nitriding time using XPS by Heinlein \textit{et al.}\textsuperscript{21,34} who identified two regimes of nitridation, (i) a linear increase in N 1s peak intensity as the surface is initially exposed to N\textsuperscript{+}, followed by (ii) a saturation regime with a slight increase in N 1s peak intensity. At 600° C the linear increase can last through the first 200 min of N\textsuperscript{+} exposure.\textsuperscript{34} In comparing sample P to sample F, the extra hour sample F spent nitriding at 600 W did not appear to increase the nitriding layer thickness, suggesting that the additional time F spent nitriding was within the saturation regime rather than the linear region.

The time length of the linear increase regime (i) appears to be dependent on substrate temperature. At 400° C, the linear increase can last through the first 300 min of exposure to N\textsuperscript{+}.\textsuperscript{21} This suggests that sample F, with a nitriding temperature 150° C lower than samples W and P, could have been still nitriding within the linear region. If this were the case, with the N 1s

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intensities of F and P being similar, the nitriding layer of sample F grew slower. However, without additional data, there is insufficient evidence to determine the nitriding regime of sample F at the end of 210 min. This does infer that the nitriding time should be maximized to insure the saturation regime is reached.

As for sample Q, having no ions influencing the nitridation, the 1 s N binding energy peak was centered at ~398 eV. Normalizing the Q binding energy peak indicated that it was about half the intensity of P. There was no RHEED pattern to assess the chemistry and AlN onset time. After XPS characterization, nitriding samples P and Q were returned to the deposition chamber for AlN film growth.

As Figure 4.13 illustrates, P and Q were grown using a constant Al flux rate of ~1.1 Å/s, and a gas flow of 1 sccm, placing this within the N-rich regime, as described in §2.4.3. AlN was grown on both films simultaneously to a XRR measured thickness of 120 nm, at temperature of 450° C, using a 600 W plasma power. The XRD \( \theta-2\theta \) scan presented in Figure 4.13(b), with lower intensity peaks augmented by the log intensity scale, indicated both AlN films were \( c \)-axis oriented. Sample P had a \( \theta-2\theta (002) \) FWHM of 0.39° with an intensity ~1.5 times the intensity of
Sample Q had a slightly narrower (002) FWHM, 0.35°, but also showed the presence of a (101) AlN orientation. The results of the XRD scans are listed in Table 4.5 along with calculated grain size. Rocking curves for P and Q were 3.4° and 4.0°, respectively. These are narrower rocking curves than the 4.4° achieved on a 100 nm AlN film grown at 600° C and the 5.7° RC of a 300 nm AlN film grown at 400° C, both grown on Si by Auner et al.67

Table 4.5 Nitriding ions assessment XRD FWHM values. Corresponding θ-2θ lateral grain sizes are calculated from the Scherrer equation. Intensities of (101) peaks were too close to background intensity to determine a FWHM value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>θ-2θ FWHM (°)</th>
<th>AIN (002) Lateral Grain Size (nm)</th>
<th>RC FWHM (°)</th>
<th>AIN (101) Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.39</td>
<td>23.1</td>
<td>3.4</td>
<td>undetermined</td>
</tr>
<tr>
<td>Q</td>
<td>0.35</td>
<td>21.8</td>
<td>4.0</td>
<td>undetermined</td>
</tr>
</tbody>
</table>

The SEM images of samples P and Q presented in Figure 4.13(c) appear similar, and are devoid of the surface formations seen on W and X. The smoother surface is attributed to having grown the samples within the N-rich regime using an Al/N~0.9. Because many mechanical properties of GaN and AlN are similar, both share similar growth parameters. A common consensus is that a technique or condition that applies to GaN growth will also apply to AlN.36,71,74,99 If this is the case, the plasma ion influence on nitriding found in this study does not appear to agree with that reported by Yao et al.19 GaN films grown by Yao on sapphire nitrided without the influence of ions were reported to have narrower (002) θ-2θ and RC FWHM than GaN grown on sapphire nitrided with the influence of ions. Additionally, the surface morphology of the GaN samples was affected by ions in the plasma. The GaN grown on the ion influenced nitridation layer showed a surface of flat mesas separated by deep ditches. The GaN grown on an ion-free nitridation layer showed an atomically flat surface. Growth parameters of the GaN were not reported.
The texture of both films was investigated using pole figures. A comparison of the P and Q (002) planes is presented in Figure 4.14, plotted on a square-root scale. The peak intensity of P was approximately twice the intensity of Q, which follows the intensity difference of P and Q seen in the $\theta$-2$\theta$ plot. Additionally, the (002) planes were plotted on Figure 4.15, using a linear scale with the high and low intensities removed.

![Figure 4.14 Nitriding ions assessment (002) plane pole figures. The center peak indicates the (002) plane parallel to the surface. The 3 additional peaks at 38.2° $\chi$ indicate the sapphire (104) plane.](image1)

Figure 4.14 (a) and (b) indicate that both plots have a strong center peak and no other AlN peaks, indicating a single orientation texture with the (002) plane parallel to the surface. The 3 sapphire (104) plane peaks are present. The sample pretreated with ions (P) has a narrower and more intense peak than the sample pretreated with ions deflected away (Q). The truncated plots of Figure 4.15 did not reveal any additional orientations.

![Figure 4.15 Nitriding ions assessment (002) pole figures without high and low intensities. The center hole and three surrounding holes indicate an intensity greater than 250.](image2)

Figure 4.16 presents a (101) plane pole figure comparison of samples P and Q, both plotted using a linear scale. Both plots show the hexagonal symmetry of wurtzite, and both
indicate the outlines of a circular ridge at 61.6°χ connecting the (101) peaks. The high intensity of the 6 peaks at 61.6°χ on Figure 4.16(a) is evidence that most of the c-axis oriented AlN grains of P are oriented and not polycrystalline about the c-axis. The small center peak of P indicates a minimal number of grains are oriented with (101) plane parallel to the surface. This indicates an orientation that the θ-2θ scan results of Figure 4.13(a) did not detect. The large center peak observed on Figure 4.16(b) indicates that Q has more grains with the (101) plane parallel to the surface, which corroborates the θ-2θ scan. The less intense set of 6 peaks along 61.6°χ is evidence that there are fewer c-axis oriented grains than P, which is in line with the center peak intensities of the (002) pole figures (Figure 4.14).

Below each PF on Figure 4.16 is an intensity vs. φ plot of the circumscribed line at 61.6°χ. The intensity plots indicate much stronger and narrower peaks for the sample pretreated with exposure to ions. The average FWHM of the ion-pretreated peaks (P) was 7.5°. The average FWHM for sample Q peaks was 10.1°. The determination from the XRD analysis is that sample P, the AlN film grown on the sapphire nitrided with the ion plates off, shows a stronger texture than sample Q.

![Figure 4.16 Nitriding ions assessment (101) plane pole figures. The six peaks at 61.6°χ indicate an oriented (101) plane. A center peak indicates (101) plane parallel to the surface. Below each PF is an intensity vs. φ plot of a circumscribed line at 61.6°χ showing intensity comparison of the (101) peaks.](image-url)
4.4 Chapter conclusions

Nitriding pretreatment is an essential step in growing high quality AlN. The formation of the nitriding layer on sapphire can be influenced by substrate temperature, plasma ions, and plasma power. What made this study unique was the treatment of plasma power. Rather than use a constant plasma power, in most instances the first 50 min of the nitriding occurred while plasma power was increased, defined as ramping.

The object of nitriding is to form a thin layer AlN or AlO$_x$N$_y$ on the sapphire surface. Ramping the plasma was found to lower the presence of oxides within the layer. Oxides within the layer were further reduced when plasma ions were utilized along with the ramping. Oxides were minimized when the plasma was ramped, ions were utilized, and the nitriding was at high temperature (775°C).

Assessments of the nitriding verified that nitriding is crucial for growing high quality AlN. Nitriding at low temperatures (≤600°C) may require over 90 min at ≤300 W for an adequate nitriding layer to form. The crystallinity of the AlN films improved when ions were utilized in the nitriding pretreatment. As this was a nitriding study, further discussions on the growth and surface morphology of the AlN growth assessment will be included in the growth chapter.
CHAPTER 5

GROWTH OF LOW TEMPERATURE AlN

The objective of this portion of the research was to grow high quality AlN thin films at low temperatures, below 500 °C. A growth method in which the Al flux was periodically interrupted was developed for this purpose. This method was compared with two conventional uninterrupted growth methods. All growth methods utilized RF PAEBE. The two conventional methods involve (A), using an Al/N flux >1, and (B), using an Al/N flux <<1. The interrupted growth method (C), involves using an Al/N flux >1 and periodically interrupting the Al flux. This method is a modification of existing interrupted growth methods used in growing InN at comparable temperature, and AlN at temperature above 700 °C. Samples of all groups were grown on c-plane sapphire, and were pretreated with a nitrogen plasma. Common growth parameters for the 3 groups included substrate temperature, plasma power, nitrogen gas flow, and Al rate. Fluctuations in the Al flux rate were also recorded. The AlN film stoichiometry of all samples in all groups, measured by x-ray photoelectron spectroscopy (XPS), indicated that the samples were stoichiometric.

5.1 Group A: LT AlN growth with constant Al flux and Al/N ratio >1

Group A AlN films, displayed in Table 5.1, were grown by plasma-assisted electron beam epitaxy (PAEBE) at low temperature. Prior to the growth of AlN, group A samples were pretreated with a nitrogen plasma using procedure (a) of §3.3.2. Samples were nitrided at 450° C for a minimum of ~70 minutes at a RF plasma power ≥300 W, which included a time at 600 W of 31 min for A-1 and 40 min for A-2. The two samples were grown at 450° C, using a RF power of 600 W and a gas flow of 1.0 standard cubic centimeters per minute (sccm), using an uninterrupted Al flux ~1.65 Å/s as per §3.3.3. Sample A-2 was grown to about three times the
thickness of A-1. Figure 5.1(a) shows the timeline of the growth procedure indicating the relative amounts of Al and N flux.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitriding Time at plasma power</th>
<th>Growth Plasma Power</th>
<th>Al Rate (ave.)</th>
<th>XRR Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp °C</td>
<td>W min</td>
<td>≥ 300W</td>
<td>Temp. °C</td>
</tr>
<tr>
<td>A-1</td>
<td>450</td>
<td>600</td>
<td>31</td>
<td>69</td>
</tr>
<tr>
<td>A-2</td>
<td>450</td>
<td>600</td>
<td>40</td>
<td>75</td>
</tr>
</tbody>
</table>

Given that a monolayer (ML) of (0001) AlN is about 2.5Å, the Al flux rates for A-1 and A-2 correspond to an AlN growth rate ~$\frac{2}{3}$ ML/s. Relating the Al rate with the N gas flow results in an Al/N ratio ~1.38, placing the growth conditions within the metal-rich regime as described in §2.4.3. The A-1 and A-2 $\theta$-2$\theta$ plots of Figure 1(b), plotted with log intensity scales to augment low intensity peaks, indicate both (002) and (101) AlN peaks on both samples. The FWHM for sample A-1 peaks were 0.54° for the (002) plane and 0.73° for the (101) plane. The A-2 FWHM values for the (002) and (101) planes were 0.31° and 0.79°, respectively. The rocking curve (RC) peak of sample A-1 was not intense enough above background to determine a value. The RC of A-2 was 3.2° (not displayed). Table 5.2 shows the 002 and 101 FWHM and corresponding grain sizes. The mean lateral grain size, $L$, was determined using the Scherrer equation. The improvement in (002) FWHM and grain size of sample A-2 over A-1 can be attributed to it being a thicker sample.
The SEM (scanning electron microscope) of both surfaces shown in Figure 5.1 (b) indicate a rough surface in addition to the formation of triangular hillocks, similar to those described by Kaneko et al.\textsuperscript{176} seen on AlN grown at 650° C. At low temperatures, the low adatom mobility of Al results in an effective Al-rich growth flux ratio (Al/N\textgtr\textless 1), even when the Al and N flux are at near stoichiometric conditions. For the samples in this growth study (450° C, 600 W, and 1.0 sccm), large AlN surface features rather than Al metal droplets appeared for Al rates >1.1 Å/s (0.44 ML/s), which infers that the Al/N flux ratio was >1. These features were triangular in nature. As noted in §4.3.1, triangles are also indicative of the (101) orientation seen on sputtered AlN films grown under low temperatures, caused by high deposition rates.\textsuperscript{207,208}

### Table 5.2 Group A XRD FWHM values. Corresponding 0-20 lateral grain sizes are calculated from the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>0-20 FWHM (°)</th>
<th>AIN (002) Lateral Grain Size (nm)</th>
<th>RC FWHM (°)</th>
<th>AIN (101) 0-20 FWHM (°)</th>
<th>Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>0.54</td>
<td>18.1</td>
<td>undetermined</td>
<td>0.73</td>
<td>13.8</td>
</tr>
<tr>
<td>A-2</td>
<td>0.31</td>
<td>32.1</td>
<td>3.2</td>
<td>0.79</td>
<td>12.7</td>
</tr>
</tbody>
</table>

A-2 was compared with the nitriding pretreatment growths. Relevant nitriding, growth, and film parameters of the pretreatment assessment growths W, P, and Q are displayed with A-2.
in Table 5.3. A comparison of W and P, both pretreated using plasma ions indicate that the additional pretreatment time improved the crystallinity of P. A-2 and Q were pretreated without ions. The lower temperature pretreatment of A-2 appears to have improved the crystallinity of A-2. The Al rate does not appear to have had an effect on the crystallinity of the films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ion Plates</th>
<th>Nitriding Time at plasma power</th>
<th>Growth Plasma Power</th>
<th>Al Rate (A/s)</th>
<th>XRR Thickness</th>
<th>(002) FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. °C</td>
<td>W min</td>
<td>min</td>
<td>Flow Temp. °C W</td>
<td>sccm</td>
<td>Power A</td>
</tr>
<tr>
<td>W</td>
<td>off 600</td>
<td>600</td>
<td>65</td>
<td>90</td>
<td>1</td>
<td>450</td>
</tr>
<tr>
<td>P</td>
<td>off 600</td>
<td>600</td>
<td>65</td>
<td>90</td>
<td>1</td>
<td>450</td>
</tr>
<tr>
<td>Q</td>
<td>on 600</td>
<td>600</td>
<td>120</td>
<td>150</td>
<td>1</td>
<td>450</td>
</tr>
<tr>
<td>A-2</td>
<td>on 450</td>
<td>600</td>
<td>40</td>
<td>75</td>
<td>1</td>
<td>450</td>
</tr>
</tbody>
</table>

Pole figure X-ray scans were taken on both samples. Since both films showed a c-axis orientation, the (002) plane pole figure was used to verify the c-axis orientation, and show evidence of other orientations. Figure 5.2 presents the pole figure projection of the (002) AlN plane for A-1 and A-2. Figure 5.2 a) and (b) are plotted on separate scales since the maximum intensity of A-2 is ~5 times the maximum intensity of A-1. Both are plotted using square-root scales to augment any lower intensity features. Both samples indicate a center peak, revealing the c-axis orientation. They both also have three sapphire (104) plane peaks, spaced 120° apart, and located at about 38.2° χ. The (104) sapphire peaks are present on all (002) AlN pole figure scans due to the spacing of the sapphire (104) plane which is within 1° of the AlN (002) plane.\(^{197}\)

![Figure 5.2 Group A (002) plane pole figures. The center peak indicates the (002) plan parallel to the surface. The 3 peaks at 38.2° χ indicate the sapphire (104) plane.\(^{197}\)
An analysis of the A-1 (002) pole figure in Figure 5.2(a) confirms much of the information determined from the $\theta$-2$\theta$ scan of Figure 5.1(a). The center peak gives an indication of how much of the film is c-axis oriented. The center peak of A-1 is less intense than the sapphire peaks. The ring located about $61.6^\circ \chi$ is evidence that some of the film is oriented with the (101) plane parallel to the sapphire surface. The ring indicates that the (101) oriented grains are randomly aligned about the (101) axis. This coincides with the information determined from the $\theta$-2$\theta$ (002) peak, that both orientations are present. The A-2 (002) pole figure in Figure 5.2(b) shows an intense double peak at the center. This indicates at least one (002) plane not parallel with the sapphire surface. The interference of the multiple planes give the peak a hexagonal widening at its base. The intensity of A-2’s center peak prevents a more detailed analysis of the (101) orientation.

To provide a more detailed analysis of the (101) orientation, the pole figures for A-1 and A-2 were plotted on the same scale, as shown in Figure 5.3. Since all pole figure scans used the same incident and diffracted optics, and similar instrument settings, the cross section of intensity between 90 and 250 was similar for all pole figure scans. By removing the high and low intensities, the ring of A-1 presented in Figure 5.3(a) is more pronounced. As for A-2, in Figure 5.3(b) removal of the peripheral intensities shows evidence of the (101) orientation. There are indications of a ring at about $61.6^\circ \chi$, as well.

![Figure 5.3 Group A (002) pole figures without high and low intensities. The center hole and three surrounding holes indicate an intensity greater than 250.](image-url)
Pole figures of the (101) plane for both A-1 and A-2 are presented in Figure 5.4. The (101) pole figure of A-1 of Figure 5.4(a) only has a center peak. There is an absence of any peaks or ring at $\chi$ of 61.6°. This denotes that the c-axis textured portion of the film has no orientation about the (002) axis. The A-2 (101) pole figure in Figure 5.4(b) has a six strong peaks at 61.6° $\chi$, confirming the hexagonal symmetry of wurtzite. The peaks appear connected by a ring indicating that some of the c-axis oriented grains of A-2 are randomly oriented about the (002) axis.

![Figure 5.4 Group A (101) plane pole figures. The six peaks at 61.6° $\chi$ indicate an oriented (101) plane. A center peak indicates (101) plane parallel to the surface. Below each PF is an intensity vs. $\phi$ plot of a circumscribed line at 61.6° $\chi$ showing intensity comparison of the (101) peaks.](image)

### 5.2 Group B: LT AlN growth with constant Al flux and Al/N ratio $<<1$

A conclusion reached by Koblmueller *et al.*\(^6^4\) in constructing the AlN growth diagram presented in Figure 2.11 of §2.4.3, is that very high Al fluxes or low growth temperatures are responsible for Al droplet formation, referred to as the Al droplet regime (Al/N$>>1$). This suggests that lowering the Al rate would reduce the formation of surface features. The three representative samples of group B, shown in Table 5.4, were grown at three different low substrate temperatures, 400° C for B-1, 450° C for B-2, and 500° C for B-3. B-1 and B-2 were pretreated at their respective temperatures with a nitrogen plasma using procedure (a) as
described in §3.3.2 for a minimum of ~35 min at a RF plasma power ≥300W, which included ~5 min at 600 W. Gas flow for both was 5 sccm. Sample B-3 was pretreated at 500°C using a modification of procedure (c), described in §3.3.2. The sample shutter was opened when plasma power was 350 W. The maximum plasma power was 400 W. Of the 19 min nitriding at ≥350W, 13 min were at 400 W.

At the time B-3 was grown, a quartz sleeve was inserted within the discharge tube of the OAR HD25, and the alumina aperture was replaced with a quartz aperture. The quartz components were intended to alleviate the Na contamination of the alumina components. Their installation imposed a maximum RF power limit of 400 W. The quartz aperture and sleeve were removed after the sleeve expanded and broke the discharge tube. The quartz components were replaced by the existing alumina aperture and PBN discharge tube.

Table 5.4 Group B AlN films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitrating Time at plasma power ≥300W</th>
<th>Growth Plasma Power</th>
<th>Al Rate (ave.)</th>
<th>XRR Thickness nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>400</td>
<td>600</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>B-2</td>
<td>450</td>
<td>600</td>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>B-3</td>
<td>500</td>
<td>400</td>
<td>13</td>
<td>19</td>
</tr>
</tbody>
</table>

After pretreatment, the three samples were grown at their respective temperatures. Figure 5.5 shows the growth cycle timelines for group B samples indicating the relative amounts of Al and N flux. B-1 and B-2 were grown using a gas flow of 5 sccm, and similar uninterrupted Al flux rates as per §3.3.3. The Al rates of ~0.21 Å/s for B-1 and ~0.17 Å/s for B-2 were equivalent to an AlN growth of 1 ML/~12–15s. As samples B-1 and B-2 were grown using similar parameters, the growth times were similar, about 30 min for each. B-3 was grown with a 400 W plasma and gas flow of 1 sccm, using an uninterrupted Al flux ~0.04 Å/s in accordance with
§3.3.3. The AlN growth rate was roughly 1 ML/min. At this rate, B-3 took over 2 hours to grow. Each had an Al/N ratio \( \sim 0.03 \), placing them well within the N-rich regime as described in §2.4.3.

![Figure 5.5 AlN growth cycles for a) B-1, b) B-2, and c) B-3.](image)

The \( \theta-2\theta \) scans of group B samples in Figure 5.6(a) indicate a single (002) AlN orientation. The (002) AlN FWHMs were within 0.03° of each other, and the (002) lateral grain sizes presented in Table 5.5 were 21.2–23.0°. The rocking curves in Figure 5.6(b) had FWHMs of 1.8–1.9°, narrower than the 3.2° of sample A-2. In comparison to other studies, the RC FWHMs were narrower than the 4.4° and 5.7° rocking curves of the 100 nm and 300 nm AlN films grown by Auner et al.,\(^{67}\) and close to the 1.2° and 1.4° rocking curves of the 400 nm films grown by Stevens et al.,\(^{68}\) presented in Table 2.10 in §2.4.3.

![Figure 5.6 Group B (a) \( \theta-2\theta \) plots, (b) rocking curves, and (c) SEM images.](image)
All group B samples were grown with approximately the same Al/N ratio, and from Figure 2.11, the AlN growth diagram in §2.4.3, the growth of the 3 films was within the N-rich regime. As such, the surface morphologies of the 3 films were expected to be similar, with little evidence of surface droplets or hillocks. SEM surface images presented in Figure 5.6(c) showed B-1 with surface features, which are 50-100 nm in diameter, dotting the otherwise smooth surface. B-2 had a smooth, featureless surface. The surface of B-3 was smooth with small pits. Both mounds and pits seen on AlN films grown at high temperature have been attributed to growth in the Al droplet regime. Group B films growth parameters were within the N-rich regime, so the films were likely N-polar. For N-polar AlN, Northrup et al. has estimated the energy binding an Al-adatom on the surface to be 9.4 eV. With the ion deflection plates energized, ions are prevented from interacting with the surface, and neutral atomic nitrogen is the species with the highest energy impacting the growth. The lowest energy of atomic nitrogen is greater than the energy binding the Al-adatom to the surface. If the AlN is indeed N-polar, the atomic nitrogen has sufficient energy to break bonds binding the adatom to the surface, allowing the adatom to be moved to an available site.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$-20 FWHM (°)</th>
<th>AlN (002) Lateral Grain Size (nm)</th>
<th>RC FWHM (°)</th>
<th>AlN (101) $\theta$-20 FWHM (°)</th>
<th>Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>0.43</td>
<td>23.0</td>
<td>1.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-2</td>
<td>0.45</td>
<td>21.7</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B-3</td>
<td>0.46</td>
<td>21.2</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Pole figure X-ray scans of the (002) and (101) planes were also taken on group B samples. The films were already established as $c$-axis oriented, with no other identifiable orientations. The (002) plane pole figure was used to verify the $c$-axis orientation, and to identify any previously unseen orientations. Figure 5.7 presents the pole figure projections of the (002)
AlN plane for group B samples. The three samples show an intense and narrow center peak, indicating that the films are all strongly c-axis oriented. The figures were plotted on a square-root intensity scale to augment any lower intensity features. The intensity of the B-3 center peak was the lowest of the three, about half the intensity of the B-1 center peak. The center peak intensity of B-2 was nearly as intense as B-1. Other than the three sapphire (104) peaks on each sample, there were no other distinguishing features.

Figure 5.7 Group B (002) plane pole figures. The center peak indicates the (002) plan parallel to the surface. The 3 additional peaks at 38.2°χ indicate the sapphire (104) plane.

Again, for a more detailed analysis of the (101) orientation, the pole figures were plotted with the high and low intensities removed. Figure 5.8 presents the Group B sample plots on the same scale. Possible evidence of the (101) orientation is seen by a small grouping of intensity at the intersections of 61.6°χ and 0°φ, and 61.6°χ and 180°φ on Figure 5.8(a), sample B-1. Sample B-2 also has a small intensity grouping near the 61.6°χ and 180°φ intersection, indicating the (101) orientation shown on Figure 5.8(b). Evidence for the (101) orientation on sample B-3 (Figure 5.8(c)) is inconclusive. Any grouping of intensity along the 61.6°χ circumference is not immediately evident.
Figure 5.8 Group B (002) pole figures without high and low intensities. The center hole and three surrounding holes indicate an intensity greater than 250.

Pole figures of the (101) plane for group B films are presented in Figure 5.9. All three group B samples show the hexagonal distribution of 6 peaks, each spaced 60° $\phi$ apart, located radially from the center at 61.6° $\chi$. Directly below each PF is an intensity vs. $\phi$ plot of the circumscribed line at 61.6° $\chi$. The average FWHM of the (101) peaks along the 0–360° $\phi$ line for the three samples is, 4.3° for B-1, 3.6° for B-2, and 5.3° for B-3. There appears to be a small center peak is visible on all three plots, which would verify that some grains have the (101) orientation parallel to the surface.

B-1 and B-2 were both nitrided and grown using similar Al flux rates, plasma powers, and gas flows. The difference between B-1 and B-2 was the growth temperature. It was difficult to distinguish much difference in the crystalline quality of these 2 samples. The smoother surface
morphology of B-2 may be due to the growth temperatures, as B-2 was grown at a temperature 50°C greater than B-1. B-3 was nitrided and grown using lower plasma power, lower gas flow, lower Al flux rate, but at a higher temperature. The pits on the surface of B-3 may be the result of the low Al flux rate combined with the long growth time. As the Al influx was low compared to the N flux, there was always an overabundance of N to chemically react with Al. The surplus N was free to interact with the surface and disrupt existing bonds. These conditions lasted for over 2 hours, nearly 4 times longer as those for B-1 and B-2. The lower crystalline quality of B-3 was attributed to the shorter nitriding pretreatment.

5.3 Group C: LT AlN growth with an interrupted Al flux and Al/N ratio >1

Group C AlN films were grown using an interrupted growth procedure, which consisted of cycles of AlN growth, followed by a nitriding recovery time. This interruption procedure is described in §3.3.3 and is similar to those used to grow AlN\textsuperscript{60,63} and InN,\textsuperscript{61} devised to eliminate metal droplets through nitrogen plasma irradiation. The recovery nitriding after depositing serves to eliminate Al droplets and allow the newly formed AlN layer to orient. The final film thickness is the result of depositing multiple thin layers of AlN.

Of the six representative group C samples grown, three – samples C-1, C-2, and C-3 – are shown in Table 5.6. Prior to the AlN growth, group C samples were pretreated with a nitrogen plasma using procedure (a) of §3.3.2. Samples were nitrided at 450°C. Samples C-1 and C-2 were nitrided ~40 minutes at a RF plasma power ≥300 W, which included a time at 600 W of 9 min for C-1 and 5 min for C-2. Including the initial ramp-up time, as the plasma power is increased from 100 W to 300 W, the total nitriding time for C-1 and C-2 was ~60 min. C-3 was nitrided 90 minutes at a RF plasma power ≥300W, including ~50 min at 600 W. Including the ramp-up time, sample C-3 was nitrided for a total of ~110 min. Samples C-1, C-2, and C-3 were
grown at 450° C, using a RF power of 600 W and a gas flow of 1.0 sccm, using an interrupted Al flux ~1.85 Å/s as per §3.3.3. All group C samples used an AlN deposition rate of ~0.67–0.83 ML/s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitriding Time at plasma power</th>
<th>Growth Al</th>
<th>Recovery Cycles</th>
<th>XRR Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp °C W min</td>
<td>Max min</td>
<td>N Flow sccm</td>
<td>Temp °C W</td>
</tr>
<tr>
<td>C-1</td>
<td>450 600 9</td>
<td>39</td>
<td>1</td>
<td>450 600</td>
</tr>
<tr>
<td>C-2</td>
<td>450 600 5</td>
<td>41</td>
<td>1</td>
<td>450 600</td>
</tr>
<tr>
<td>C-3</td>
<td>450 600 53</td>
<td>90</td>
<td>1</td>
<td>450 600</td>
</tr>
</tbody>
</table>

Table 5.6 C-1, C-2, and C-3 AlN films.

Figure 5.10 shows the growth cycle timeline for C-1, C-2, and C-3 indicating the relative amounts of Al and N flux. The corresponding Al/N ratio ~1.54, is within the Al-rich regime as described in §2.4.3. With a stable Al flux rate ~1.85 Å/s, the amount of Al deposited was controlled by controlling the time the e-beam shutter was open. The width of each Al bar corresponds to the time duration the e-beam shutter was open. For C-1, 20–22 Å of Al (8–9 ML) were deposited each time the shutter was opened. Figure 5.10(a) shows the shutter cycling sequence of C-1. After each Al deposit of C-1, the shutter was closed for 1 min. The cycle was repeated 19 more times, growing a 42 nm AlN film. Figure 5.10(b) indicates that for C-2, each cycle lasted 1 min. Beginning each cycle with an Al deposit of 7–8 Å (3–4 ML), the e-beam shutter was closed for the remainder of the minute. C-2 was grown to 50 nm with sixty cycles. Figure 5.10(c) shows the growth cycles for C-3. After 23–27 Å of Al (9–11 ML) were deposited, the e-beam shutter was closed for the remainder of each two-minute cycle. C-3 was grown to a thickness of 25 nm using 10 cycles.
Figure 5.10 AlN growth cycles for a) C-1, b) C-2, and c) C-3.

Figure 5.11 shows the $\theta$-2$\theta$ plots and SEM surface pictures for C-1, C-2 and C-3. The AlN (002), (101), and rocking curve FWHM values are displayed in Table 5.7, along with the corresponding lateral grain size values. The $\theta$-2$\theta$ scans of Figure 5.11(a) indicated both (002) and (101) AlN orientations on each sample. The (002) $\theta$-2$\theta$ FWHM values of samples C-1 and C-2 were very similar to those of samples B-1 and B-2. The (002) $\theta$-2$\theta$ FWHM value of sample C-3 was much less intense and wider and wider than the C-1 and C-2 peaks. The increase in nitriding time did not appear to improve the crystallinity of C-3. The additional AlN deposited per growth cycle for C-3 resulted in a less oriented (002) and more oriented (101).

Figure 5.11 C-1, C-2, and C-3 a) $\theta$-2$\theta$ plots and b) SEM images.
The surface SEM images of C-1 and C-2 shown in Figure 5.11(b) indicate two distinctly different surfaces. The surface of C-1 had the formation of triangular features, similar to those described by Kaneko et al.\(^{176}\) with outer dimensions of 2-3 \(\mu m\). The area enclosed by each triangle appeared to be relatively flat. The surface morphology of the area surrounding the triangles appeared flat. The nitriding recovery for C-1 appeared to reduce the density of hillocks. For C-2 this wasn’t the case. The surface of C-2 was rough. A possible explanation is that not enough Al was deposited per cycle to promote complete and uniform adatom surface migration. With fewer adatoms placed on the surface, they were less influenced by any surrounding oriented growth and more likely to create independent domain orientations. The initial adatoms placed on the surface had a strong influence on any subsequent adatoms. The nitriding recovery was insufficient to move adatoms into a more ordered state. Any disorder created by the initial adatoms was compounded over the 60 additional cycles of the growth.

Table 5.7 C-1, C-2, and C-3 XRD FWHM values. Corresponding \(\theta-2\theta\) lateral grain sizes are calculated from the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\theta-2\theta) FWHM ((^{\circ}))</th>
<th>AIN (002) Lateral Grain Size (nm)</th>
<th>RC FWHM ((^{\circ}))</th>
<th>AIN (101) (\theta-2\theta) FWHM ((^{\circ}))</th>
<th>Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1</td>
<td>0.43</td>
<td>23.1</td>
<td>3.7</td>
<td>undetermined</td>
<td>undetermined</td>
</tr>
<tr>
<td>C-2</td>
<td>0.45</td>
<td>21.8</td>
<td>1.8</td>
<td>0.59</td>
<td>16.9</td>
</tr>
<tr>
<td>C-3</td>
<td>0.74</td>
<td>13.3</td>
<td>undetermined</td>
<td>0.67</td>
<td>14.0</td>
</tr>
</tbody>
</table>

The C-3 SEM surface image (Figure 5.11(c)) appeared flat, with the presence of a few small mounds, each 100-150 nm in diameter. The increased time exposure to the plasma brought by increasing the nitriding recovery time smoothed the surface and eliminated surface features. It appears that, as with the growth of group B samples, the additional energy supplied by the atomic nitrogen compensated for the low growth temperature. Since the Al deposition rate for Group C samples was >1 \(\AA/s\), making the Al/N flux ratio >1, the samples are possibly Al-polar.\(^{74}\) Northrup et al.\(^{212}\) estimated the Al-adatom binding energy on the Al-polar surface to be 4.0 eV.
This is less than the energy of \( \text{N}_2(\text{A}^3\Sigma_u^+) \) molecules, and less than half the energy of atomic nitrogen.\(^{128}\) If this is the case, both atomic and molecular nitrogen should take part in breaking adatom bonds and Al mobility, resulting in better surface morphology than N-polar films.

Figure 5.12 presents pole figure plots of C-1, C-2 and C-3. C-1, in Figure 5.12(a) shows a center peak with a slight hexagonal widening at the base. No other discernable features are noted. C-2, presented in Figure 5.12(b) has a more intense center peak with a hexagonal widening at the base, the outlines of a ring at 61.6° \( \chi \), and six low intensity peaks located at about 70° \( \chi \). The hexagonal symmetry of the six peaks suggests the presence of an oriented (302) AlN plane parallel to the surface. C-3, shown in Figure 5.12(c) has a much lower center peak, and also has the outline of a ring at 61.6° \( \chi \).

![Figure 5.12](image)

Figure 5.12 C-1, C-2, and C-3 (002) plane pole figures. The center peak indicates the (002) plane parallel to the surface. The 3 additional peaks at 38.2° \( \chi \) indicate the sapphire (104) plane.\(^{197}\)

Removing the high and low intensities of the Figure 5.12 pole figures lead to the scans show in Figure 5.13. C-1, in Figure 5.13(a) shows no new features of evidence for other orientations. Sample C-2, shows much more prominent features in Figure 5.13(b). Both the ring at 61.6° \( \chi \) and peaks at 70° \( \chi \) are easily distinguished. The ring at 61.6° \( \chi \) contained in the plot of C-3 in Figure 5.13(c) is also more defined than in Figure 5.16(c).
Figure 5.13 C-1, C-2, and C-3 (002) pole figures without high and low intensities. The center hole and three surrounding holes indicate an intensity greater than 250. Intensity scale is the same for all plots. a) Sample C-1. b) Sample C-2. c) Sample C-3. d) Cross section of c-axis oriented wurtzite AlN film, noting the orientation of the (002) plane.

The peaks at 70° χ on C-2 suggest the presence of the (302) orientation parallel to the surface. The (302) plane is offset from the (101) plane by an angle of 70.2°. With the (302) plane parallel to the surface, as in Figure 5.14, the (002) PF would observe the (002) peaks at ~70° χ.

Figure 5.14 Illustration of a conceivable (302) plane formation atop (002) plane. Similar surface dimensions of (302) and (002) are compared using a side view. Images created using CrystalMaker®, CrystalMaker Software Ltd (www.crystalmaker.com)

C-1, C-2 and C-3 (101) plane pole figures are presented in Figure 5.15. All three samples show the presence of the (101) plane parallel to the surface with their center peak Samples C-1 (Figure 5.15(a)), and C-2 (Figure 5.15(b)) show the hexagonal symmetry of wurtzite. C-3 (Figure 5.15(c)) shows no indication of any peaks or ring at 61.6° χ. Directly below each PF is an intensity vs. φ plot of the circumscribed line at 61.6° χ.
Figure 5.15 C-1, C-2, and C-3 (101) plane pole figures. The six defined peaks at 61.6° χ indicate an oriented (101) plane. Any center peak indicates (101) plane parallel to the surface.

The remaining three representative group C samples – samples C-4, C-5, and C-6 – are shown in Table 5.8. Prior to the AlN growth, group C samples were pretreated with a nitrogen plasma using procedure (a) of §3.3.2. Samples were nitrided at 450° C. Samples C-4 and C-5 were nitrided ~85 minutes at a RF plasma power ≥300 W, which included a time at 600 W of 57 min for C-4 and 53 min for C-5. Including the initial ramp-up time, as the plasma power is increased from 100 W to 300 W, the total nitriding time for C-4 was 107 min and for C-5, 103 min. C-6 was nitrided 110 minutes at a RF plasma power ≥300W, including 38 min at 600 W. Including the ramp-up time, sample C-3 was nitrided for a total of 130 min. Samples C-4 and C-5 were grown at 450° C, using a RF power of 600 W and a gas flow of 1.0 sccm. Sample C-6 was grown at 450° C, using a RF power of 300 W and a gas flow of 1.0 sccm. All samples were grown using an interrupted Al flux ~1.85 Å/s as per §3.3.3. This was equivalent to an AlN deposition rate of ~0.67–0.83 ML/s.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nitriding Time at plasma power</th>
<th>Growth Al Rate (ave.)</th>
<th>Recovery Time</th>
<th>XRR Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp W min 1 450 600 67</td>
<td>14-16 5-6 120 20 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-4</td>
<td>450 600 37 87 1 450 600 1.85</td>
<td>1-16 5-6 120 20 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-5</td>
<td>450 600 53 85 1 450 600 1.85</td>
<td>15-16 5-6 180 20 31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-6</td>
<td>450 600 38 110 1 450 300 1.85</td>
<td>13-15 5-6 120 20 27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.16 shows the growth cycle timeline for C-4, C-5, and C-6 indicating the relative amounts of Al and N flux. For the three, ~13–16 Å of Al (5–6 ML) were deposited each time the shutter was opened. Figure 5.16(a) shows the shutter cycling sequence of C-4 and C-6. After each Al deposit, the shutter was closed for 2 min. Figure 5.16(b) indicates that for C-5, the shutter was closed for 3 min after each Al deposit. C-4 was grown to 30 nm, C-5 grown to 31 nm, and C-6 to 27 nm.

Figure 5.16 AlN growth cycles for a) C-4 and C-6, and b) C-5.

Figure 5.17 shows the \(\theta-2\theta\) plots and SEM surface pictures for C-4, C-5 and C-6. The AlN (002), (101), and rocking curve FWHM values are displayed in Table 5.7, along with the corresponding lateral grain size values. The \(\theta-2\theta\) scans of Figure 5.19(a) indicated only (002) AlN orientations on each sample. The (002) \(\theta-2\theta\) FWHM values of C-4, C-5 and C-6 were all similar to each other, as well as similar to those of samples B-1 and B-2. The (002) RC FWHM values of samples C-4 and C-5 were similar and in the same range as group B samples. Sample C-6 had a narrower RC of 1.2°. This suggests that for these growth conditions, there is an optimal amount of AlN deposited per cycle that results in a singly oriented film. This optimal amount appears to be in the range of ~5-6 ML for each cycle. An increase or reduction in this amount resulted in multiple orientations.
Figure 5.17 C-4, C-5, and C-6 a) $\theta$-2$\theta$ plots, b) rocking curves, and c) SEM images.

The $\theta$-2$\theta$ scans of C-4, C-5, and C-6 indicate only the (002) orientation. C-4 and C-5 had smooth surface morphology, but the surface of C-6 was not. The additional nitriding recovery time experienced by C-5 did not appear to change the surface morphology over C-4. However, the reduced amount of atomic nitrogen C-6 received from operating the plasma at 300 W resulted in the rougher surface. An optical emission spectrum analysis of the RF plasma used in this study indicated that when operating at 600 W, the plasma produced about 20% more molecular nitrogen, and nearly 3 times more atomic nitrogen than when operating at 300 W. The total amount of N$_2$ produced by the 300 W plasma over 2 minutes was greater than the amount of N$_2$ produced by the 600 W plasma over 1 minute; The total amount of atomic nitrogen produced by the 300 W plasma over 2 minutes was less than the total amount of atomic nitrogen produced by the 600 W plasma over 1 minute. Relating this to the surface improvement C-3 and C-4 experienced with an increased nitriding recovery time indicates that atomic nitrogen was responsible for the smooth surface morphology.
Table 5.9 C-4, C-5, and C-6 XRD FWHM values. Corresponding $\theta$-$2\theta$ lateral grain sizes are calculated from the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$-2$\theta$ FWHM ($^\circ$)</th>
<th>AIN (002) Lateral Grain Size (nm)</th>
<th>RC FWHM ($^\circ$)</th>
<th>AIN (101) Lateral Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-4</td>
<td>0.46</td>
<td>21.3</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>C-5</td>
<td>0.42</td>
<td>23.3</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>C-6</td>
<td>0.42</td>
<td>23.5</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>

An analysis of the pole figures for films C-4, C-5, and C-6 verify that these films are highly oriented. The (002) pole figures are presented in Figure 5.18. C-4 (Figure 5.18(a)), C-5 (Figure 5.18(b)) C-6 (Figure 5.18(c)) all show intense, narrow, center peaks. There are no other distinguishable features present. Plots with the high and low intensities removed are shown in Figure 5.19. A close inspection of the plots does not reveal any obvious indications of other orientations in any of the films. However, on Figure 5.19(c), an interpretation of an area of intensity near the intersection of $70^\circ \chi$ and $180^\circ \phi$ on C-6 suggests the possibility of the (302) orientation. If the (302) plane is present, the rough surface of C-2 supports the supposition that the (302) orientation is a product of the rough surface.

Figure 5.18 C-4, C-5, and C-6 (002) plane pole figures. The center peak indicates the (002) plane parallel to the surface. The 3 additional peaks at $38.2^\circ \chi$ indicate the sapphire (104) plane.
Pole figures of the (101) plane for C-4, C-5, and C-6 are presented in Figure 5.20. Sample C-4 (Figure 5.20(a)), C-5 (Figure 5.20(b)), and C-6 (Figure 5.20(c)) all have the hexagonal symmetry of wurtzite and have a small peak in the center. Figure 5.20(b) is only displayed to $80^\circ \chi$ due to interference with the sapphire (110) peak. Directly below each PF is an intensity vs. $\phi$ plot of the circumscribed line at $61.6^\circ \chi$.

5.4 LT AlN growth summary

LT AlN was grown on $c$-plane sapphire by EBE with 300–600 W RF plamsa powers at temperatures 400–500 °C using three separate methods. 1) Using a constant Al flux with $\text{Al/N}>1$, 2) a constant Al flux with $\text{Al/N}\ll 1$, and 3) an $\text{Al/N}>1$ and interrupting the Al flux, using the interruption to expose the growth surface to the nitrogen plasma. Figure 5.21 indicates...
the temperature and Al/N flux parameters used for these growth methods, as well as the growth temperature and Al/N flux for AlN grown by others using interrupted Al flux methods.

![Diagrams of AlN growth parameters](image)

Figure 5.21 LT AlN plotted on AlN growth diagram. Diagram adapted from Koblmüller et al. Markers W/X, P/Q, and A–C refer to AlN films grown in this work. Markers F & J refer to previous AlN grown using interrupted Al flux methods.

Figure 5.22 compares the rocking curves of AlN samples grown in this work to other AlN films found in the literature found on Table 2.10 in §2.4.3.1.

![Rocking curve comparison](image)

Figure 5.22 Rocking curves of LT AlN plotted vs. growth temperature. Additional films found in the literature are included for comparison.

Two AlN films were grown using a constant Al flux, plasma power of 600 W, and Al/N>1, Figure 5.21(A). This method resulted in AlN films with (002) and (101) orientations parallel to the substrate surface and rough surface morphology. XRD θ-2θ scans FWHM of the 002 planes were between 0.31 for an 86-89 nm sample and 0.54° for a 29-31 nm sample.
Three films were grown to between 28 and 44 nm using a constant Al flux, plasma power of 400-600W, and Al/N<<1, Figure 5.21(B-1), (B-2), and (B-3). These films were mostly (002) orientation parallel to the substrate surface and had relatively smooth surface morphology. The respective (002) θ-2θ and rocking curve FWHMs were 0.43-0.46°, and 1.8-1.9°. There was some evidence of a (101) oriented plane parallel to the surface on the samples.

Six films were grown using an interrupt method, Figure 5.21(C). Three were between 23 and 55 nm, using a plasma power of 600 W, and depositing different amounts of AlN between each interruption. The film grown by depositing 3-4 ML of AlN and interrupting the deposition for nearly a minute, resulted in a film with a rough surface, (002) and (101) orientations parallel to the surface, and a (002) θ-2θ FWHM of 0.45°. The film grown by depositing 8-9 ML of AlN and interrupting the deposition for a minute, resulted in a film with large triangular features on an otherwise smooth surface, (002) and (101) orientations parallel to the surface, and a (002) θ-2θ FWHM of 0.43°. The film grown by depositing 9-11 ML of AlN and interrupting the deposition for nearly two minutes, resulted in a film with smooth surface, and (002) and (101) orientations parallel to the surface. The (002) θ-2θ FWHM was 0.74°.

Three of the six films were grown between 26 and 32 nm, by depositing 6 ML of AlN between interruptions. All three films were strongly (002) oriented. The film grown using a 600 W plasma with a two-minute interruption, resulted in a film with a smooth surface, no other orientations, and respective (002) θ-2θ and rocking curve FWHMs of 0.46° and 2.0°. By increasing the interruption to three minutes, the (002) θ-2θ and rocking curve FWHMs improved to 0.42° and 1.7°. Using a 300 W plasma, and a two-minute interruption, resulted in a (002) θ-2θ and rocking curve FWHM of 0.42° and 1.2°, but with an additional (302) orientation and rough surface morphology. Figure 5.23 plots the (002) RC values as a function of nitriding
pretreatment time. The RC for C-3 could not be determined. Sample C-2 included both the (002) and (101) orientations parallel to the surface. In calculating the linear regression best fit line, C-2 was considered an outlier.

![Figure 5.23 Group C rocking curves plotted as a function of nitriding pretreatment time. RC for C-3 was undetermined. Linear regression best fit line drawn without C-2 RC.]

Of the three methods, the interrupted method produced the most crystalline film with a smooth surface morphology. Crystallinity was effected by Al amount, Al flux rate, and Al/N ratio. For LT AlN growth, the formation of high-quality films appears to be a coordination of the amount of Al that arrives at the surface, combined with the amount of available $N^*$, and the time irradiated by the RF plasma. Pretreatment time has an effect on the crystallinity. Longer nitriding time time improves crystallinity. Surface morphology was directly impacted by plasma power and exposure time, suggesting that the higher energies of atomic N are necessary for adatom mobility.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

Highly oriented AlN thin films approximately 30 nm thick were grown on c-plane sapphire at 450 °C by RF PAEBE. Two separate growth techniques were employed to overcome the low adatom mobility of Al at low temperatures. One method was to lower the Al flux rate to make the Al/N flux ratio <<1. The second method involved depositing 5-6 ML of Al, interrupting the deposition with a nitriding recovery time. Each technique included a nitriding pretreatment of the sapphire. The interruption growth method resulted in strongly textured polycrystalline AlN films. The role of the RF plasma in both nitriding and growth cannot be overstated.

6.1 Conclusions

Nitriding pretreatment is essential in growing high quality AlN. The object of nitriding is to form a thin layer AlN or AlOxNy on the sapphire surface. A direct comparison of sapphire substrates, nitrided under varying conditions, found that the formation of the nitriding layer on sapphire is influenced by substrate temperature, plasma ions, and plasma power.

The nitriding pretreatment procedure used for most of the AlN films grown in this study involved ramping the plasma – initiating the nitriding as the plasma was struck at 100 W, and gradually increasing plasma power in 50W increments to the maximum 600 W power. Ramping the plasma was found to lower the presence of oxides within the layer. Oxides within the layer were further reduced when plasma ions were utilized along with the ramping. Oxides were minimized when the plasma was ramped, ions were utilized, and the nitriding was at high temperature (775° C).
A pretreatment comparison of AlN films grown on sapphire, pretreated with RF plasma that was ramped, found that the nitriding parameters of substrate temperature, plasma ions, and nitriding time directly influenced AlN film crystallinity.

The nitriding assessment study described in §4.3.2, evaluated the influence of plasma ions on the pretreatment process. During the nitriding pretreatment of sample P, plasma ions were allowed to interact with the sapphire surface. While sample Q was pretreated, plasma ions were deflected away from the surface. Both were nitrided at 600° C using a RF power ≥300 W for 150 min. A post-pretreatment XPS indicated the N 1s peak of sample P centered at binding energy ~397.3 eV, indicating a lower oxide content than Q, which was centered at ~398 eV. AlN films were grown on both samples concurrently using an Al flux rate of ~1.1 Å/s. The XRD measured θ-2θ (002) FWHM for P was 0.39°, and 0.35° for Q. However, the intensity of the sample P θ-2θ (002) peak was ~1.5 times the intensity of the sample Q θ-2θ (002) peak. Sample P had a RC FWHM of 3.4°, and sample Q a RC FWHM of 4.0°. The influence of plasma ions in the pretreatment improved the growth of the AlN film. Ramping of the plasma may have an affect on ion influence.

The pretreatment substrate temperature was found to have an influence on the crystallinity by comparing sample A-2 of the AlN growth study with sample Q of the nitriding assessment study. Both samples were pretreated without the influence of ions, but sample A-2 was nitrided at was nitrided at 450° C, lower than 600° C nitriding temperature of Q. Sample A-2 was nitrided at ≥300 W for 75 min, half the time spent for the nitriding of Q. AlN was grown on A-2 using an Al flux rate of ~1.65 Å/s, compared with the Al flux rate of ~1.1 Å/s for Q. The θ-2θ (002) FWHM for A-2 was 0.31°, and the RC FWHM was 3.2°. The improvement in crystallinity was due to the lower substrate temperature of the pretreatment.
A comparison of sample P with the results of sample W, described in §4.3.2, assessed the influence of nitriding time on the pretreatment process. Sample W was pretreated using similar parameters as sample P. The exception was that P was nitrided at \( \geq 300 \) W for 150 min, an hour longer than W. W was grown using an Al flux rate of \(~1.8\) Å/s. The XPS results of W indicated the N 1s peak centered at binding energy \(~397.3\) eV similar to sample P. The \( \theta-2\theta \) (002) peak of W was \(0.53^\circ\), but the RC of W was not intense enough above background to determine a FWHM value. The improvement in crystallinity was due to the added nitridation time of the pretreatment.

Growing LT AlN on \(c\)-plane sapphire at \(450\) °C, using an Al/N flux ratio \(<1\), results in textured polycrystalline AlN films. Highly ordered AlN films of thickness \(~30\) nm were grown at temperatures \(400–500\) °C with a significantly low Al flux rate. FWHM \(\theta-2\theta\) values were \(0.43–0.46^\circ\) and rocking curve FWHM values were \(1.8–1.9^\circ\). The \(c\)-axis AlN films were well ordered with a relatively smooth surface morphology as observed by SEM.

The goal was to grow low temperature AlN films with near perfect orientation as well as smooth surface morphology. The energy requirements of moving adatoms to appropriate growth sites are usually supplied via the growth temperature, typically \(~800\) °C. At similar high temperatures, AlN growth using Al/N\(>1\) typically results in the formation of Al droplets on the surface. The growth flux ratio in this work was reduced to Al/N\(<1\) to minimize the creation of adatoms. The high energy N* species within the RF plasma was utilized to provide the energy during the AlN growth.

An initial nitriding pretreatment of the surface was done at growth temperature, using a RF plasma at \(400–600\) W to increase the concentration of N*, and achieve an optimal pretreated surface. B-1 and B-2 were both nitrided and grown at 600 W and 5 sccm using similar Al flux.
rates. B-3 was nitrided and grown using 400 W and 1 sccm, a lower Al flux rate, but at a higher temperature.

The resulting films had the (002) orientation parallel to the sapphire surface, but some samples showed indication of the (101) plane parallel to the surface. From the resulting time frame taken in growing AlN films using a very low Al flux rate, any formations attributed to adatom mobility that initially formed were substantially eliminated through the extended bombardment of high energy N⁺. The pits on the surface of B-3 may be the result of the low Al flux rate combined with the long growth time. As the Al influx was low compared to the N flux, there was always an overabundance of N to chemically react with Al. The surplus N was free to interact with the surface and disrupt existing bonds. These conditions lasted for over 2 hours, nearly 4 times longer as those for B-1 and B-2. The lower crystalline quality of B-3 was attributed to the shorter nitriding pretreatment.

Strongly textured polycrystalline AlN films can be grown at LT on $c$-plane sapphire using the method of interrupting the Al flux with a periodic nitriding recovery time. Highly ordered AlN films of thickness $\sim$30 nm were grown at 450 °C using a process of interrupting the Al flux with a recovery time. FWHM values of 0.42–0.46° for $\theta$-2$\theta$, and rocking curve FWHM values of 1.2–2.0° were obtained. The films were strongly textured polycrystalline, c-axis AlN, with smooth surface morphology as observed by SEM.

As stated earlier, the goal was to grow low temperature AlN films with near perfect orientation as well as smooth surface morphology. The use of a growth flux ratio of Al/N>1 has been shown to grow films with higher epitaxy. Using this Al/N ratio results in Al-polar films, which have been noted as being of higher quality than N-polar AlN films. At temperatures $>$700 °C, AlN growth using Al/N>1 can result in the formation of Al droplets on the surface, a result
of the low mobility of Al adatoms. A solution is to grow AlN using an interrupted method. At low temperatures, (<600 °C) hillocks, rather than droplets are formed on the surface. The high energy N* species within the RF plasma was again utilized to provide the energy during the AlN growth.

An initial nitriding pretreatment of the surface was done at growth temperature, using a RF plasma at 600 W for maximum concentration of N* to achieve an optimal pretreated surface.

Each growth cycle began with depositing 5–6 monolayers (ML) of Al on the substrate using a flux ratio of Al/N>1. The Al flux was interrupted and the growth surface was irradiated with the 600W plasma for 2 min. Upon completion of the cycle, the Al was again applied and the cycle repeated. Using these parameters resulted in a highly oriented AlN film with smooth surface morphology. When the AlN deposited each cycle was increased or decreased by 50%, the resulting film was more polycrystalline and showed additional orientations parallel to the surface.

Shortening the recovery time to one minute resulted in surface morphology that contained visible surface features. One minute does not appear to be enough time for the N* to mobilize surface adatoms for growth at 450 °C. Increasing the recovery time from 2 min to 3 min did not appear to change the surface morphology or the crystalline structure.

When the plasma was reduced to 300 W, a two-minute recovery time resulted in rough surface morphology. At 300 W, the N/N₂ is less, meaning less N* is available for effecting the film surface. However, the crystalline structure was more strongly textured due to the additional nitriding time.
6.2 Recommendations for future research

Further investigation of ramping the plasma for nitriding.

The plasma was ramped for most of the samples in this study. Ramping the plasma is not a technique found in the literature. The results of this study, regarding the influence of ions in the pretreatment were counter the results reported by Yao et al.\textsuperscript{19} The ramping of the plasma may have had an effect on how the ions influenced the nitriding process. Nitrogen plasma-assisted cleaning has been shown to be an efficient technique for the removal of oxides from surfaces.\textsuperscript{204} By starting the nitriding at low RF power, the plasma may be initially cleaning the sapphire surface rather than creating a nitriding layer. The discussion of the nitriding study in §4.2.2 reports that the AlN onset for sample F, nitrided at 450 °C occurred sooner than the onset of AlN for samples nitrided at a much higher temperature. This also runs counter to Yao et al.\textsuperscript{19}

Optimizing the growth parameters for LT AlN growth.

Three variables suitable for further investigations of the interrupted Al flux method are: gas flow, Al flux rate, and amount of Al deposited per cycle. These parameters are all interrelated in the growth process. Small changes in the Al flux resulted in significant changes in crystalline quality. A higher gas flow may allow for a higher Al flux rate or shorter recovery time.

Verify the polarity of LT AlN films grown using the interruption method.

The convention wisdom of AlN film growth is that AlN films grown in N-rich conditions are N-polar, and Al-polar films are grown when the film is grown in Al-rich conditions. Although the Al flux was greater than the N flux as the film was deposited, during Al interruption the Al/N ratio may have been different.
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BIOGRAPHY OF THE AUTHOR

Roger Eastman Feeley was born in Lewiston, Maine on August 27, 1956. He was raised in Auburn (a far cry from his birth city across the river) and was rumored to have graduated from Edward Little High School in 1974. In 1977 he joined the US Navy’s Nuclear Power Program and spent much of the next 6 years verifying that 70% of the Earth’s surface is indeed covered with water. After discharge from the Navy, Roger spent two years at the University of Arizona in Tucson before transferring to UMaine. In 1989 he graduated with a BS in Engineering Physics.

Before returning to UMaine, Roger worked for the University of Wisconsin – Madison as a Physics Outreach Specialist, presenting over 525 demonstrations to nearly 100,000 people in fifteen different states and provinces. While in Madison, he also taught a course in Radioisotopes at Madison Area Technical College, and was a Radon Analyst for the State of Wisconsin.

He has a Master of Science in Teaching from U Maine in 2007, and also a Master of Engineering – Engineering Physics from U Maine in 2011

Roger is a member of ΣΠΣ, a physics honor society, as well as the engineering honor society, ΤΒΠ. Roger is a devotee of Coast to Coast AM – the ‘heavy boots’ in a world unencumbered by gravity. He also enjoys cooking, playing the piano, singing, and running. In addition to his world travels, he has visited 49 of the 50 states. Roger is a candidate for the Doctor of Philosophy degree in Physics from the University of Maine in May 2019