DEPOSITION AND CHARACTERIZATION OF AMORPHOUS GAN THIN FILMS

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DEPOSITION AND CHARACTERIZATION
OF AMORPHOUS GAN THIN FILMS

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Theoretical study by Stumm and Drabold [P. Stumm and D. A. Drabold, Phys. Rev. Lett 79, 677 (1997).] showed that amorphous GaN could be a promising wide bandgap semiconductor material for electronic and optoelectronic device applications. In this dissertation, a-GaN and a-GaN:Er thin films were prepared by means of ion beam assisted evaporation at room temperature in an ultra-high vacuum chamber. The properties of as-deposited and thermal annealed films were studied by a variety of characterization methods.

X-ray diffraction, electron diffraction, and Raman spectroscopy results confirmed that the films are amorphous. Depending on the deposition condition, films with Ga to N ratio of 1.0:0.5 to 1.0:1.4 were obtained. The film with the Ga:N ratio of 1.0:1.3±0.1 has an optical bandgap of ~2.5eV measured at the absorption coefficient of $10^4$ cm$^{-1}$, whereas the optical bandgap is ~2.0eV from a Tauc plot. The film is highly transparent for light with energy lower than the bandgap energy, while gallium rich films showed much higher absorption in the same region, which indicate that a clean band gap can be obtained for a-GaN film by preparing nitrogen rich films. Oxidation at room temperature has been observed for some films, while others are stable against oxidation until annealed above 500°C. The densities of the a-GaN and a-GaN:O films in this work are 62 to 78 at % and 68 to 85 at %.
% respectively, of that of crystalline GaN, and the more the N or N+O in the film, the lower the density of the film. XPS and AES results showed that the binding energies for N and Ga to be consisted with Ga-N bonding. The XPS valence band spectrum showed that the highest valence band state is about 1.5eV below the Fermi level. Both as-deposited and annealed (at 900°C in N₂) a-GaN:Er film showed IR emissions in the range of 950-1000nm by PL measurement. The annealed film also showed visible emissions near 700nm by PL measurement.

Approved ________________________________

Associate Professor of Physics and Astronomy
To my grandmother, my mother, and my sister.
Acknowledgments

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<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>µc-</td>
<td>microcrystalline</td>
</tr>
<tr>
<td>a-</td>
<td>amorphous</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>ERD</td>
<td>elastic recoil detection</td>
</tr>
<tr>
<td>ERS</td>
<td>elastic recoil spectroscopy</td>
</tr>
<tr>
<td>FET</td>
<td>field effect transistor</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>HOPG</td>
<td>highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
</tr>
<tr>
<td>NRA</td>
<td>nuclear reaction analysis</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>SAM</td>
<td>scanning Auger microscopy</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeters per minute</td>
</tr>
<tr>
<td>TBN</td>
<td>total beam neutralization</td>
</tr>
<tr>
<td>TED</td>
<td>transmission electron diffraction</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TFT</td>
<td>thin film transistor</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>UPS</td>
<td>ultra-violet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>WZ</td>
<td>wurtzite</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZB</td>
<td>zincblende</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

In a perfect single crystal, atoms (or groups of atoms) are arranged in a periodic array. The underlying microscopic periodic structure (the Bravais lattice) and the electron configuration of the atoms sitting in the Bravais lattice give rise to a periodic potential that determines the fundamental physical properties of the system. In the real crystal materials, there exist defects such as impurities and the deviations from perfect periodicity so that the properties of the real crystalline materials are greatly affected by the scattering processes caused by defects when respond to the electrical or optical signals.

In the amorphous materials, no long-range periodic ordering is preserved, while there does exist some degree of local order on the atomic scale. Joffe and Regal’s empirical rule [12] stated that an amorphous semiconductor retains its semiconducting properties in spite of the destruction of the long-range order if only the
non-crystalline phase conserves the short-range order present in the related semiconductor crystal. This rule holds well so far in that there exist band gaps in amorphous semiconductors close in energy to their crystalline counterparts. While in the amorphous materials, there is no translation symmetries so that some forbidden transitions between energy levels in crystals restricted by the periodicity are relaxed.

In this chapter, some physical properties of crystalline GaN will be listed for comparison. Then the proposed researches for amorphous GaN in this dissertation will be discussed.

1.1 Properties of crystalline GaN

GaN was first synthesized by Juza and Hahn [13] in 1938. While due to the lack of a good substrate for epitaxy, high background n-type doping, and the lack of p-type dopant, the development of GaN based devices was slow until early 1980s. Intensive study in the area was inspired again after the growth of good quality epilayers by Yoshida et al in 1983 [14] and the first p-type doping of GaN by Amano et al in 1988 [15]. GaN-based FETs were first reported by Khan et al in 1993 [16], and the first GaN-based laser diode was reported by Nakamura et al in 1995 [17]. The performance of GaN-based devices has improved rapidly since then. Recent review papers and books in GaN materials and devices can be found in Ref.
The equilibrium crystalline structure for GaN is the wurtzite structure while GaN has also been reported to form zincblende structure when grow on a cubic substrate. Some fundamental properties of GaN are listed in Table 1.1. The zincblende and wurtzite bonding between Ga and N atoms in adjacent planes are shown in Figure 1.1. In both structures, every atom is tetragonally coordinated with four atoms of the opposite species. The crystal structure differ only in their stacking sequences along the (111) axis. The three tetrahedral bonds are 60° rotated in the zincblende structure and mirror images in the wurtzite structure. GaN has a direct band-gap of 3.4eV so that it can be used for violet, blue and green light emitting devices. By alloying with InN and AlN, the band gap and emission wavelength can be tuned from 1.9eV for InN to 6.2eV for AlN. GaN has high thermal conductivity so that GaN-based devices are possible to work at high temperature environment. The breakdown voltage for Si and GaAs are $2 \times 10^5 V/cm$ and $4 \times 10^5 V/cm$. Compared
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$6.15 \text{g/cm}^3$</td>
<td>[25]</td>
</tr>
<tr>
<td>Band-gap Energy</td>
<td>$E_g(300K) = 3.39 \text{eV}$</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>$E_g(1.6K) = 3.50 \text{eV}$</td>
<td>[27]</td>
</tr>
<tr>
<td>Temperature Coefficient</td>
<td>$dE_g/dT = -6.0 \times 10^{-4} \text{eV/K}$</td>
<td>[28]</td>
</tr>
<tr>
<td>Pressure Coefficient</td>
<td>$dE_g/dP = 4.2 \times 10^{-3} \text{eV/kbar}$</td>
<td>[29]</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>$a = 3.189\text{Å}$</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>$c = 5.185\text{Å}$</td>
<td></td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>$\Delta a/a = 5.59 \times 10^{-6} / \text{K}$</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>$\Delta c/c = 3.17 \times 10^{-6} / \text{K}$</td>
<td></td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$\kappa = 1.3 \text{W/cm K}$</td>
<td>[30]</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>$n(1\text{eV}) = 2.33$</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>$n(3.38\text{eV}) = 2.67$</td>
<td></td>
</tr>
<tr>
<td>Dielectric Constants</td>
<td>$\varepsilon_0 = 9.5$</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon_\infty = 5.35$</td>
<td></td>
</tr>
<tr>
<td>Electron Mobility</td>
<td>$1000 \text{cm}^2/\text{V s (bulk)}$</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>$2000 \text{cm}^2/\text{V s (2D-gas)}$</td>
<td></td>
</tr>
<tr>
<td>Hole Mobility</td>
<td>$30 \text{cm}^2/\text{V s}$</td>
<td>[34]</td>
</tr>
<tr>
<td>Breakdown field</td>
<td>$&gt; 5 \times 10^6 \text{V/cm}$</td>
<td>[34]</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>$&gt; 1700 \text{°C}$</td>
<td>[34]</td>
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<tr>
<td>Zincblende Polytype</td>
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<tr>
<td>Band-gap Energy</td>
<td>$E_g(300K) = 3.2 \text{eV}$</td>
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<td>$E_g(300K) = 3.45 \text{eV}$</td>
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<td>Lattice Constant</td>
<td>$a = 4.52\text{Å}$</td>
<td>[35]</td>
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<tr>
<td></td>
<td>$a = 4.531\text{Å}$</td>
<td>[36]</td>
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<tr>
<td></td>
<td>$a = 4.51\text{Å}$</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>$a = 4.5\text{Å}$</td>
<td>[14]</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>$n(3.2\text{eV}) = 2.91$</td>
<td>[38]</td>
</tr>
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Table 1.1: Properties of GaN.
to Si and GaAs, GaN has a higher breakdown voltage ($> 5 \times 10^6 \text{V/cm}$) so that GaN is also a good candidate material for high power electronic devices.

1.2 Proposed researches and the organization of this dissertation

In 1997, Stumm and Drabold [4] studied the structural and electronic properties of amorphous GaN by ab initio molecular dynamic calculations. Their results showed that amorphous GaN is a promising electronic material with a wide bandgap of 2.8eV. Inspired by their theoretical work, I proposed an experimental study of amorphous GaN thin films.

For this dissertation, amorphous GaN thin films and Er doped amorphous GaN thin films were prepared by means of ion beam assisted evaporation at room temperature in an ultra-high vacuum (UHV) chamber. The structural, electronic, and optical properties of the amorphous GaN thin films were studied experimentally by a variety of characterization methods.

In chapter 2, the recent work related to amorphous GaN will be reviewed. In chapter 3, I will give a brief introduction to the methods used to characterize the properties of amorphous GaN thin films in this dissertation. The characterization methods used in this work include Rutherford Backscattering Spectroscopy (RBS), Elastic Recoil Detection (ERD), mechanical thickness measurement, X-ray diffrac-
tion, electron diffraction, Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), UV-visible transmittance measurement, and photoluminescence (PL) measurement. In chapter 4, I will describe the thin film deposition system and the thermal annealing system as well as the testing results of the performance of the equipments and the experimental parameters. In chapter 5, I will list the experimental results and discuss the results. In chapter 6, I will summarize my work and give some suggestions for future work.
Chapter 2

Literature review

Crystalline GaN has been studied intensively as a wide bandgap semiconductor material for short-wave length optoelectronic device, high temperature device and high power device applications during last twenty years. Great success has been achieved. Compared to its crystalline counterpart, amorphous GaN has received little attention. The first reactive sputtered a-GaN thin film was studied by Hariu et al in 1977 [1]. Several other experimental studies have been performed since then in reactive sputtered a-GaN [39, 2, 3, 40], MBE a-GaN [6], ion-assisted deposition of a-GaN [7], and hydrogenated a-GaN [41]. Theoretical studies of a-GaN have also been done by Stumm and Drabold in 1997 [4], and by Yu and Drabold in 1998 [5]. In this chapter, I will review the work on a-GaN. In this dissertation, I am not going to discuss the amorphous phase of GaN caused by ion beam bombardment of crystalline GaN, or amorphous phase of GaN formed when Ga or N ions implant
into materials containing Ga or N atoms. Therefore, I will not list a-GaN related works in those areas in this chapter.

2.1 Theoretical studies of a-GaN

In 1997, Stumm and Drabold [4] proposed two 64 atom amorphous structural models for GaN. One had the density of the experimental wurtzite GaN density (6.06g/cm$^3$) and the other had the density of 82% of the wurtzite GaN experimental density. They used these models to calculate the optical and electronic properties of a-GaN from approximate ab initio molecular dynamics. They obtained highly disordered network models with large state-free optical band gaps. The structural and electronic properties of their models are shown in Figure 2.1. The calculation showed that there were more threefold coordinated atoms in the lower density model, while no homopolar bonds were observed in both models which indicated the strong ionicity of a-GaN. They found that the band gap is almost constant at 2.8eV for both materials, and there are no midgap states. However they claimed that it is possible that their estimate for the gap is somewhat overestimated. Their calculation showed that the valence band tail is barely broadened relative to the crystalline state density, while the conduction tail states are significantly broadened. Their results also showed that the band tail states are more weakly localized in the lower density material which should result in a higher mobility.
(a) Number density function $n(r)$ for higher density model (upper line) and lower density model (lower line).

(b) Electronic density of states for higher density model (solid line) and lower density model (dotted line). The vertical dashed line is the Fermi level.

(c) Localization of the higher density model.

(d) Localization of the lower density model.

Figure 2.1: Structural and electronic properties of a-GaN from Ref. [4].
In 1998, Yu and Drabold [5] performed quantum molecular dynamics to simulate the density dependence of the structural and electronic properties of a-GaN to find the most probable density for the existence of a-GaN, and the possibility of the existence of the novel electronic properties at that density. Compared to the previous study [4], they employed the self-consistency for the charge transfer throughout the simulation. They constructed 64 atom structural models of a-GaN at the densities of 100%, 94%, 92%, 90%, 88%, and 86% of that of wurtzite GaN (6.06g/cm$^3$). The properties of the simulated a-GaN are shown in Figure 2.2 and 2.3. Their results showed the strong ionicity of a-GaN since no homopolar bonds was observed in all models. In analyzing the ring statistics, they found that their models are rather ordered. Thus, the effect of ionicity is important in a-GaN and leads to the networks with strong chemical short-range order, which is very different from known crystalline phase of GaN. The simulated bandgaps were 3.605eV, 3.339eV, 2.964eV, 2.847eV, 2.764eV and 2.616eV corresponding to the materials with decreasing density. No midgap defect states were observed for all models. Their method resulted in a bandgap of 4.145eV for zincblende GaN compared to the value of 3.4eV at room temperature from experimental measurements. If we assume that their method overestimate the bandgap at a constant shift, the bandgap of a-GaN should range from 1.9eV to 2.9eV for the proposed models. The estimation of the electronic localization of the band tail states showed that the valence band (VB) states in a-GaN are mostly localized on N sites, and the conduction
(a) The coordination defects and the ring statistics at different densities $\rho$.

<table>
<thead>
<tr>
<th>$\rho/\rho_0$</th>
<th>Ring size</th>
<th>Coordination</th>
<th>Average bond length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>10 64</td>
<td>30 34</td>
<td>1.87</td>
</tr>
<tr>
<td>0.94</td>
<td>8  64</td>
<td>25 39</td>
<td>1.91</td>
</tr>
<tr>
<td>0.92</td>
<td>64</td>
<td>28 36</td>
<td>1.92</td>
</tr>
<tr>
<td>0.90</td>
<td>64</td>
<td>28 36</td>
<td>1.93</td>
</tr>
<tr>
<td>0.88</td>
<td>64</td>
<td>30 34</td>
<td>1.94</td>
</tr>
<tr>
<td>0.86</td>
<td>64</td>
<td>39 25</td>
<td>1.92</td>
</tr>
<tr>
<td>1.00*</td>
<td>64</td>
<td>64</td>
<td>1.95</td>
</tr>
</tbody>
</table>

(b) The total energy per atom and the band gap at different densities $\rho$.

<table>
<thead>
<tr>
<th>$\rho/\rho_0$</th>
<th>Total/atom (eV)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>-168.397</td>
<td>3.605</td>
</tr>
<tr>
<td>0.94</td>
<td>-168.468</td>
<td>3.339</td>
</tr>
<tr>
<td>0.92</td>
<td>-168.487</td>
<td>2.964</td>
</tr>
<tr>
<td>0.90</td>
<td>-168.492</td>
<td>2.847</td>
</tr>
<tr>
<td>0.88</td>
<td>-168.493</td>
<td>2.764</td>
</tr>
<tr>
<td>0.86</td>
<td>-168.457</td>
<td>2.616</td>
</tr>
<tr>
<td>1.00*</td>
<td>-168.664</td>
<td>4.145</td>
</tr>
</tbody>
</table>

Figure 2.2: Properties of a-GaN from Ref. [5]. $\rho_0$ is the experimental density of wurtzite GaN. (*: ZB-GaN)
(a) Pair-distribution function of a-GaN at different densities.

(b) Electronic density of states of a-GaN at different densities.

(c) Partial-pair distribution function of a-GaN at 0.9\(\rho_0\) for (A) NN pairs, (B) GaGa pairs, and (C) GaN pairs.

(d) The electronic localization of a-GaN at different densities.

Figure 2.3: Structural and electronic properties of a-GaN from Ref. [5]. \(\rho_0\) is the experimental density of wurtzite GaN.
band (CB) states on Ga sites. The comparison of the electronic localization of a-
GaN at different densities showed that the eigenstates at both VB an CB edges are
more localized in the range of 0.88-0.94\(\rho_0\). By calculating the total energies of the
ground state defined in Harris expression as a function of density, they found that
a-GaN may exist in a small range of the density around 90\(\pm\)2\% of the experimental
wurtzite GaN density.

2.2 Experimental studies of a-GaN

Amorphous GaN thin films have been experimentally studied by several groups.
In this section, I will briefly review the preparation methods, electronic properties,
and optical properties of a-GaN thin films.

2.2.1 Reactive sputtered a-GaN

Hariu et al [1] prepared a-GaN thin films by reactive sputtering of gallium in
nitrogen ambient in 1977. In their experiments, the substrates were water-cooled,
and the typical deposition rate was 150Å/min. They claimed that AES analysis
sometimes detected several percents of oxygen in the GaN film. The films were
considered to be amorphous since no X-ray diffraction lines were detected. The
properties of the a-GaN films depended on the \(N_2\) pressure which ranged from
\(10^{-2}\)Torr to 1Torr during the deposition, and some properties of their a-GaN are
listed in Table 2.1. The optical bandgaps of the films ranged from 3.1eV to 3.3eV

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Band Gaps</td>
<td>3.1 – 3.3eV</td>
<td>Absorption</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.0 – 2.2 at 5461Å</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>3.71 and 5.06</td>
<td>Poole-Frenkel effect</td>
</tr>
<tr>
<td></td>
<td>3.65 and 4.75</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>Surface-state Density</td>
<td>$7.6 \times 10^{11} cm^{-2}eV^{-1}$</td>
<td>Conductance Method</td>
</tr>
<tr>
<td>at 0.45eV above VB top</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.1: Properties of a-GaN from Ref. [1].

which are smaller than that of crystalline GaN (3.4eV), and the refractive indices of the films ranged from 2.0 to 2.2 at a wavelength 5461Å for the larger values corresponds to the higher deposition pressures.

Yaji et al [39] prepared a-GaN and a-AlN thin films by reactive ion beam sputtering using N₂ gas, and studied the crystal structure, electrical and optical properties of the films. The X-ray diffraction results showed that the films were amorphous. The XPS results showed that the films contained some oxygen impurities, and the a-GaN films contained 8-12% Al due to the contamination of the Ga target. The optical absorption edge had the form $(h\nu - E_g)^{1/2}$, where $h\nu$ is photon energy and $E_g$ the band gap. The $E_g$ obtained by the extrapolation of the linear parts of the absorption edges were 5.20eV and 4.24eV for AlN and GaN respectively. They claimed that the higher optical band gap for GaN was due to the incorporation of Al which might indicate that the possibility of bandgap engineering of AlₓGa₁₋ₓN. The resistivity of the film was higher than $10^{11} \Omega$cm, and the thermoelectricity measure-
ment showed that the films were n-type. They claimed that the annealing at 1000°C for 30 min did not change resistivity appreciably.

Nonomura et al [2, 3] studied the optical and electrical properties of a-GaN and microcrystalline GaN (μc-GaN) films prepared by radio frequency (RF) reactive sputtering and their application to transparent thin film transistor (TFT). The deposition conditions are listed in Table 2.2. X-ray diffraction results showed when

<table>
<thead>
<tr>
<th>Target</th>
<th>Metal Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>N₂+Ar</td>
</tr>
<tr>
<td>Sputtering Pressure (mTorr)</td>
<td>N₂=5, Ar=195</td>
</tr>
<tr>
<td>Background Pressure (Torr)</td>
<td>( \leq 1 \times 10^{-6} )</td>
</tr>
<tr>
<td>Input RF-power ( P_{rf} ) (W)</td>
<td>80-120</td>
</tr>
<tr>
<td>Substrate Temperature ( T_s ) (°C)</td>
<td>200, 300, and 400</td>
</tr>
</tbody>
</table>

Table 2.2: Deposition conditions of a-GaN and μc-GaN from Ref. [2, 3].

\( P_{rf} \) was 80W and \( T_s \) was 200°C, the sample had an amorphous structure, while a value of \( P_{rf} \) over about 100W produced microcrystalline GaN with the crystalline size increased as the \( T_s \) increased. The XPS analysis showed that the ratio of Ga:N was about 1:1.15 at the surface. While XPS could not determine the ratio of Ga:N in bulk because Ar ion tend to sputter nitrogen out more easily than gallium. The films showed semiconducting tendency by the temperature dependence of dark conductivity measurement. The activation energy and the dark conductivity at room temperature were about 0.7eV and \( 3 \times 10^{-11} \) S/cm respectively for a-GaN. The conductivity of the films changed dramatically from about \( 10^{-11} \) S/cm for a-GaN to
about $10^{-3}$S/cm for microcrystalline GaN. GaN films showed n-type conduction by thermoelectric measurement. Photoconductivity was observed in a-GaN with $\Delta\delta_{\text{photo}}=5.7 \times 10^{-8}$S/cm under a light illumination of 100mW, and $\Delta\delta_{\text{photo}}$ has a dependence on illumination intensity $F$ in the form of $\Delta\delta_{\text{photo}} = CF^{0.77}$ where $C$ is a constant. The persistent photoconductivity was observed in both a-GaN and microcrystalline GaN films above room temperature. Electron spin resonance (ERS) spectra showed the spin densities in a-GaN and microcrystalline GaN are less than about $3 \times 10^{16}$ and $7 \times 10^{16}$cm$^{-3}$. They claimed that the relative low spin density suggested a low mid-gap density of states and an activation type electron transport process above 350K in a-GaN. The optical bandgaps measured at absorption coefficient of 5000cm$^{-1}$ were 3.95 and 2.96eV for a-GaN and microcrystalline GaN respectively. While the optical bandgaps determined by Tauc plot were about 2.8eV for both. A bottom gate type thin film transistor (TFT) was made by using a-GaN and the operation as a TFT was observed. The gate electrode and the insulator were n-type c-Si and SiO$_2$ respectively. The operation as a TFT was obtained by change of drain current depended on gate and drain voltage. The order of drain current was $10^{-8}$A and its mobility was about $10^{-4}$cm$^2$/V·s.

Chen et al [40] alloyed a-GaN and a-AlN to form Al$_x$Ga$_{1-x}$N with $x$ ranging 1 to 100 at % by reactive sputtering at a substrate temperature of 100K. They claimed the optical bandgaps varied linearly with composition ranging from 3.27eV for pure a-GaN to 5.95eV for pure a-AlN. They also performed ab initio calculations of
electronic properties for 216-atom models a-Al$_x$Ga$_{1-x}$N with $x$ being 0, 25, 50, 75 and 100 at %. The theoretical calculations showed that the slope of band gap versus $x$ is around 0.026eV/% compared to the experimental value of 0.027eV/%.

### 2.2.2 MBE a-GaN

Kuball et al [6] prepared a-GaN by room temperature molecular beam epitaxy and investigated their properties by transmission electron microscopy/diffraction and micro-Raman spectroscopy. The nitrogen source used was a RF plasma source for the production of atomic nitrogen. The transmission electron diffraction pattern showed broadened diffraction rings along with a considerable amount of diffuse background scattering which implies a significant amount of a-GaN in the film and the additional presence of crystalline GaN. The ring broadening suggested an average crystallite size of 30-40Å. The Raman spectra for room temperature (RT) GaN and GaN grown at 340°C under 488nm excitation and 325nm excitation are shown in Figure 2.4. They attributed the broad Raman peak centered at 650cm$^{-1}$ to a-GaN since it is not the characteristic of poly- and nano-crystalline GaN. The Raman spectrum deviates significantly from the phonon density of states of wurtzite and cubic GaN. They claimed that this observation suggested that the local short range bonding structure in the investigated a-GaN deviates from both wurtzite and cubic GaN in contrast to amorphous Si, Ge, and GaAs where a similar short range bonding structure is present in the amorphous and crystalline phase. They also
claimed that using Raman spectroscopy they did not find any indications for the presence of a large amount of N-N bonds and no indication for the presence of metallic Ga was found in the TED pattern.

### 2.2.3 IAD a-GaN

Bittar et al [7] prepared a-GaN films by ion-assisted deposition (IAD) and studied the Raman and optical properties of the films. A Kaufman type source was used to produce nitrogen ions and nitrogen ions were accelerated through 750V towards the substrate. The deposition rate was 0.7-0.8Å/s and there were possible resputtering of material during film formation. Rutherford backscattering spectroscopy
(RBS) and nuclear reaction analysis (NRA) showed that the Ga:N ratio in the films were within 10% of unity, and the films had O concentration lying between 10 and 20 at %. They claimed that within this level of variation of oxygen there were only minor differences measured among the optical responses and none at all in Raman. A typical Raman spectrum of a-GaN deposited on Si after Si background correction is shown in Figure 2.5. They found that the Raman spectrum in Figure 2.5 consists of three broad features, centered on 220, 580, and 700 cm\(^{-1}\) which contrasts strongly with crystalline wurtzite GaN which shows a set of much narrower Raman lines in the same range. They claimed that there is a clear correspondence between the measured spectrum and the frequencies at which bands appear in the calculated vibrational density of modes, while the bands appear very much broadened in the a-GaN spectrum, and the various bands have quite different Raman scattering cross

![Figure 2.5: Raman spectrum of a-GaN film on Si with a thickness of 200nm [7]. The first order Si signal at 520 cm\(^{-1}\) and the second order Si signal have been subtracted. The wurtzite GaN vibrational density of states is shown below the spectrum.](image-url)
sections. The optical band gaps of the films were \((3.1 \pm 0.3)\)eV by absorption measurement in the photon energy ranging from 1eV to 6eV. They claimed that the absorption coefficient vs. energy curve did not fit a simple power law in the range of measurement. A small subband gap absorption was presented in films produced with low nitrogen flow rate and was effectively minimized in high flow rate films.

### 2.2.4 Hydrogenated a-GaN

Hydrogenated amorphous and microcrystalline GaN films were studied by Yagi [41]. The films were grown by remote-plasma metalorganic chemical vapor deposition at a substrate temperature between 100°C to 300°C. They investigated the chemical bonds, compositions, structure and photoelectrical properties of the films. TED patterns showed amorphous and polycrystalline structures of the films. Atomic composition of the films was investigated by RBS. The N:Ga ratio for the films deposited at temperatures of 200°C and 300°C were \(1.18 \pm 0.03\) and \(1.01 \pm 0.03\) respectively. The corresponding hydrogen contents were 30 and 17 at \% respectively and oxygen and carbon contents were less than 10 at \%. The film prepared at 100°C exhibits a high oxygen content of more than 40 at \% within 50nm from the surface. The IR spectra showed that the Ga-N bond formation increased with the decreasing of hydrogen, which resulted in crystallization. All the GaN:H films were transparent with the optical bandgap of 3.0 to 3.3eV at an absorption coefficient of \(10^4\)cm\(^{-1}\). The photoluminescence (PL) measurement showed a broad peak between
360nm and 700nm for both amorphous and microcrystalline films. The photoresponse of a microcrystalline GaN:H film was 0.012A/W at 330nm monochromatic light of the incident intensity of 5µW/cm² with a 3V bias. The dark current and photocurrent of microcrystalline GaN:H films were two orders of magnitude larger than those of amorphous films. The photocurrent to dark current ratio was 10^4. The photoresponse time of microcrystalline GaN:H was inversely proportional to the intensity of Ga-H and N-H IR absorption which indicates that hydrogen performed the role of passivation of traps. The photodegeneration phenomena had never been observed for the GaN:H films in their investigation.

2.3 Summary

The simulation of a-GaN [4, 5] showed that a-GaN has a wide bandgap of 2.6-3.6eV with no deep gap states (without defect passivating H) and weakly localized band tail states. Therefore, a-GaN is believed to be a promising novel electronic material in its own right.

Experimental studies of a-GaN thin films have been performed by several groups which showed that the a-GaN films are transparent in the visible light range with an optical band gap in the range of 2.8-3.95eV [1, 39, 2, 7, 41, 40]. The refractive index of a-GaN films was reported to be about 2.0-2.2 above 400nm [1, 39] which is close to the value of crystalline GaN. The a-GaN films deposited at different con-
ditions showed different characteristics. Raman spectrum of a-GaN deposited by IAD showed a clear correspondence between the measured spectrum and the calculated vibrational density of states of wurtzite GaN [7], while Raman spectrum of MBE a-GaN deviates significantly from the phonon density of states of wurtzite GaN [6]. Nonomura et al reported low mid gap density of states for a-GaN by ESR measurement [2]. Yaji et al [39] reported insulator a-GaN with an electrical resistivity higher than $10^{11} \Omega \text{cm}$. While Nonomura et al [2, 3] reported a-GaN films with semiconducting tendency by temperature dependence of dark conductivity measurement. Amorphous GaN showed n-type conductivity reported in Ref. [39, 2, 3]. Photoconductivity has been observed for a-GaN by some groups [2, 3, 41]. Transparent TFT was made by using a-GaN [3] and the operation as a TFT was observed, while the performance was very poor. Several groups reported that oxygen contamination was detected in a-GaN films [1, 39, 7, 41].

In summary, progresses have been made both in theoretical and experimental studies of a-GaN. While the studies are far from complete and no films with high quality for optical and electronic device applications has been reported so far. Therefore, more studies in the area might be needed in the future to broaden the area of wide bandgap amorphous semiconductors.
Chapter 3

Film characterization techniques

Thin film characterization is used to determine the properties of the thin film. The structural properties, optical properties, and electrical properties are three main categories which are of interest for electronic and optoelectronic thin film devices. Fundamentally, the composition and structure of a thin film determines its other properties. Therefore, it is important to control the process to obtain thin films with known composition and structure for specific applications.

In this work, I mainly focused on studying compositional, structural, optical, and electronic properties of GaN thin films prepared at room temperature by ion beam assisted molecular beam evaporation with varieties of characterization techniques. X-ray diffraction and electron diffraction measurements were used to determine the structure of the films. The elemental composition and the stoichiometry of the films were obtained by Rutherford backscattering spectroscopy (RBS), elas-
tic recoil detection (ERD), and X-ray photoelectron spectroscopy (XPS). RBS and ERD were also used to determine the area densities of each element in the thin films. When combined with mechanical thickness measurement, RBS and ERD were used to determine the densities of the thin films. XPS and AES were employed to determine the chemical binding states of the top layers of the thin films.

GaN has a predicted band gap in the range of ultra-violet (UV) and visible light so that UV-visible light transmittance measurement were used to study optical band gaps of GaN thin films. The Er doped films were also studied by photoluminescence (PL) spectroscopy. Raman spectroscopy were used to study phonon density of states (DOS) as well as the structure of GaN films.

### 3.1 RBS and ERD

Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD) employ ion beams with energies in the MeV range to determine the stoichiometry, elemental area density, and impurity distributions in thin films. RBS and ERD measure the number of backscattered ions and forward recoiled ions as a function of energy. ERD can detect atoms lighter than the incident ions such as hydrogen when α particles are used as incident ions. RBS can detect atoms heavier than the incident ions. The sensitivity of RBS varies as $Z^2$, where $Z$ is the atomic number of the target, so that RBS is most sensitive for heavier atoms. The detection limit
is about $10^{12}$ atoms/cm$^2$. When careful measurements are made the typical uncertainties in the results are ±3% for areal density and 1% for average stoichiometric ratios. General references on RBS and ERD can be found in Zhu [42] and Tesmer et al [43].

Both RBS and ERD analysis involves interactions between incident ions and target materials. The surface elemental identification is based on the two-body elastic collision theory. Let $E_0$ and $M_1$ be the energy and atomic mass of the incident ions, let $M_2$ be the atomic mass of the target material, and let $E_1$ and $E_2$ be the energy of $M_1$ and $M_2$ after collision; and define the kinematic factor $K \equiv E_1/E_0$ which is a function of $M_1$, $M_2$ and the scattering angle $\theta$. Thus $M_2$ can be identified if $K$, $M_1$, and $\theta$ can be determined. When a uniform beam impinges at normal incidence on a uniform target that is larger than the area of the beam, the total number of detected particles $A$ is a function of scattering cross section $\sigma$, detector solid angle $\Omega$, total number of incident particles $Q$, and the area density $Nt$ of the target:

$$A = \sigma \Omega \cdot Q \cdot Nt \quad (3.1)$$

Where $N$ is the number of atoms per unit volume, and $t$ is the thickness of the film. This equation shows that when $\sigma$, $\Omega$, $A$, and $Q$ are known, the area density for each element in the target can be determined.

In this work, the incident ions were collimated $\alpha$ beams with an area of $1mm \times$
2mm generated by the 4.5MV tandem accelerator at Ohio University. The energy of \( \alpha \) beam for RBS and ERD was typically 2.2MeV. Detectors were Si barrier detectors with energy resolution of 15-20 keV. The stopper foil for ERD detector was a mylar foil. The vacuum in the measurement chamber was in the range of \( 10^{-6} \) Torr during the experiments. Figure 3.1 illustrates the set up for RBS and ERD measurements. The RBS and ERD detectors were at 168° and 30° to the incident beam respectively.

![RBS and ERD measurement set up.](image)

**Figure 3.1: RBS and ERD measurement set up.**

The distances from the samples to the detectors were about 10cm. The solid angles of the detectors were 3-6 mili-steradians.

The RBS and ERD spectra were analyzed by simulating the data with RUMP[44] and comparing the experimental results with simulated results. The best match was assumed when the difference in total counts in the interested area was less than the square root of the total counts in the interested area which was then considered as the statistical error. The uncertainty in RBS and ERD results in this work did not
consider the errors caused by errors in collision cross sections, errors in stopping powers of the incident ions in the target materials, and the possibility of the failure of Bragg’s rule for compound target materials [44]. Typically, the errors in cross section and stopping power are within 1%, the error caused by the failure of the Bragg’s rule depends on the configuration of electrons of the elements in the target material [42]. When the glassy carbon was used as substrate, the RBS and ERD spectra were analyzed by normalizing to the substrate, i.e., the total counts from substrate of simulated spectra matched the experimental results within the statistical error. The results showed that when normalized to the substrate spectra, the simulated Ga and N peaks also matched the experimental spectra both in heights and widths. Therefore, we concluded that the Bragg’s rule holds for amorphous GaN. When the substrate was crystal Si or HOPG, the channeling effect is a potential error source if the data are normalized to the substrate. Therefore, for crystal substrates, the analysis was done by normalizing to Ga and N peaks, i.e, matching the height and the width of the simulated and experimental Ga and N peaks within the statistical errors. Usually, the channeling effect can be alleviated by rotating the sample by 7° relative to the incident beam. The proton recoil cross section data used for simulation was the data measured by Ingram et al [45].

Figure 3.2 is a typical RBS spectrum of amorphous GaN. The RUMP simulation result is listed in table 3.1. The composition of the film is $Ga_{1.0}N_{1.41\pm0.01}$ with an area density of $(760\pm3)\times10^{15}$ molecules/cm². The film contains 0.12 at % of
Figure 3.2: A RBS spectrum of an amorphous GaN thin film on HOPG substrate.

Table 3.1: RUMP simulation result for the spectrum in Figure 3.2.
W atoms relative to the number of Ga atoms due to the ion source has W wires as cathode and neutralizer filaments. The film surface is covered by a thin layer of absorbed O.

### 3.2 Thickness measurement

The physical thickness of the films was measured by a mechanical thickness profilometer, Dektak IIA, Veeco Instruments Inc. This kind of measurement uses a mechanical stylus probe to trace the topography of a film with a sharp edge on a substrate. The sharp edge was obtained by partially masking the substrate with scotch tape prior to the film deposition and removed the mask before thickness measurement. The accuracy of this instrument is ±100Å with 200Å being the lowest measurable thickness.

Figure 3.3 shows a typical curve measured by the profilometer for GaN film on Si(100) substrate. The thickness of this film was calculated by subtracting the average height of the lower region (640µm-960µm) from the average height of the higher region (100µm-500µm). The measured thickness of this film was 1803Å±61Å (mean±standard deviation).
In crystalline materials, atoms (or groups of atoms) are arranged in a pattern that repeats periodically in three dimensions. When an X-ray or electron beam is scattered by a crystalline material, a diffraction pattern, which reflects the symmetry of the crystal, will be observed. The diffraction patterns from single crystals are usually discrete bright spots, and that from polycrystalline materials are sharp concentric bright rings. In amorphous materials, there is no long range periodic ordering preserved. In other words, there is no translation symmetry in amorphous materials. The atomic environment around any atom is different from each other, but a small degree of local order does exist such that the distance between atoms...
cannot be smaller than that of the radii of two atoms, and the number of nearest neighbors is limited by some constraints. Thus, X-ray diffraction and electron diffraction generate only one or more broad diffuse halos [46] for amorphous materials. In this work, X-ray diffraction and electron diffraction were employed to confirm the amorphous structure of the GaN thin films.

X-ray diffraction was performed by using powder X-ray diffractometer (Rigaku Geigerflex DMAX-B) with Cu Kα line (1.542Å) as X-ray source. θ-2θ scans were performed in the range of 2θ = 20° to 90°. The thickness of the films used for X-ray diffraction measurement were in the range of 1000Å to 5000Å. The films were assumed to be amorphous if no diffraction peak related to crystalline GaN was observed.

The electron diffraction patterns were taken on a Zeiss EM 109 electron microscope with electron energy of 80keV, and camera length 650mm or 390mm. The thickness of the films used for electron diffraction measurement were in the range of 100Å to 800Å. Only broad diffuse halos have been observed in the electron diffraction patterns.

### 3.4 Raman spectrum

Raman scattering is an inelastic scattering process experienced by light passing through a material which involves absorption or emission of one or more phonons.
Inelastic scattering must satisfy conservation of energy and momentum which is given by

\[ \omega_s = \omega - \omega' \]  
\[ k_s = k - k' \]  

(3.2)  
(3.3)

Where \( \omega \) and \( \omega' \) are frequencies of the incident light and scattered light, \( k \) and \( k' \) are wave vectors of incident light and scattered light, \( \omega_s \) and \( k_s \) are scattering frequency and wave vector of the phonon involved. If \( \omega > \omega' \), the process is a Stokes process which involves emission of phonons; if \( \omega < \omega' \), the process is an anti-Stokes process which involves absorption of phonons.

In a first-order Raman process, only a single phonon participates the process. In crystalline materials, momentum conservation requires \( k_s = q \) where \( q \) is crystal momentum. Since the magnitude of the wave vector in a Raman process is usually much smaller than the value corresponding to the Brillouin zone boundary of typical crystals [47], a Raman process only involves the wave vector at or near the center of the Brillouin zone and a Raman spectra show sharp peaks for crystal materials. Wave vector conservation breaks down for amorphous materials when no translation symmetry is preserved, and the Raman spectra are expected to display features reflecting the participating phonon density of states in amorphous materials. Further information on the application of Raman scattering in materials science can be found in Ref. [48].
In this dissertation, the Raman spectra were taken at room temperature using the 140mW 488nm line from an Ar-ion laser.

### 3.5 UV-Visible transmittance measurement

When the UV-visible light incident on a material, the light interact with the material by reflection, transmission, and absorption. Assume that we have a system with a uniform thin absorbing film on a thick but finite transparent substrate (no absorption) as shown in Figure 3.4. Let the thickness of the film be \( d \), the complex refractive index of the film be \( n_1 = n - ik \), the absorption coefficient of the film be \( \alpha \), the refractive index of the substrate be \( s \), and the incident wavelength be \( \lambda \). By considering the multiple reflection and interference of the light caused by the film

\[
\begin{align*}
&\text{Film} \quad d \\
&\text{Substrate} \\
&\text{Transmittance} \\
\end{align*}
\]

\( I_0 \)

\( n_0 = 1 \)

\( n_1 = n - ik \)

\( s \)

\( T \)

\( n_0 = 1 \)

Figure 3.4: An absorbing thin film on a finite transparent substrate.
and the multiple reflection of the light caused the substrate, the transmittance of the light with normal incidence on the film is given by [49]:

\[
T = \frac{Ax}{B - Cx + Dx^2}
\]  

(3.4)

where

\[
A = 16s(n^2 + k^2)
\]

\[
B = [(n + 1)^2 + k^2][(n + 1)(n + s^2) + k^2]
\]

\[
C = [(n^2 - 1 + k^2)(n^2 - s^2 + k^2) - 2k^2(s^2 + 1)]2\cos\phi
\]

\[
- k[2(n^2 - s^2 + k^2) + (s^2 + 1)(n^2 - 1 + k^2)]2\sin\phi
\]

\[
D = [(n - 1)^2 + k^2][(n - 1)(n - s^2) + k^2]
\]

\[
\phi = 4\pi nd/\lambda \quad x = \exp(-\alpha d) \quad \alpha = 4\pi k/\lambda
\]

In the region of weak and medium absorption, \(k \ll n\), \(\alpha \neq 0\) and \(x < 1\), The real refractive index is:

\[
n = \left[N + (N^2 - s^2)^{1/2}\right]^{1/2}
\]  

(3.5)

where

\[
N = 2s \frac{T_M - T_m}{T_MT_m} + \frac{s^2 + 1}{2}
\]
and $x$ is:

$$x = \frac{E_M - [E_M^2 - (n^2 - 1)^3(n^2 - s^4)]^{1/2}}{(n - 1)^3(n - s^2)}$$  \hspace{2cm} (3.6)$$

where

$$E_M = \frac{8n^2s}{T_M} + (n^2 - 1)(n^2 - s^2)$$

Therefore if we can determine $T_M(\lambda)$ and $T_m(\lambda)$ as continuous functions, the complex refractive index of the film can be determined and thus the absorption coefficient of the film can be obtained.

If the attenuation of the intensity of the incident light is mainly caused by the one way absorption of the light by the thin film and all the other effects can be neglected, the reflection and interference free transmittance can be calculated by:

$$T = I_0 \exp(-\alpha d)$$ \hspace{2cm} (3.7)$$

thus the absorption coefficient can be obtained if the transmittance and the thickness of the film are known.

In semiconductor materials, the optical absorption behavior in the UV-Visible light range is closely related to the electronic band structure. Semiconductors absorb lights with energy larger than their bandgap energy, so the absorption measurements can be used to estimate their bandgap energy. In direct bandgap crystalline semiconductors, the direct band-to-band transition dominates, and the absorption
The absorption coefficient has the following form at the band edge:

\[ \alpha h\nu = A(h\nu - E_g)^B \]  \hspace{1cm} (3.8)

where \( A \) is a constant related to the material, \( E_g \) is the bandgap energy, and \( B \) is 1/2 for dipole-allowed transitions which is the case for most direct gap materials, and \( B \) is 3/2 for the dipole-forbidden transitions. In indirect bandgap crystalline semiconductors, the indirect transitions have phonons involved, and the absorption coefficient at the band edge has the following forms:

\[ \alpha h\nu = C \left[ \frac{(h\nu - E_g + E_p)^D}{e^{E_p/k_B T} - 1} + \frac{(h\nu - E_g - E_p)^D}{1 - e^{-E_p/k_B T}} \right] \]  \hspace{1cm} (3.9)

Where \( C \) is a constant, \( E_p \) is the participating phonon energy, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( D \) is 2 for allowed transitions and 3 for forbidden transitions.

The fundamental absorption edge in most amorphous semiconductors follows an exponential law, i.e. \( \ln \alpha \) is proportional to the photon energy \( h\nu \). Above the exponential tail, the band-to-band transition for many amorphous materials is observed to obey a form given by Tauc [50] which is obtained under the assumption of parabolic bands:

\[ \alpha = \frac{C(h\nu - E_g)^2}{h\nu} \]  \hspace{1cm} (3.10)
where $C$ is a constant.

In this dissertation, the transmittance of a-GaN thin films on quartz substrates were measured by using HP 8451A Diode Array Spectrophotometer in the wavelength range of 200nm to 800nm with a resolution of 2nm. In this study, the absorption coefficient of the films will be derived from the transmittance measurement, and the optical absorption edge will be studied to find out the optical bandgap energy.

3.6 XPS and AES

Monoenergetic X-rays such as Mg Kα (1253.6eV) or Al Kα (1486.6eV) can penetrate a distance of the order of 1-10µm into the surface region of a material. The incident X-ray interact with atoms in the material causing photoelectrons to be emitted. X-ray photoelectron spectroscopy (XPS) involves analysis of emitted electrons which carry information about elemental composition of the surface and the chemical state of the elements. Since only the photoelectrons from atoms near the surface (typically from the top 5-50Å) can escape from the surface without inelastic loss, XPS is only sensitive to the top layers of most materials. XPS can be used to detect lithium and heavier elements. The detection limit ranges from 1% of a monolayer for light elements to 0.1% of a monolayer for heavy elements.

Auger electron spectroscopy (AES) involves the detection of Auger electrons
emitted from a material surface caused by the incidence of electrons or other radiations with sufficient energy to ionize an atomic core level electron. Conventionally, AES normally uses an electron beam to take the advantage of the ability to focus and scan the incident beam. This allows imaging specific element of surface region in scanning Auger microscopy (SAM). Lateral resolution as good as 50nm can be achieved in commercial instruments. Like XPS, AES is only sensitive to the top few monolayers. AES can be used to detect all elements except hydrogen and helium. The detection limit ranges from 1 to 0.1 at atomic %.

Figure 3.5 [8] schematically shows the related processes that involved in the ejection of a photoelectron or an Auger electron. The kinetic energy of photoelectron is given by:

$$E_k = h\nu - E_b - \Phi_{sp}$$

(3.11)

Where $h\nu$ is the incident photon energy, $E_b$ is the electron binding energy, and $\Phi_{sp}$ is the spectrometer work function. Since the work function can be compensated electronically, it can be eliminated. The Auger electron energy is given by:

$$E_{Auger} = E_x - E_y - E_z - \Phi_{sp}$$

(3.12)

Where $E_x$, $E_y$, $E_z$ are the binding energies of the three participating electrons. Sometimes XPS spectra are used to obtain Auger parameter $\alpha$, which is defined as the sum of core level photoelectron binding energy and the kinetic energy of
Auger electron:

$$\alpha = E_b + E_{Auger}$$  \hspace{1cm} (3.13)

The auger parameter can be used to investigate the chemical state of the atoms, and the measured value of the Auger parameter is independent of any electrostatic charging of the sample.

Since the binding energy of the electrons depends not only on the atoms which bind to but also on the environment of the surrounding atoms, XPS and AES can be
used to determine the elemental composition of the surface as well as the chemical binding information between atoms. Depth profiles can be obtained for XPS and AES by sputtering and measuring at successive depths.

In this work, XPS and AES were used in three areas: (1) the core level XPS and AES were employed to identify the surface elements and the chemical environment of the elements; (2) X-ray excited valence band spectroscopy was used to study the amorphous GaN valence band DOS; and (3) the kinetic energy of X-ray excited Auger electron were studied and the Auger parameter for Ga in a-GaN was obtained.

The XPS/AES spectra were taken and processed on an XSAM 800 XPS/UPS/AES/SAM with the VISION2 control and information handling system, Kratos Analytical Ltd. The general arrangement of the system is shown in Figure 3.6. The samples were mounted on a stainless steel sample holder.

To acquire XPS spectra, The system is equipped with a dual anode X-ray gun which produces Mg Kα X-ray with line energy 1253.6eV and approximate FWHM of 0.7eV, and Al Kα X-ray with line energy 1486.6eV and approximate FWHM of 1.0eV. The system is also equipped with an X-ray monochromator of the capability to produce monochromatic Al Kα X-ray with approximate FWHM of 0.2-0.3eV. The system consists of a UV-lamp which illuminates the inside of the spectrometer chamber to neutralize the charge on the insulator samples.

The analyser is a conventional hemispherical analyser with a radius of 127mm
combined with a lens system consisting of a combination of magnetic and electrostatic elements. The paths of the photoelectrons are as show in Figure 3.7. The analyser was operated at a constant pass energy mode for XPS spectra and constant retard ratio mode for AES spectra. At a pass energy of 10eV and using the monochromatic X-ray source, the spectrometer has a resolution of 0.5eV. The accuracy with which a peak energy may be measured is better than 0.1eV.

The Tougaard background correction [51], the Shirley background correction [52], and the linear background correction, which is a straight line between the data values at the start and the end of the interested region, were used to determine the XPS and Auger peaks. The energy peak positions were obtained by least-square fit-
ting each peak shape by a combination of Gaussian and Lorentzian with adjustable percentage of Lorentzian from 0 to 100, and sometimes an additional tail function was added on the low energy side of the peak to get the best fit of the peak shape [10].

Figure 3.7: AXIS Spectrometer Schematic [10].
3.7 PL spectrum for Er doped a-GaN

Photoluminescence is the luminescence caused by the absorption of light. The rare-earth doped semiconductors are potential materials for optoelectronic applications due to that the rare-earth luminescence depends very little on the nature of the host and the ambient temperature. Er-doped semiconductors are of great interests for its luminescence at 1540nm which is the wavelength corresponds to a window of minimum attenuation in silica based optical fibers for optical fiber communication.

In this dissertation, Er-doped a-GaN thin films were studied by photoluminescence spectroscopy. The concentration of the Er in the films were studied by RBS. The concentration of the Er was less than 5 at percent compared to Ga contents. The spectra for both as-deposited and annealed films were taken at 11K by using 325nm line from a He-Cd laser.
Chapter 4

Film deposition and thermal annealing

4.1 Film Deposition

The GaN thin films were prepared in an ultra-high vacuum (UHV) chamber by means of an evaporated Ga molecular beam and a low energy N ion beam. In this method, during Ga vapor deposition, N ions bombard the growing film surface, and the reaction between Ga and N is supposed to take place. The principle advantage of this method is that the operator has control over the relative arrival rates of each species at the sample surface, as well as control over the ion energy. This is quite unlike a plasma based reactive deposition, where the flux and energy of energetic species are strongly coupled, and the arrival rate of the reactive species is affected
by the deposition rate and gettering effects on the walls.

4.1.1 Deposition system

The film deposition was performed in the MeV chamber which is a part of W. M. Keck Thin Film Analysis Facility (Keck system) in Edwards Accelerator Laboratory, Ohio University. The layout of the Keck system is shown in Figure 4.1. Keck

![W.M. Keck Thin Film Analysis Facility](image)

Figure 4.1: W. M. Keck Thin Film Analysis Facility at Ohio University.

system is a UHV thin film deposition and analysis system which includes an MeV ion beam analysis chamber (MeV chamber), an XSAM800 XPS/UPS/AES/SAM chamber (XPS chamber), a load-lock sample transfer system, and two MOCVD deposition chambers. The MeV chamber is attached to a beam line from the 4.5MV
tandem accelerator that provides MeV ion beams to do Rutherford Backscattering Spectroscopy (RBS), Nuclear Reaction Analysis (NRA), and Elastic Recoil Spectroscopy (ERS). The films deposited in the MeV chamber or MOCVD chambers can be moved around the chambers without exposing the sample to air for ion beam analysis or electron spectroscopy.

The MeV chamber is a 61cm (24inches) outside diameter, 106cm (41.75inches) high stainless steel UHV chamber. A cryo-pump is employed to pump down the MeV chamber. The base pressure in the MeV chamber is around $2 - 3 \times 10^{-9}$ Torr without baking, and the pressure during the deposition is about $10^{-4}$ Torr due to the nitrogen gas flow for the ion source. A 2-grid 3-cm defocused broad beam Kaufman-type ion source from Commonwealth Scientific Corporation, and a 10cc single filament effusion cell from EPI are mounted on MeV chamber side wall port flanges to provide N ions and Ga molecules. A water-cooled $7.5 \times 7.5$cm$^2$ copper sample holder is mounted vertically in the center of the chamber. The sample holder is water cooled and can be moved up and down vertically, as well as rotated respect to the center axis of the cylindrical chamber. The sample holder was facing the evaporation cell during the deposition. To dope the films with erbium, an tantalum evaporation boat is mounted on the bottom of the chamber. A quartz crystal thickness monitor is in the vicinity of the substrate holder to monitor the film deposition rate. A quadrupole mass spectrometer is mounted on the top of the chamber to monitor the residual gas composition. The layout of the growth chamber is shown
schematically in Figure 4.2. The distances from the ion source, effusion cell, and

the evaporation boat to the sample holder are about 30cm, 30cm, and 50cm respectively.

4.1.2 Equipment performance

1. Performance of the ion source

The ion source is a Kaufman-type double molybdenum dish gridded 3cm defocused broad beam ion source. Figure 4.3 is the schematic diagram of the ion source
Figure 4.3: Schematic diagram of gridded, broad beam ion source and power supplies.

and the power supplies [53]. The diameter of the ion source is 64mm (2.5in). Both the standard cathode and neutralizer use tungsten wires with a diameter of 0.25mm (0.010in). The ions from the ion source can be accelerated to an energy up to 1500eV.

The 99.999% ultra high purity nitrogen gas was fed to the ion source through a Mass Flow Controller (MFC). The gas was filtered by a 0.5 microns particle filter before introduced into the MFC. The variation of nitrogen ion-beam current with nitrogen gas flow rate is plotted in figure 4.4. The measurement was done at
constant discharge current 0.53A, constant discharge voltage 40V, constant beam voltage 500V, and constant accelerator voltage 75V. The beam current increased rapidly at low flow rate, then the increment slowed down. An optimal condition can be selected in between the two regions. The N gas flow was set to be 9sccm (standard cubic centimeter per minute) for most depositions in this dissertation.

The ion beam profile is measured vertically along the MeV chamber center axis by moving a probe attached to gonimeter, and measuring the beam current passed through a small hole with a diameter of 2mm. Figure 4.5 shows typical beam profiles at beam current $I_b=7.0mA \pm 0.5mA$ and $4.0mA \pm 0.5mA$, beam volt-
age $V_b=150V \pm 3V$ and $100V \pm 3V$, and accelerator voltage $V_a=30V$ without beam neutralization. Two independent measurements were performed for each of the two operations of the ion source at $I_b=4.0mA \pm 1.0mA$, $V_b=150V$ and $I_b=4.0mA \pm 1.0mA$, $V_b=100V$. The results showed that the beam profiles are approximately reproducible (Figure 4.5). The discharge voltage was set at 40V to eliminate the production of doubly charged ions [54]. The ion arrival rate is calculated by assuming single charged ions. The $z$ axis is along the chamber center axis where positive direction is pointed up. The origin is the point where the axis of the ion source crosses the axis of the chamber. The uncertainty in the distance measurement is within 1mm. The results showed that the shapes of the beam profiles depend on the beam voltage and the beam current. In this work, the films were deposited at beam voltage

![Figure 4.5: Ion beam profile.](image-url)
50, 100, or 150V, accelerator voltage 30V, and beam current ranging from 0.5mA to 9.0mA with total beam neutralization or without beam neutralization. The ion arrival rate was in the range of $10^{15}$ ions/cm$^2$/s.

2. Performance of the evaporation sources

The gallium molecules were evaporated by a Knudsen-type effusion cell (Figure 4.6). The effusion cell is a water cooled 10cc BN crucible single filament effu-

![Figure 4.6: Effusion cell [11].](image)

sion cell from EPI. The effusion cell has an integral pneumatically activated shutter which can be rotated 90°. The 99.9999% metal basis gallium splatters were fed less than 2/3 of the crucible. The effusion flux is determined by the effusion cell temperature that is controlled by a tungsten-rhenium thermocouple feeding a temperature controller. The highest temperature that can be reached by this effusion cell
is 1600°C. The temperature fluctuation was ±0.1°C during the film depositions.

The Ga molecular beam deposition rate at substrate surface was measured by depositing Ga films on Si substrate and measuring the area density of the film by RBS. The deposition rate was about $1.9 \times 10^{14}$ atoms/cm$^2$/s at evaporation temperature of 1100°C on a 1cm diameter substrate which was placed on the substrate holder at the position facing the center of the evaporation cell. The variation of Ga molecular beam arrival rate at substrate surface as a function of temperature was measured by using the crystal thickness monitor, and the result is shown in figure 4.7. The deposition rate was about $5.6 \times 10^{12}$ atoms/cm$^2$/s at 900°C, and increased to about $1.9 \times 10^{14}$ atoms/cm$^2$/s at 1100°C.

The variation of Ga molecular beam flux as a function of substrate position was

![Figure 4.7: Ga beam flux as a function of temperature.](image)

Figure 4.7: Ga beam flux as a function of temperature.
measured by depositing films on glass slides, and measuring the area density of Ga by RBS. The result is shown in Figure 4.8. and Table 4.1. The position of the measured point on the substrate in the deposition chamber was described by Cartesian coordinates (x, z) in a right-hand Cartesian coordinate system in which the origin is the position where Ga beam center intersects the substrate surface, and the x-z plane is the plane of the substrate surface with the positive z direction pointed up. The uncertainty in the position measurement was less than 5mm. The variation in an area of 56mm-by-36mm was from a minimum value of 650 to a maximum value of 1317 in arbitrary units. The variation was about 68% relative to the average value of the minimum and the maximum values.

Figure 4.8: Ga beam flux as a function of substrate position.
Table 4.1: Ga deposition rate (arbitrary unit) as a function of substrate position.

A home-made tantalum evaporation boat was used to evaporate erbium metal which has a purity of 99.99%. The Ta boat was heated by an alternating current supplied from a variable transformer. The Er deposition rate as a function of heating current was measured by depositing Er on Si substrate and measuring the area density of the film by RBS. The Er deposition rate was controlled by setting proper heating current.

4.1.3 Film deposition

Thin films were deposited on a variety of substrates including HOPG (highly oriented pyrolytic graphite), glassy carbon, glass slides, Si(100), Si(111), fused quartz, and NaCl crystal, depending on the type of characterization to be done. Films deposited on HOPG and glassy carbon have good sensitivity for RBS measurement of the nitrogen content. Films deposited on quartz were mostly used for UV-visible light transmittance measurement since quartz substrates are transparent.

\[
\begin{array}{ccccccccc}
 z(\text{mm}) & -28 & -20 & -4 & 4 & 20 & 28 \\
 x(\text{mm}) & & & & & & & \\
 -18 & 910 & 1102 & 1103 & 1152 & 973 & 818 \\
 -12 & 1041 & 1129 & 1218 & 1142 & 1063 & 881 \\
 -6 & 1169 & 1231 & 1302 & 1268 & 1071 & 907 \\
 0 & 1133 & 1252 & 1302 & 1268 & 997 & 877 \\
 6 & 1116 & 1207 & 1300 & 1247 & 957 & 650 \\
 12 & 1135 & 1236 & 1307 & 1247 & 894 & 650 \\
 18 & 924 & 1073 & 1073 & 998 & 718 & 657 \\
\end{array}
\]
for photons in the visible and part of ultra-violet range. Films deposited on glass slides or NaCl substrate were floated in water and caught with TEM grids to take electron diffraction patterns.

Before loading into the growth chamber, all substrates except NaCl were ultrasonically cleaned in semiconductor grade acetone and alcohol for 15 minutes in each, and blow dried. The substrates were mounted on substrate holder by using double side conducting carbon tapes. The substrate holder was cooled with cooling water with a temperature of 18-22°C. The temperature of the substrate was monitored by placing Cole-Parmer Color-Change temperature indicators on the back of the substrates. The three indicators used in the experiments were supposed to change colors at the lowest temperature of 40°, 60°, and 88° respectively. None of them changed color during the deposition. Therefore we conclude that the substrates were close to room temperature during the film deposition.

The base pressure in the MeV chamber was lower than $6.0 \times 10^{-8}$ Torr before each film deposition started. When 9sccm nitrogen gas flow was introduced to the ion source, the pressure ranged between $9.0 \times 10^{-5}$ Torr and $1.3 \times 10^{-4}$ Torr. The residual gas pressure in the chamber was monitored by the quadrupole mass spectrometer and some typical spectra are shown in figure 4.9. Figure 4.9 (a) is a spectrum obtained before nitrogen gas was introduced into the ion source. The pressure read from ion gauge was $3.2 \times 10^{-9}$ Torr, and the total pressure read from quadrupole mass spectrometer was $2.84 \times 10^{-9}$ Torr during the scan. Figure 4.9 (b) was the spec-
(a) Before nitrogen gas was introduced.

(b) At nitrogen 0.75sccm gas flow.

Figure 4.9: Partial gas pressures in the MeV chamber.
trum obtained when 0.75sccm nitrogen gas flow was introduced into the ion source. The pressure read from ion gauge was $1.5 \times 10^{-5}$ Torr, and the total pressure read from quadrupole mass spectrometer was $4.30 \times 10^{-6}$ Torr. The difference is due to the sensitivity of the quadrupole mass spectrometer working at different pressures. Other than nitrogen, the dominate residual gas in the chamber was water vapor.

### 4.2 Thermal annealing

Some amorphous GaN films have been thermal annealed in quartz tube in a nitrogen or ammonia gas environment to study the composition change and crystallization of the films. The thermal annealing setup is shown in figure 4.10. Before each annealing, the quartz tube was $N_2$ or ammonia gas purged three times with a rotary pump. During each purge, the gas line and the quartz tube were filled with $N_2$ or ammonia gas to a pressure of 10-20psi, then pumped down to $10^{-1}$ Torr by the rotary pump. During the annealing, the gases flew through the quartz tube and a 5m-long 5mm-diameter copper pipe into the exhausting gas line. The gas flow rates were 10sccm to 120sccm. The annealing temperatures ranged from 250° to 1000°.

![Figure 4.10: Thermal annealing set up.](image-url)
Chapter 5

Results and discussion

In this chapter, I will list the deposition conditions for a-GaN and a-GaN:Er films prepared by ion beam assisted deposition, present the properties of the films characterized by a variety of methods, and discuss the experimental results.

In the experiments, the deposition conditions for the films are defined by (1) the Ga evaporation temperature; (2) the N ion beam parameters that include beam voltage $V_b$, beam current $I_b$, accelerator voltage $V_a$, and beam neutralization which is either total beam neutralization (TBN) or no beam neutralization; (3) the position of the substrate in the deposition chamber; and (4) the residual impurities in gases.

The deposition condition in general were (1) the Ga evaporation temperature was in the range of 1000-1100°C; (2) the N ion source parameters were: the beam voltage $V_b$ was 50V, 100V or 150V, beam current $I_b$ was in the range of 0.5mA to 9.0mA, accelerator voltage $V_a$ was 0V or 30V, and beam neutralization was either
total beam neutralization (TBN) or no beam neutralization; (3) the substrates were on the substrate holder that was mounted vertically in the center of the chamber facing to the Ga evaporation cell and N ion source; (The position of the substrates in the deposition chamber is defined by Cartesian coordinates \((x, z)\) in a right-hand Cartesian coordinate system in which the origin is the position where Ga beam center intersects the substrate surface, and the \(x-z\) plane is the plane of the substrate surface with the positive \(z\) direction pointed up. The uncertainty in the position measurement for the samples was within 2cm.) and (4) the nitrogen gas fed to ion source was 99.999\% ultra high pure nitrogen gas, the base pressure in the deposition chamber was lower than \(6 \times 10^{-8}\)Torr before each deposition started, and the pressure during the deposition was ranged between \(9.0 \times 10^{-5}\) and \(1.3 \times 10^{-4}\)Torr. The impinge ratio of \(~10:1\) for N:Ga was chosen in our experiments to prevent the decomposition reaction which can be significantly enhanced from Ga-rich surfaces due to catalysis by metallic Ga [55]. Specific conditions will be given with particular results.
5.1 RBS and ERD results

5.1.1 Elemental composition and area density of as-deposited GaN films

RBS and ERD analyses have been performed on films deposited at different N and Ga arrival rate at the growth surface. Most RBS and ERD analyses have been done after the films had been taken out of the growth chamber and exposed to air for several days unless specified in the text. Typically, the $\alpha$ beam energy used for RBS and ERD analyses was 2.2MeV, the RBS spectra were taken at normal incidence, and the ERD spectra were taken at glancing incidence with the angle of 75° between incident beam and the sample normal unless specified in the text.

This section will include three parts: (1) two case studies of typical RBS and ERD results for a-GaN films on HOPG substrate and Si(100) substrate; (2) RBS and ERD results for samples deposited at different deposition conditions; and (3) oxygen contaminated GaN films.

1. Typical GaN films deposited on HOPG and Si(100) substrate

Figure 5.1 shows RBS and ERD spectra and RUMP simulation results of a typical a-GaN film on HOPG substrate. The deposition condition was: $I_b=4.0\pm 1.0$mA, $V_b=150\pm 3$V and $V_a=30$V without beam neutralization; and the Ga evaporation temperature was $1075.0 \pm 0.1^\circ$C. The HOPG substrate was centered at about (0,
(a) RBS spectrum and RUMP simulation result.

(b) Substrate, N, and O region.

(c) Ga region.

(d) W and Mo region.

(e) ERD spectrum and simulation of H by assuming that H was on the GaN surface and in the interface between GaN and substrate.

(f) ERD spectrum and simulation of H by assuming that H was in the GaN film.

Figure 5.1: RBS and ERD spectra and RUMP simulation results for a-GaN on HOPG substrate.
4cm) in the deposition chamber. The RUMP simulation result for RBS spectrum is listed in Table 5.1. The simulation of H content was done by assuming that (1) the H was on the surface of GaN film and in the interface between GaN film and substrate; or (2) the H was completely in the GaN film. For the first case, the composition of H in layer 1 and layer 3 were 0.7±0.3 and 1.8±0.2 respectively. For the second case, the composition of H in layer 2 was 0.30±0.05. The ERD spectrum and RUMP H content simulation results are shown in Figure 5.1 (e) and (f). Comparing the two simulations with the experimental results, it is likely that the H was on the GaN film surface and in the interface between the GaN film and the substrate since the first case simulation result matched the shape of the experimental spectrum better. The results also showed that there was a small amount of O on the GaN film surface and at the interface between the GaN film and the substrate.

Figure 5.2 shows RBS and ERD spectra and RUMP simulation results of a typical a-GaN film on Si(100) substrate. Both spectra were taken at glancing incidence.

<table>
<thead>
<tr>
<th>Layer #</th>
<th>Area density ( \times 10^{15} \text{molecules/cm}^2 )</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7±4</td>
<td>O 1.0</td>
</tr>
<tr>
<td>2</td>
<td>256±13</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 1.19±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W 0.00025±0.00005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo 0.0006±0.0001</td>
</tr>
<tr>
<td>3</td>
<td>39±7</td>
<td>O 1.0</td>
</tr>
</tbody>
</table>

Table 5.1: RUMP simulation results for RBS spectrum in Figure 5.1.
Figure 5.2: RBS and ERD spectra and RUMP simulation results for a-GaN on Si(100) substrate.
with an angle of 76.3° between incident beam and the sample normal. The energy of α beam was 2.387MeV. The deposition condition was: $I_b=7.0\pm1.0\text{mA}$, $V_b=150\pm3\text{V}$ and $V_a=30\text{V}$ with total beam neutralization; and the Ga evaporation temperature was $1015.0\pm0.1^\circ\text{C}$. The center of the substrate in the deposition chamber was close to (4cm, -5cm). The RUMP simulation results are listed in Table 5.2.

In Table 5.2, the simulation of H was done by assuming that the H was on the surface of GaN film, in the interface between GaN film and substrate, and in the GaN film (Figure 5.2 (e)). The simulation has also been done by assuming that the H was totally in the GaN film (Figure 5.2 (f)). For this case, the composition of H in layer 2 was $0.022\pm0.005$ to get the total counts match. It is likely that the H was also on the GaN film surface and in the interface between the GaN film and the substrate since the second simulation did not match the width of the experimental spectrum. Due to the heavy substrate mass, the possible small amount of O on the GaN film surface and in the interface between the GaN film and the substrate was

<table>
<thead>
<tr>
<th>Layer #</th>
<th>Area density $\times 10^{15}$ molecules/cm$^2$</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6±1</td>
<td>H 1.0</td>
</tr>
<tr>
<td>2</td>
<td>609±8</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N 1.1±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H 0.005±0.002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>W 0.0006±0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo 0.0010±0.0005</td>
</tr>
<tr>
<td>3</td>
<td>2±1</td>
<td>H 1.0</td>
</tr>
</tbody>
</table>

Table 5.2: RUMP simulation results for RBS spectrum in Figure 5.2.
not detectable in this case.

The RBS results also showed that GaN films contained a small amount of W and Mo due to the ion source had W wires as cathode and neutralizer filaments, and Mo dishes for extracting ion beam.

2. RBS and ERD results for films deposited at different deposition conditions

Table 5.3 and Table 5.4 listed the growth conditions and the RUMP simulation results of RBS spectra of GaN films deposited at different Ga evaporation temperature and N ion beam parameters. Total beam neutralization was applied for films’ #

<table>
<thead>
<tr>
<th>Sub. #</th>
<th>Substrate position (cm, cm)</th>
<th>Ga temperature (°C)</th>
<th>N ion beam parameters</th>
<th>Deposition time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_b$</td>
<td>$I_b$</td>
</tr>
<tr>
<td>HOPG 3</td>
<td>(0, 2)</td>
<td>1075.0±0.1</td>
<td>50±1</td>
<td>0.5±0.5</td>
</tr>
<tr>
<td>HOPG 2</td>
<td>(0, 2)</td>
<td>1075.0±0.1</td>
<td>100±3</td>
<td>1.5±1.0</td>
</tr>
<tr>
<td>HOPG 9</td>
<td>(0, 2)</td>
<td>1100.0±0.1</td>
<td>100±3</td>
<td>3.0±1.0</td>
</tr>
<tr>
<td>HOPG 8</td>
<td>(0, 2)</td>
<td>1100.0±0.1</td>
<td>100±3</td>
<td>5.0±1.0</td>
</tr>
<tr>
<td>Si(100) 10</td>
<td>(0, 2)</td>
<td>1100.0±0.1</td>
<td>100±3</td>
<td>6.0±1.0</td>
</tr>
<tr>
<td>HOPG 1</td>
<td>(0, 2)</td>
<td>1075.0±0.1</td>
<td>150±3</td>
<td>0.5±0.5</td>
</tr>
<tr>
<td>HOPG 44</td>
<td>(0, -3)</td>
<td>1015.0±0.1</td>
<td>150±3</td>
<td>7.0±1.0</td>
</tr>
<tr>
<td>HOPG 43</td>
<td>(0, -4)</td>
<td>1020.0±0.1</td>
<td>150±3</td>
<td>7.0±0.5</td>
</tr>
<tr>
<td>HOPG 52-1</td>
<td>(-3, -6)</td>
<td>1050.0±0.1</td>
<td>150±3</td>
<td>5.0±1.0</td>
</tr>
</tbody>
</table>

Table 5.3: GaN thin film deposition conditions. Total beam neutralization was applied for films’ # greater than 10, no beam neutralization was applied for others. All the films listed in the tables contained no detectable O content by RBS analysis. The results showed
Table 5.4: RBS results of the composition and area density for a-GaN deposited at different experimental conditions listed in Table 5.3.

<table>
<thead>
<tr>
<th>Sub.</th>
<th>#</th>
<th>Ga:N ratio</th>
<th>Area density (×10^{15} \text{m/cm}^2)</th>
<th>Deposition rate (×10^{15} \text{m/cm}^2/\text{hr})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>3</td>
<td>1:0.48±0.02</td>
<td>445±2</td>
<td>445±2</td>
</tr>
<tr>
<td>HOPG</td>
<td>2</td>
<td>1:0.94±0.03</td>
<td>353±99</td>
<td>353±99</td>
</tr>
<tr>
<td>HOPG</td>
<td>9</td>
<td>1:0.67±0.04</td>
<td>581±14</td>
<td>581±14</td>
</tr>
<tr>
<td>HOPG</td>
<td>8</td>
<td>1:0.86±0.02</td>
<td>612±18</td>
<td>583±17</td>
</tr>
<tr>
<td>Si(100)</td>
<td>10</td>
<td>1:1.1±0.1</td>
<td>1362±355</td>
<td>545±142</td>
</tr>
<tr>
<td>HOPG</td>
<td>1</td>
<td>1:1.25±0.04</td>
<td>254±17</td>
<td>254±17</td>
</tr>
<tr>
<td>HOPG</td>
<td>44</td>
<td>1:1.41±0.01</td>
<td>740±23</td>
<td>56±2</td>
</tr>
<tr>
<td>HOPG</td>
<td>43</td>
<td>1:1.43±0.03</td>
<td>938±10</td>
<td>69±1</td>
</tr>
<tr>
<td>HOPG</td>
<td>52-1</td>
<td>1:1.05±0.02</td>
<td>815±33</td>
<td>178±7</td>
</tr>
</tbody>
</table>

that the composition, the area density, and the growth rate of the films depend on the growth conditions. The higher the Ga evaporation temperature, the higher the growth rate since the Ga evaporation rate increases as the Ga evaporation temperature increases. At any fixed temperature, the higher the N ion energy, the lower the growth rate. This might be due to the sputtering effect. At any fixed temperature, the higher the N ion beam current or ion energy, the higher the N to Ga ratio in the film.

In general, the films deposited with total beam neutralization stays on the substrates better than the films deposited without beam neutralization. Sometimes, films deposited without beam neutralization fell off the substrate when taken out from the deposition chamber. This is possibly due to the charging effect on insulator surfaces.
The films deposited on the fused quartz substrate showed that the films with highest Ga:N ratio had black appearances, which had an electrical resistivity lower than $10^{10}\Omega cm$. The films deposited on fused quartz at same deposition conditions as that of film #44 and #43 are transparent with a clear green or yellow color, which had an electrical resistivity higher than $10^{10}\Omega cm$. The absorption of the light by the films affect the color of the films. The dark appearance of the film could be the reflection of the smaller optical bandgap of the film or the higher density of bandgap states of the film. There will be more discussions of the optical bandgap and bandgap states when the UV-Visible light transmittance measurements of the films are presented later in this chapter.

3. Oxygen contaminated films

It was found that the films prepared at some positions in the chamber sometimes contained significant amount of oxygen, as well as hydrogen. The contamination mechanism is not clear yet. Figure 5.3 shows the RBS and ERD spectra, and RUMP simulation for a-GaN film #49-7 on HOPG with O and H contamination. The deposition condition for this film was the same as that of film #44 which was listed in Table 5.3 except the substrate was centered at about (0, -8cm) in the deposition chamber. The RBS spectrum showed a significant amount of the O all through the film. The ERD spectrum also showed that the film contained a significant amount of H. The RUMP simulation result is listed in Table 5.5.
Figure 5.3: RBS and ERD spectra and RUMP simulation results for a-GaN:O on HOPG substrate.
Table 5.5: RUMP simulation results for RBS spectrum in Figure 5.3.

Since the films with O contamination were deposited at a position that was in the lower part of the N beam, it is possible that the N beam there contained more N species that could form relatively weaker bonds in the film, therefore when such a film is exposed to O, the film react with the O, and get contaminated. The reason that it might not be caused by less N in the region is that I had deposited films with low N contents that was not contaminated by oxygen. To test the hypothesis that the film might oxidized after the deposition, two RBS analyses have been done for a-GaN film #62 which was deposited on glassy carbon substrate at the same deposition condition as that of film #49-7 for which O contamination was observed. The first RBS spectrum was taken immediately after the deposition without having the film exposed to air. The second RBS spectrum was taken a few days after the film exposed to air. The RBS spectra and RUMP simulation results are shown in Figure 5.4. The RUMP simulation results are listed in Table 5.6. The RBS
(a) RBS spectrum taken immediately after deposition without having the film exposed to air.

(b) RBS spectrum taken a few days later after the film has been exposed to air.

Figure 5.4: RBS spectra and RUMP simulation results for a-GaN:O on glassy carbon substrate.
Table 5.6: RUMP simulation results for RBS spectra in Figure 5.4.

results showed that the number of Ga atoms in the film did not change after the film exposed to air, but the film lost some N atoms and gained some O atoms after exposed to air. Therefore it is likely that the film was oxidized after the deposition.

5.1.2 Elemental composition and area density of thermal annealed a-GaN films

Amorphous GaN films have been thermal annealed in N ambient at the temperature of 250, 500, 700, 900, and 1000°C. The annealing condition and RBS analysis before and after annealing are listed in Table 5.7. The ERD spectra were also taken for annealed films #44 on HOPG, #43 on HOPG and #49-2 on HOPG. The H composition in the films were 0.05±0.02, 0.6±0.2 and 0.25±0.05 in films #44 on HOPG, #43 on HOPG and #49-2 on HOPG respectively. The RBS results showed that the film annealed at 250°C had no observable change in area density and composition (Figure 5.5). In Figure 5.5 the surface element positions for Ga, O,
Table 5.7: Annealing condition and RBS results of as-growth and annealed a-GaN films.

<table>
<thead>
<tr>
<th>Sub.</th>
<th>#</th>
<th>Temp. (°C)</th>
<th>Time (minutes)</th>
<th>Area density (×10^{15} m/cm²)</th>
<th>Composition</th>
<th>Area density (×10^{15} m/cm²)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG</td>
<td>44</td>
<td>250±10</td>
<td>210</td>
<td>740±23</td>
<td>Ga 1.0</td>
<td>786±42</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.41±0.01</td>
<td>N 1.41±0.02</td>
<td></td>
</tr>
<tr>
<td>HOPG</td>
<td>49-4</td>
<td>500±15</td>
<td>175</td>
<td>527±19</td>
<td>Ga 1.0</td>
<td>507±28</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.20±0.04</td>
<td>N 1.15±0.05</td>
<td></td>
</tr>
<tr>
<td>HOPG</td>
<td>43</td>
<td>700±5</td>
<td>90</td>
<td>938±10</td>
<td>Ga 1.0</td>
<td>904±45</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.43±0.03</td>
<td>N 0.9±0.1</td>
<td>O 0.3±0.1</td>
</tr>
<tr>
<td>Si(100)</td>
<td>46</td>
<td>900±5</td>
<td>70</td>
<td>609±8</td>
<td>Ga 1.0</td>
<td>412±40</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.1±0.1</td>
<td>N 0.9±0.2</td>
<td>O 0.3±0.1</td>
</tr>
<tr>
<td>Si(100)</td>
<td>46</td>
<td>900±5</td>
<td>190</td>
<td>609±8</td>
<td>Ga 1.0</td>
<td>28±5</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.1±0.1</td>
<td>N 1.0±0.5</td>
<td>O 1.0±0.5</td>
</tr>
<tr>
<td>HOPG</td>
<td>49-2</td>
<td>900±5</td>
<td>30</td>
<td>740±30</td>
<td>Ga 1.0</td>
<td>374±9</td>
<td>Ga 1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 1.41±0.01</td>
<td>O 1.5±0.1</td>
<td></td>
</tr>
</tbody>
</table>

(a) As-growth film.  
(b) Annealed at 250°C.

Figure 5.5: RBS spectra of as-growth film #44 on HOPG and the same film annealed at 250°C.
N and C are labeled. No oxidation of the film was observed. The films annealed at 500, 700, and 900°C lost some N, and gained some O. At 500°C, the oxygen seems to start to build up at the interface between the film and the substrate (Figure 5.6). At 700°C, oxygen was observed all through the film (Figure 5.7). At 900°C, the film was oxidized completely (Figure 5.8) or partly and evaporated if annealed long enough. If the films annealed at 900°C are compared, it seems the film on HOPG is more likely to be oxidized. (RBS analysis showed no oxygen content in the substrate before deposition). The oxygen gained during the annealing could come from the residue gases in the quartz tube or in the pipes. The annealing results showed that the a-GaN is reactive to oxygen when heated to 500°C or above. Amorphous GaN films also get evaporated at 900°C. Some films have also been annealed at

Figure 5.6: RBS spectra of as-growth film #49-4 on HOPG and the same film annealed at 500°C.
Figure 5.7: RBS spectra of as-growth film #43 on HOPG and the same film annealed at 700°C.

Figure 5.8: RBS spectra of as-growth film #49-2 on HOPG and the same film annealed at 900°C.
1000°C, the films were completely evaporated at this temperature in 30 minutes.

Some a-GaN films have also been annealed in ammonia at 700 and 900°C. No significant oxidation has been observed. RBS measurement showed that after annealing in ammonia at 700°C the composition of the film did not change much; and at 900°C, film lost nitrogen completely, and only a thin layer of gallium (less than the Ga content in the GaN film before annealing) was left on the substrate. Therefore, oxidation of a-GaN during thermal treatment can probably be avoided by annealing in ammonia.

## 5.2 Physical density of the films

The physical densities of the films have been calculated from the area density measured from RBS and ERD spectra and the physical thickness measured by mechanical thickness profilometer Dektak IIA. The calculation was done as follows. Let $M_{Ga}=69.723\text{gm/mol}$ be the mass of Ga, $M_N=14.00674\text{gm/mol}$ be the mass of N, $M_O=15.9994\text{gm/mol}$ be the mass of O, $M_H=1.00794\text{gm/mol}$ be the mass of H, $A$ and $dA$ be the area density and the uncertainty in the area density of the film in molecules/cm², $t$ and $dt$ be the physical thickness and the uncertainty in the thickness of the film in cm, and $A_v=6.0221 \times 10^{23}\text{atoms/mol}$ be the Avogadro constant. Assume the composition of the film is $\text{Ga}_{1.0}N_{x \pm dx}:O_{y \pm dy}:H_{z \pm dz}$, then the density $D$
of the film is calculated by:

\[ D = (M_{Ga} + xM_N + yM_O + zM_H) \times \frac{A}{t/A_v} \]  

(5.1)

and due to the independence of the variables the uncertainty \( E_D \) in the density \( D \) is calculated by:

\[ E_D = \sqrt{\left( \frac{\partial D}{\partial x} \right)^2 dx^2 + \left( \frac{\partial D}{\partial y} \right)^2 dy^2 + \left( \frac{\partial D}{\partial z} \right)^2 dz^2 + \left( \frac{\partial D}{\partial A} \right)^2 dA^2 + \left( \frac{\partial D}{\partial t} \right)^2 dt^2} \]  

(5.2)

The calculated results are listed in Table 5.8.

The lattice constant of the zincblende (ZB) GaN is \( a=0.451 \text{nm} \) [37], which results a density of 6.06gm/cm\(^3\). The lattice constants of the wurtzite (WZ) GaN are \( a=0.3189 \text{nm} \) and \( c=0.5185 \text{nm} \) [26], which give a density of 6.09gm/cm\(^3\). Compared to crystal GaN, the densities of the amorphous GaN films are smaller. By using the density of 6.1gm/cm\(^3\) for crystal GaN, the densities of the amorphous GaN films without O are 62% to 78% that of the crystal GaN. The oxidized films had densities of 68% to 85% of the crystal GaN. The density of the films depends on the composition of the films, the larger the N or N+O to Ga ratio, the lower the density of the film.
<table>
<thead>
<tr>
<th>Sub.</th>
<th>#</th>
<th>Area density ((\times 10^{15}\text{m/cm}^2))</th>
<th>Composition</th>
<th>Thickness (Å)</th>
<th>Density (gm/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(111)</td>
<td>46</td>
<td>624±77</td>
<td>Ga 1.0</td>
<td>1870±51</td>
<td>4.76±0.61</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N 1.15±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 0.05±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(111)</td>
<td>55</td>
<td>118±5</td>
<td>Ga 1.0</td>
<td>405±52</td>
<td>4.19±0.57</td>
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<tr>
<td></td>
<td></td>
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<td>N 1.20±0.10</td>
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<td></td>
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<tr>
<td></td>
<td></td>
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<td>H 0.08±0.04</td>
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</tr>
<tr>
<td>Si(100)</td>
<td>55</td>
<td>221±12</td>
<td>Ga 1.0</td>
<td>763±92</td>
<td>4.17±0.56</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>N 1.20±0.10</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 0.12±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(111)</td>
<td>51</td>
<td>467±43</td>
<td>Ga 1.0</td>
<td>1818±55</td>
<td>3.78±0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N 1.35±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 0.05±0.05</td>
<td></td>
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</tr>
<tr>
<td>Si(100)</td>
<td>46</td>
<td>687±24</td>
<td>Ga 1.0</td>
<td>1856±136</td>
<td>5.21±0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N 0.95±0.10</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>O 0.10±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 0.18±0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(100)</td>
<td>53</td>
<td>175±38</td>
<td>Ga 1.0</td>
<td>570±97</td>
<td>4.67±1.29</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>N 0.80±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O 0.60±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 1.10±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(100)</td>
<td>51</td>
<td>412±12</td>
<td>Ga 1.0</td>
<td>1527±74</td>
<td>4.15±0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N 0.90±0.10</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O 0.60±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>H 0.73±0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.8: Physical density of the films.
5.3 X-ray diffraction and electron diffraction results

Figure 5.9 shows a typical $\theta - 2\theta$ X-ray diffraction spectrum of a-GaN film on Si(100) substrate. The deposition condition for the film in Figure 5.9 was: $I_b=7.0 \pm 1.0\text{mA}$, $V_b=150 \pm 3\text{V}$ and $V_a=30\text{V}$ with total beam neutralization; and the Ga evaporation temperature was $1015.0 \pm 0.1^\circ\text{C}$. The approximately $1\text{cm} \times 1\text{cm}$ Si(100) substrate was centered at about $(0, -4\text{cm})$ in the deposition chamber. The thickness of the film is about $4300\text{Å}$, and the estimated Ga:N ratio of the film is $1.0:1.3 \pm 0.1$. The X-ray diffraction spectrum was taken on powder X-ray diffractometer (Rigaku Geigerflex DMAX-B) with Cu K$\alpha$ line ($1.542\text{Å}$) as X-ray source. The RSM, RM, SS, and DS slits were $0.45\text{mm}$, $0.3\text{mm}$, $1^\circ$ and $1^\circ$ respectively. In all X-ray diffraction spectrum...
tion measurements, only diffraction peaks related to the substrates have been ob-
served, no diffraction peaks related to crystal GaN have been observed in any X-ray
diffraction spectrum.

Figure 5.10 shows two electron diffraction patterns for amorphous GaN thin
films. The deposition condition for the film in Figure 5.9 (a) was: $I_b=7.0\pm1.0$mA,

![Electron diffraction patterns](image)

(a) (b)

Figure 5.10: Electron diffraction patterns of GaN thin films.

$V_b=150\pm3$V and $V_a=30$V with total beam neutralization; and the Ga evaporation
temperature was $1015.0\pm 0.1^\circ$C. The substrate was centered at about (0, 2cm) in
the deposition chamber. The thickness of the film is about 200Å, and the estimated
Ga:N ratio of the film is $1.0:1.3\pm0.1$. The electron energy was 80keV, and the
camera length was 390mm for the electron diffraction measurement. The depo-
sition condition for the film in Figure 5.9 (b) was: $I_b=6.0\pm 1.0$ mA, $V_b=100\pm 3$ V and $V_a=30$ V without beam neutralization; and the Ga evaporation temperature was $1100.0\pm 0.1$ °C. The substrate was centered at about (0, 0) in the deposition chamber. The thickness of the film was about 300 Å, and the estimated Ga:N ratio of the film is $1.0:1.1\pm 0.1$. The electron energy was 80 keV, and the camera length was 650 mm for the electron diffraction measurement. In both spectra, no sharp rings related to GaN crystalline structure have been observed.

### 5.4 Raman spectra

Figure 5.11 shows a first order Raman spectrum for an amorphous GaN thin film. The Raman spectrum was taken at room temperature using 140 mW of the 488 nm line of an Ar-ion laser. The dominate feature at $\sim 520$ cm$^{-1}$ is due to the
optical mode from the Si substrate. The RBS spectrum showed that the composition of the film was GaN$_{1.1\pm0.1}$; the area density of the film was $(646\pm34)\times10^{15}$ molecules/cm$^2$ which corresponds to a physical thickness of about 1500Å to 2000Å. The Raman spectrum of the GaN film showed continuums that roughly contains the main features in the phonon DOS of hexagonal GaN from \textit{ab initio} calculation [56], which is a strong indication that the film is amorphous since in the amorphous materials the crystal momentum is not a good quantum number and, as a result, all vibrations participate in first-order scattering.

The Raman spectra of amorphous GaN are different from the Raman spectra of the crystalline GaN for which only narrow peaks have been observed because of the conservation of lattice momentum. For comparison, the Raman frequencies of hexagonal GaN and cubic GaN modes are listed in Table 5.9 and Table 5.10.

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
$E_2^+$ & $E_2^-$ & $A_1$(TO) & $A_1$(LO) & $E_1$(TO) & $E_1$(LO) & Ref. \\
\hline
145 & 568 & 533 & & 559 & & [57] \\
& 568 & 533 & & 559 & & [58] \\
144 & 569 & 532 & & 560 & & [59] \\
143 & 568 & 533 & & 559 & 726 & [60] \\
& 570 & & & 738 & & [61] \\
144 & 569 & 533 & 735 & 561 & 743 & [62] \\
142 & 567 & 530 & & 558 & & [63] \\
\hline
\end{tabular}
\caption{Raman frequencies (cm$^{-1}$) of the WZ-GaN modes.}
\end{table}

[48]. Comparing the Raman frequencies of crystalline GaN and amorphous GaN, the frequencies are in the same range. The structure in a-GaN Raman spectra be-
Table 5.10: Raman frequencies (cm\(^{-1}\)) of the ZB-GaN modes.

<table>
<thead>
<tr>
<th>Frequency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>730</td>
<td>64</td>
</tr>
<tr>
<td>554</td>
<td>65</td>
</tr>
<tr>
<td>555</td>
<td>66</td>
</tr>
</tbody>
</table>

low \(\sim400\text{cm}^{-1}\) and in the range of \(550-750\text{cm}^{-1}\) are roughly corresponds to the acoustic and optical phonons.

### 5.5 UV-visible transmittance measurement results

UV-Visible transmittance spectra were taken on an HP 8451A Diode Array Spectrophotometer in the wavelength range of 300nm to 820nm with a resolution of 2nm for a-GaN thin films deposited on fused quartz substrate. The quartz substrate is transparent in the wavelength range of 300nm-820nm with a refractive index of \(\sim1.46\). The optical properties of one film with estimated Ga:N ratio of \(1.0:1.3\pm0.1\) will be given in the following paragraphs. The thicknesses of the film is \(3503\pm55\text{Å}\) measured by surface profilometer.

The complex refractive index of the films were calculated by using the method proposed by Swanepoel [49] in the range of weak and medium absorption. From the calculated refractive index, the calculated transmittance spectra were obtained. The thicknesses of the films were manually adjusted near the value measured by surface profilometer to get the best fit of the calculated spectrum to the experimen-
tal spectrum. The experimental spectrum, the envelope function, and the calculated spectra are shown in Figure 5.12. The simulation showed that the best results were

Figure 5.12: UV-Visible spectra, the envelope $T_M$ and $T_m$, and the calculated spectra from $T_M$ and $T_m$ at the film thickness near the value measured by mechanical method.

obtained at the film thicknesses near 3550Å, which is very close to the value of 3503Å measured by surface profilometer. Thus the thickness of the film was assumed to be 3550Å for further study.

The accuracy of the method partly depends on the accuracy of the determination of functions $T_M(\lambda)$ and $T_m(\lambda)$. To test the effect of the variation of the functions $T_M(\lambda)$ and $T_m(\lambda)$ on the resulted values of $n$ and $k$, the simulations were performed by increasing or decreasing the value of functions $T_M(\lambda)$ or $T_m(\lambda)$ by 1%. The results showed that the change in the value of $n$ was within 0.08, and the change
in the value of $k$ was within 0.003. The refractive index and the extinction coefficient of the film vs. the wavelength of the incident light are shown in Figure 5.13. Compared to the refractive index of crystalline GaN [38, 67], the results showed

![Figure 5.13: Refractive indices of the films determined from the envelope $T_M$ and $T_m$ shown in Figure 5.12.](image)

that the refractive indices of the a-GaN film are close to that of crystalline GaN.

The absorption coefficient $\alpha$ as a function of the photon energy $E$, which is shown in Figure 5.14, was calculated from the extinction coefficient $k$ by using $\alpha(E) = \frac{4\pi k(E)}{\lambda}$, where $\lambda$ is the wavelength of the incident photon. The absorption coefficient increased slowly as the energy increasing at the low energy, and the increment was getting more abrupt at the higher energy. The optical band gap of the film measured at the absorption coefficient of $10^4\text{cm}^{-1}$ is about 2.5eV. The optical band gap of the film was also determined by least-square fitting of a straight line in
the region of 2.4eV to 2.9eV from Tauc plot [50] which is shown in Figure 5.15. The bandgap derived from Tauc plot is \(~2.0eV\). The absorptions above those energies are probably due to the band to band absorption. The absorptions at lower energies are probably due to the band gap states.

To compare the optical properties of films with different Ga:N ratio, two transmittance spectra for films with different Ga:N ratio are shown in Figure 5.16. In the region of 550-820nm which is below bandgap energy, film (A) showed much higher transmittance than film (B) though the first one is thicker than the second one. Therefore the absorption coefficient for film (A) is lower than that of film (B) in this region. Assume that the absorption of the photons in the region of UV-visible light is due to electronic transitions, the absorption coefficient $\alpha$ is related to

Figure 5.14: Absorption coefficient vs. energy.
Figure 5.15: Tauc plot.

Figure 5.16: Transmittance of (A) a film with estimated Ga:N ratio of 1.0:1.3±0.1 and measured thickness of $3503\pm55\text{Å}$; (B) a film with estimated Ga:N ratio of 1.0:0.9±0.1 and estimated thickness of $2200\pm300\text{Å}$. 
the occupancy of the initial state \( n_i \) and final state \( n_f \) by 
\[
\alpha \propto \sum P_{if} n_i n_f,
\]
where \( P_{if} \) is the optical transition matrix. From this relation, the low absorption coefficient for photons with energies lower than the band gap energy implies a lower density of band gap states. Therefore, we can conclude that by incorporating more nitrogen into the film, the band gap of a-GaN film is getting cleaner.

### 5.6 XPS/AES results

XPS/AES spectra have been taken for an amorphous GaN sample deposited on glassy carbon substrate. The deposition condition was: \( I_b = 7.0 \pm 1.5 \text{mA}, V_b = 150 \pm 3 \text{V} \) and \( V_a = 30 \text{V} \) with total beam neutralization; and the Ga evaporation temperature was \( 1015.0 \pm 0.1 \degree \text{C} \). The glassy carbon substrate was centered at about \((0, 4 \text{cm})\) in the deposition chamber. An RBS spectrum was taken immediately after the deposition without exposing the sample to air. The RUMP simulation result for RBS spectrum was: the composition of the film was \( \text{Ga}_{1.0}\text{N}_{1.37\pm0.02}\text{W}_{0.0022\pm0.0001}\text{Mo}_{0.0023\pm0.0001} \); and the area density of the film was \((213 \pm 2) \times 10^{15} \text{molecules/cm}^2\). The sample was left in the transfer chamber for 30 days before the XPS chamber was ready, then transferred into the XPS chamber for analysis without exposing to air. The vacuum in the transfer chamber and XPS chamber was in the range of \(10^{-9} \text{Torr}\).
5.6.1 XPS analysis

XPS spectra were taken on the as-deposited film; then the film was sputtered by 4000eV Ar ions, and the XPS spectra were taken on the sputtered film. The spectra were taken at a pass energy of 80eV, 40eV or 20eV, and the energy steps were 1eV for survey spectra and 0.1eV to 0.5eV for core level XPS regional spectra and valence band XPS spectra. The survey XPS spectra were taken in the binding energy range of 0-1200eV to identify the surface elements; the regional core level XPS spectra for selected core levels were taken to obtain the atomic ratio of the atoms in the film; and the valence band XPS spectra were taken to study the valence band structure of the film. The binding energy of the electrons were measured relative to the Fermi level of the system.

1. XPS analysis of as-deposited film

The XPS survey spectra were taken with Mg Kα, Al Kα, and monochromatic Al Kα (mono Al Kα) with or without UV-lamp on. Some typical spectra are shown in Figure 5.17 and Figure 5.18. Figure 5.17 showed that by turning on the UV-lamp, there were no shift in core level electron energy peak positions, therefore we concluded that no charging up effect took place on the film surface. The regional core level XPS spectra taken with mono Al Kα X-ray showed that the spectra are usually broadened by turning on the UV-lamp compared to the spectra taken without the UV-lamp on. Figure 5.17 and Figure 5.18 showed that the surface elements of
Figure 5.17: XPS survey spectra excited by (A) Al Kα, (B) monochromatic Al Kα and (C) monochromatic Al Kα with UV lamp on.

The film contained Ga, N, O, and C. Since RBS analysis did not show any O and C contents in the film, the O and C were assumed to be due to surface contamination.

When Al Kα X-ray is used as excitation source, N 1s and O 1s peaks overlap Ga LMM Auger series; when Mg Kα X-ray is used as excitation source, C 1s and Ga 3s peaks overlap Ga LMM Auger series. Therefore, core level XPS regional spectra for N 1s and O 1s peaks were taken with Mg Kα X-ray; while core level XPS regional spectra for C 1s peaks were taken with Al Kα X-ray.

The C 1s peak was used as the reference for monitoring the charging effect that can take place on the surface of insulator materials. The peak positions were determined by fitting the peak shape with a combination of Gaussian and Lorentzian.
(a) Binding energies of electrons excited by (A) Al Kα and (B) Mg Kα.

(b) Kinetic energies of electrons excited by (A) Al Kα and (B) Mg Kα.

Figure 5.18: XPS survey spectra.
Three different kinds of background correction algorithms, linear, Shirley [52], and Tougaard [51], were used for comparison. Figure 5.19 shows a typical Al Kα XPS spectra of C 1s electrons, the Tougaard background correction and the fitted peak. Table 5.11 listed eleven C 1s binding energy peak positions from regional scans taken at different stage during the analysis over a period of about two months. The average peak position values, the standard deviation of the values, and the minimum and the maximum values determined from different background correction algorithms are listed in Table 5.12. The fitted peak positions are slightly affected by the statistics of the data, the background correction algorithms, and the energy steps of each individual case. The average binding energies determined from three
Table 5.11: C 1s peak positions determined from different background correction algorithms.

<table>
<thead>
<tr>
<th>Background correction</th>
<th>Average values (eV)</th>
<th>Standard deviation (eV)</th>
<th>Minimum (eV)</th>
<th>Maximum (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>285.42</td>
<td>0.14</td>
<td>285.24</td>
<td>285.70</td>
</tr>
<tr>
<td>Shirley</td>
<td>285.41</td>
<td>0.15</td>
<td>285.15</td>
<td>285.69</td>
</tr>
<tr>
<td>Tougaard</td>
<td>285.42</td>
<td>0.16</td>
<td>285.16</td>
<td>285.73</td>
</tr>
</tbody>
</table>

Table 5.12: Average C 1s peak positions determined from different background correction algorithms.

The small variation in the exact peak positions does not mean the shift of the C 1s peak positions. The average value was taken as the reference, and the small variation was not considered to be due to surface charging effect. Comparing to the reported values from 284.8eV to 285.2eV for C 1s electrons when referenced to the Au 4f7/2 line at 84.0eV [68], the C 1s electron peak
position is slightly higher on amorphous GaN film surface. The difference is possibly due to the difference in the environment around the C atoms rather than the surface charging effect since no large relative shift in C 1s binding energy has been observed in different spectra.

The Tougaard background correction [51] algorithm was used to determine the binding energy peak positions for the rest of this work. In this work, the N 1s, O 1s, Ga 2p, Ga 3p, and Ga 3d core level XPS spectra were taken with Mg Kα X-ray, and C 1s, Ga 2p, Ga 3s, Ga 3p, and Ga 3d core level XPS spectra were taken with Al Kα X-ray. Several spectra have been taken for each peak region over a period of several weeks and a good reproducibility was found.

The quantitative analysis of Ga 2p, N 1s and O 1s peak areas from five Mg Kα survey spectra taken at different stage of the investigation showed that the surface elemental atomic ratio is Ga:N:O=1:0.89±0.13:0.07±0.05. Since no oxygen was detected by RBS analysis, the O was considered to be due to the surface contamination. The result showed that the film surface was a little bit richer in Ga content, converses the RBS data showed that this film was N rich. The possible reason for the disagreement might be due to that the deposition employed energetic N ions as the N source, and some N ions might penetrate into the surface and the reaction between Ga and N not only take place at the deposition surface but also a few angstrom under the surface region. It is also possible that the surface is tend to lose N after deposition. Therefore the N content is richer under the surface region
compared to the film surface.

In this section, I will give regional spectra for N 1s, O 1s, C 1s, Ga 2p, Ga 3s, Ga $3p_{1/2}$, Ga $3p_{3/2}$, Ga 3d, and N 2s electrons and list the peak positions obtained by fitting each peak shape by a combination of Gaussian and Lorentzian.

Figure 5.20 shows a typical Mg Kα spectrum, the background correction, and the fitted peak for N 1s electrons. Table 5.13 listed the binding energy peak positions for N 1s electrons. The average binding energy peak position for N 1s electrons from two spectra is 397.30eV with an uncertainty of about 0.15eV.

One spectrum was taken for O 1s electrons, and the peak position is around 532.07eV. The Mg Kα spectrum, the background correction, and the fitted peak for

Figure 5.20: Mg Kα XPS spectrum for N 1s electrons. The bounded region is the region for peak fitting.
Table 5.13: Binding energy of N 1s electrons. B.E. stands for binding energy.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<tr>
<td>B.E. (eV)</td>
<td>397.16</td>
<td>397.45</td>
<td>397.30</td>
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<tr>
<td>X-ray</td>
<td>Mg Kα</td>
<td>Mg Kα</td>
<td>N/A</td>
</tr>
</tbody>
</table>

O 1s electrons is shown in Figure 5.21.

![Figure 5.21](image)

Figure 5.21: Mg Kα XPS spectrum for O 1s electrons. The bounded region is the region for peak fitting.

Figure 5.22 shows typical XPS spectra, the background correction, and the fitted peaks for Ga 2p electrons. The average binding energy for Ga 2p electrons from seven spectra is about 1117.64eV with a standard deviation of 0.11eV. The smallest and the largest values are about 1117.53eV and 1117.83eV. The binding energy peak positions of Ga 2p electrons are listed in Table 5.14 from the seven spectra.
(a) Mg Kα.

(b) Al Kα.

Figure 5.22: Ga 2p regional XPS spectra. The bounded regions are the regions for peak fitting.
<table>
<thead>
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<th></th>
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<td>B.E. (eV)</td>
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<tr>
<td>6 7</td>
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<td>std.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B.E. (eV)</td>
<td>1117.73</td>
<td>1117.66</td>
<td>1117.64</td>
<td>0.11</td>
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<tr>
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<td>Al Kα</td>
<td>Al Kα</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.14: Binding energy of Ga 2p electrons. The std. stands for standard deviation.

Figure 5.23 shows a typical Al Kα spectrum, the background correction, and the fitted peak for Ga 3s electrons. The binding energies for Ga 3s electrons are listed in Table 5.15. The average value of the binding energy peak position for Ga 3s electrons is about 160.65eV with an uncertainty of about 0.08eV.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
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<tbody>
<tr>
<td>B.E. (eV)</td>
<td>160.73</td>
<td>160.57</td>
<td>160.65</td>
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<tr>
<td>X-ray</td>
<td>Al Kα</td>
<td>Al Kα</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 5.15: Binding energy of Ga 3s electrons

3s electrons is about 160.65eV with an uncertainty of about 0.08eV.

Figure 5.24 shows typical XPS spectra, the background correction, and the fitted peaks for Ga 3p electrons. The binding energy for Ga 3p<sub>1/2</sub> and Ga 3p<sub>3/2</sub> are listed in Table 5.16. The average binding energy peak position for Ga 3p<sub>1/2</sub> electrons is about 108.76eV with an uncertainty of about 0.11eV, and the average binding energy peak position for Ga 3p<sub>3/2</sub> electrons is about 105.33eV with an uncertainty of about 0.01eV.

The average binding energy for Ga 3d electrons from seven spectra is about
Figure 5.23: Al Kα XPS spectrum for Ga 3s electrons. The bounded region is the region for peak fitting.

<table>
<thead>
<tr>
<th></th>
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<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga 3p_{1/2} B.E. (eV)</td>
<td>108.87</td>
<td>108.65</td>
<td>108.76</td>
</tr>
<tr>
<td>Ga 3p_{3/2} B.E. (eV)</td>
<td>105.34</td>
<td>105.32</td>
<td>105.33</td>
</tr>
<tr>
<td>X-ray</td>
<td>Mg Kα</td>
<td>Al Kα</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 5.16: Binding energy of Ga 3p electrons
(a) Mg Kα.

(b) Al Kα.

Figure 5.24: Ga 3p regional XPS spectra. The bounded regions are the regions for peak fitting.
20.10eV with a standard deviation of 0.13eV. The smallest and the largest values of peak position for Ga 3d electrons are about 19.89eV and 20.26eV. The average binding energy for N 2s electrons from six spectra is about 16.32eV with a standard deviation of 0.40eV. The smallest and the largest values for N 2s peak positions are about 15.70eV and 16.89eV. The large deviation for the measurement of the N 2s peak positions is partly due to the mixing of the Ga 3d peaks and N 2s peaks, and the low intensity of N 2s electron peak compared to the Ga 3d peak. The binding energy for Ga 3d and N 2s electrons are listed in Table 5.17. Figure 5.25 shows typical XPS spectra, the background correction, and the fitted peaks for Ga 3d and N 2s electrons.

For comparison, the average binding energies in eV for N 1s, Ga 2p, Ga 3s, Ga 3p_{1/2}, Ga 3p_{3/2}, Ga 3d, and N 2s from my experiments for a-GaN and from other groups for crystalline GaN [69, 70] and Ga metal [71, 72] are listed in Table 5.18. By considering the uncertainty in the measurements, my data is in good agreement.

<table>
<thead>
<tr>
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<td>Ga 3d B.E. (eV)</td>
<td>19.89</td>
<td>20.10</td>
<td>20.00</td>
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<tr>
<td>N 2s B.E. (eV)</td>
<td>15.70</td>
<td>16.47</td>
<td>16.89</td>
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<tr>
<td></td>
<td>6</td>
<td>7</td>
<td>Average</td>
<td>std.</td>
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</tr>
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<td>Ga 3d B.E. (eV)</td>
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<td>20.19</td>
<td>20.10</td>
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<td>N 2s B.E. (eV)</td>
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<td>Al Kα</td>
<td>Al Kα</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.17: Binding energy of Ga 3d and N 2s electrons
Figure 5.25: Ga 3d and N 2s regional XPS spectra. The bounded regions are the regions for peak fitting.
with the binding energies measured for crystalline GaN studied by other groups [69, 70]. Therefore, it seems that the local chemical environment around Ga atoms and N atoms in amorphous GaN is similar to that of crystalline GaN near the surface region, and Ga atoms are likely binding to N atoms.

The valence band structure of a-GaN have also been studied by XPS. The mono Al Kα valence band spectra with and without UV-lamp on before and after background correction are shown in Figure 5.26 and Figure 5.27. The valence band electronic density of states of amorphous GaN from theoretical work [5] is shown in Figure 5.28 for comparison.

Comparing the XPS valence band spectra with and without UV-lamp on, the two spectra showed the same shape except that the spectrum with the UV-lamp on is broadened. From now on, only the valence band XPS spectrum taken without the UV-lamp on will be discussed. By linearly extrapolating the right side of the valence band (shown as the dashed line in Figure 5.26 (b)), the highest valence band state is about 1.5eV lower than the Fermi level. If the Fermi level is in the

Table 5.18: Binding energies in eV for core level electrons of GaN and Ga metal.
Figure 5.26: Mono Al Kα valence band XPS spectrum. The bounded region is the region for background correction.
(a) Mono Al Kα Valence band spectrum with UV lamp on.

(b) Mono Al Kα Valence band spectrum with UV lamp on after background correction.

Figure 5.27: Mono Al Kα valence band XPS spectrum with UV-lamp on. The bounded region is the region for background correction.
middle of the band gap, the approximate bandgap is about 3.0eV for this sample. The right side of the dashed line is not completely state free, those states are likely to be bandgap states. Compared to the DOS valence band states, the density of the bandgap states is relatively low.

Comparing the XPS valence band structure to the theoretical results in Ref. [4, 5], there are some agreements between the experimental results and the theoretical results. The calculated bandgap is ranging from 2.6eV to 3.6eV depending on the density of the simulated materials which is comparable to the bandgap measured from this experiment. The right edge of the valence band showed the similar shape in both the calculated DOS spectra and the experimental spectrum. The widths
are similar for both calculated spectra and the experimental spectrum. While the detailed structures are different in the sense that the hills and the valleys showed different relative intensity and positions in the calculated spectra and the experimental spectrum.

In this part, the XPS spectra of as-deposited a-GaN film have been studied. The core level XPS spectra showed that the Ga atoms are binding to N atoms, and the valence band XPS spectra showed that the distance between the highest VB state to the Fermi level is about 1.5eV for the a-GaN film.

2. XPS analysis of Ar ion sputtered film

The a-GaN film was sputtered by 4000eV Ar ions three times for 10 minutes each, the XPS spectra were taken between each sputtering. The XPS survey spectra taken for sputtered film are shown in Figure 5.29. After sputtering, the C contents and O contents decreased significantly. While the investigation showed that the C and O contents built up quickly to the level before sputtering over a few hours. The quantitative study also showed that the N atoms are more easily sputtered out of the surface than the Ga atoms. The ratio between the Ga and N obtained from five survey spectra taken at different stage of the investigation is Ga:N=1:0.27±0.06. Compared to the ratio before sputtering, the change is significant. The study of the valence band XPS spectra showed that the right edge of the valence band moved to very close to Fermi level after sputtering which might indicate that the Ga rich film
(a) Binding energies of electrons excited by Al Kα after sputtered film for 10min.

(b) Binding energies of electrons excited by Mg Kα after sputtered film for 30min.

Figure 5.29: XPS survey spectra for the sputtered film.
may not have a well defined clean wide band gap. The valence band spectrum of the sputtered film taken with mono Al Kα X-ray is shown in Figure 5.30. Compared to Figure 5.26, the density of states in the binding energy range from Fermi level to 1.5eV below Fermi level is increased significantly.

### 5.6.2 AES analysis

In this section, I will discuss the X-ray excited Auger electron spectra, and find out the Auger parameters. In this part, the binding energy of photoelectron peaks and kinetic energy of the Auger peaks were obtained by XPS with 1253.6eV Mg Kα X-ray from a same survey spectrum which was shown in Figure 5.18. The results are listed in Table 5.19 and Table 5.20.

<table>
<thead>
<tr>
<th>Auger process</th>
<th>Final state</th>
<th>This work</th>
<th>From Ref. [69]</th>
<th>From Ref. [70]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga L(<em>3)M(</em>{23})M(_{45})</td>
<td>(^3)D</td>
<td>979.26</td>
<td>979.2</td>
<td></td>
</tr>
<tr>
<td>Ga L(<em>2)M(</em>{23})M(_{45})</td>
<td>(^1)F</td>
<td>996.69</td>
<td>996.6</td>
<td></td>
</tr>
<tr>
<td>Ga L(<em>2)M(</em>{23})M(_{45})</td>
<td>(^3)D</td>
<td>1005.26</td>
<td>1005.6</td>
<td></td>
</tr>
<tr>
<td>Ga L(<em>3)M(</em>{45})M(_{45})</td>
<td>(^1)G</td>
<td>1064.07</td>
<td>1064.3</td>
<td>1064.2</td>
</tr>
<tr>
<td>Ga L(<em>3)M(</em>{45})M(_{45})</td>
<td>(^3)F</td>
<td>1067.39</td>
<td>1067.7</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.19: Binding energies in eV for core level electrons of GaN.

Table 5.20: Kinetic energies in eV for Auger peaks of GaN.

From the photoelectron binding energies and Auger electron kinetic energies,
Figure 5.30: Mono Al Kα Valence band XPS spectrum for the sputtered film. The bounded region is the region for background correction.
the Auger parameter was calculated. The Auger parameter obtained from Ga L$_3$M$_{45}$M$_{45}$ of 1084.15eV is very close to the reported value at 1084.05eV in Ref. [73]. Compared the XPS and AES results from this work to that from other groups [69, 70, 73], the environment around Ga atoms in a-GaN is similar to that of the crystalline GaN. Thus, Ga atoms are likely chemically binding to N atoms in a-GaN in a similar way to that of crystalline GaN.

### 5.7 Er doped films

The Er$^{3+}$ related luminescence at 1540nm with GaN as host by Er and O coimplantation into GaN were reported by several groups [74, 75, 76, 77, 78]. Visible emission from Er-doped GaN were also reported in Ref. [79, 80]. In this dissertation, the PL spectra were taken for Er doped a-GaN films excited by 325nm line from a He-Cd laser at 11K.

The film for PL spectrum was deposited on Si(100). PL spectra were recorded for both as-deposited film and the film annealed for 30 minutes at 900°C in N$_2$ ambient. The RBS analysis results for the films are listed in Table 5.21. The film was completely oxidized after annealing. The PL spectra recorded in the wavelength range of 300nm-1200nm for the as-deposited film and the annealed film are shown in Figure 5.31. The Er$^4$I$_{11/2}$ $\rightarrow$ $^4$I$_{15/2}$ emission lines in the range of 950nm-1000nm were observed in both as-deposited and annealed films, and the Er$^4$F$_{9/2}$ $\rightarrow$ $^4$I$_{15/2}$
Table 5.21: RUMP simulation results for the as-deposited film and the annealed film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness ($\times 10^{15}$ molecules/cm$^2$)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>(225±2)</td>
<td>Ga 1.0, N 1.3±0.1, O 0.1±0.1, Er 0.044±0.001</td>
</tr>
<tr>
<td>Annealed</td>
<td>(192±2)</td>
<td>Ga 1.0, O 1.5±0.5, Er 0.035±0.001</td>
</tr>
</tbody>
</table>

Figure 5.31: PL spectra for as-deposited film and annealed film.
visible emission line near 700nm were observed for the annealed film. It is interesting that the film was completely oxidized after annealing, and the visible emission was observed for the oxidized film. Therefore gallium oxide itself might be worth study for hosting Er for light emitting devices.

The UV-visible transmittance measurement was done for the as-deposited a-GaN:Er film deposited on quartz substrate at the same deposition condition as that of the film for PL measurement. The absorption coefficient was calculated by neglecting the multiple reflection and the interference effects. The UV-visible transmittance spectrum, the absorption coefficient, and the Tauc plot are shown in Figure 5.32, 5.33, and 5.34. The Tauc plot showed that the band gap of the film is about 2.1eV which is the same as that of the undoped film deposited at the similar
Figure 5.33: Absorption coefficient for the as-deposited film.

Figure 5.34: Tauc plot for the as-deposited film.
condition. While the optical bandgap is about 2.9eV measured at the absorption coefficient of $5 \times 10^4 \text{cm}^{-1}$.

In summary, a-GaN:Er is a wide band gap material with an optical band gap of about 2.1eV measurement from Tauc plot. The PL measurement showed that a-GaN:Er could be a useful material for light emitting device in the IR range, and it is possible that Er doped gallium oxide film could find application for the visible light emitting devices.
Chapter 6

Conclusions

In this dissertation, I have studied a-GaN and a-GaN:Er thin films prepared by ion beam assisted evaporation at room temperature in a UHV chamber. The properties of as-deposited and thermal annealed thin films were studied by a variety of characterization methods.

The amorphous structure of the films were examined by X-ray diffraction, electron diffraction, and Raman spectroscopy. θ-2θ X-ray diffraction spectra showed no peaks related to crystalline GaN, transmission electron diffraction patterns showed only diffusion rings, and first order Raman spectra showed continuums in the range of crystalline GaN vibration states. Those facts are strong indications that the films prepared in this work are amorphous.

The stoichiometry of the films was studied by Rutherford Backscattering Spectroscopy, Elastic Recoil Detection, and X-ray Photoelectron Spectroscopy. The
ratio of Ga to N in the films depends on the deposition conditions. In this work, I have obtained a-GaN films with Ga to N ratio ranging from 1:0.48 to 1:1.43. Tel-bizova et al [81] have reported that the composition of N$_2^+$ and N$^+$ produced by a Kaufman type ion source which is similar to the one for this work is about 80% and 20%. In this work, the nitrogen ions arrival rate at the substrate surface is about an order of magnitude higher than that of Ga atoms arrival rate. Compared to the composition of the films, it is possible that the active species to form GaN are N$^+$ ions. The properties of the films with different composition are quite different. The films with lowest N content had a black appearance and which was conducting measured by an Ohm meter. The films with the highest N content had clear yellow or green colors and which had a infinite resistance measured by an Ohm meter. These phenomena might indicate that the Ga rich films do not have a clean bandgap.

From the composition of the films measured by RBS and PRD and the thickness of the films measured by mechanical thickness measurement, the densities of the films were obtained. The a-GaN films studied in this dissertation had densities ranged from 62 to 78 at % of that of crystalline GaN. The a-GaN:O films studied in this work had densities ranged from 68 to 85 at % of that of crystalline GaN. The density of a-GaN or a-GaN:O depends on the ratio of N (or N+O) to Ga, and the higher the ratio of N (or N+O) to Ga, the lower the density of the film.

Refractive index and optical bandgap of a-GaN films were studied by UV-Visible transmittance measurement. The optical bandgap of an a-GaN thin films
with Ga:N ratio of 1.0:1.3±0.1 was about 2.5eV measured at the absorption coefficient of $10^4\text{cm}^{-1}$ which is in the visible light range, and is smaller than that of the crystalline GaN (3.4eV). While the Tauc plot yielded the optical bandgap of 2.0eV. The film is highly transparent for the light with energy lower than the bandgap energy, while the film with Ga:N ratio of 1.0:0.9±0.1 showed much higher absorption in the same region.

The chemical binding states of the a-GaN film were studied by XPS. The core level XPS spectra showed that the Ga atoms are binding to N atoms in a-GaN in a similar way to that of the crystalline GaN. The valence band structure of a-GaN film was also studied by XPS which showed that the width of valence band and bandgap of the material are close to the theoretical results in Ref. [5]. The highest valence band level was about 1.5eV below the Fermi level, and the DOS in the range from Fermi level to the highest valence band state were quite low compared to the valence band DOS. The X-ray excited Auger spectra showed that the Auger parameter of a-GaN is 1084.15eV which is in good agreement with that of the crystalline GaN. The Ar$^+$ ion sputtered film showed a Ga rich surface which resulted in the valence band XPS spectrum with much higher DOS from Fermi level to 1.5eV below the Fermi level which also indicate that Ga rich film might not have a clean band gap.

SAM over the regions of $175\mu m \times 175\mu m$ with 64×64 data points showed uniform distribution of gallium and nitrogen in the film.

The surface topography of the a-GaN films has also been examined by SEM.
(JSM-5300 Scanning Microscope) with the electron energy of 30keV and magnification of 10× to 300,000×. The films showed smooth surfaces in the regions of as small as a few micrometers.

Er doped a-GaN film has been studied by PL measurement and UV-Visible transmittance measurement. The PL spectra showed that the as-deposited film showed infrared (IR) emission at 950-1000nm, and the thermal annealed film showed both IR emission at 950-1000nm and visible emission at about 700nm. While the RBS analysis showed that the annealed film was actually gallium oxide. Therefore gallium oxide itself might be worth study for hosting rare-earth elements for light emitting devices.

The study in this dissertation showed that amorphous GaN with a clean wide bandgap can be obtained by preparing nitrogen rich films, which is very unlike a-Si in which hydrogen must be incorporated to passivate the bandgap states. To find out if a-GaN is a good candidate for electronic and optoelectronic device applications, both theoretical and experimental work will be needed in studying the dopability of the material.
Bibliography


