

STUDY OF THE EARLY STAGES OF GROWTH
AND EPITAXY OF GAN THIN FILMS ON
SAPPHIRE

A dissertation presented to
the faculty of
the College of Arts and Sciences of Ohio University

In partial fulfillment
of the requirements for the degree
Doctor of Philosophy

Eugen Mihai Trifan

August 2003

© 2003

Eugen Mihai Trifan

All rights reserved

This dissertation entitled

STUDY OF THE EARLY STAGES OF GROWTH AND
EPITAXY OF GAN THIN FILMS ON SAPPHIRE

BY

EUGEN MIHAI TRIFAN

has been approved for
the Department of Physics and Astronomy
and the College of Arts and Sciences by

David C. Ingram
Associate Professor of Physics and Astronomy

Leslie A. Flemming
Dean, College of Arts and Sciences

TRIFAN, EUGEN MIHAI. Ph.D. August 2003. Physics and Astronomy

Study of the early stages of growth and epitaxy of GaN thin films on sapphire (198 pp.)

Director of Dissertation: David C. Ingram

Due to its unique properties GaN is a material useful for a variety of applications but obtaining good quality films is still a challenge. MOCVD is the main method for epitaxial growth of GaN for mass production and the early stages of growth are decisive for the quality of the film. While extensive work has been devoted to GaN in the last decade, the *in-situ* analysis of MOCVD films has not received the same amount of attention due to experimental difficulties.

Ion beam analysis is a very powerful technique both for bulk and surface analysis that we have used in conjunction with other complementary techniques to look at the early stages of growth of GaN films grown on sapphire substrate. A new MOCVD reactor has been designed built and integrated with the W.M. Keck Thin Film Analysis Facility such that the characterization is performed *in-situ* without taking the sample out of the ultra high vacuum environment. We have extensively characterized the sapphire substrate after the preliminary preparation that consisted of cleaning and nitridation. After optimizing the growth parameters we have been able to grow wurtzite GaN films in a wide temperature range (450-1050°C) with un-reconstructed surface and of good quality. We have observed the crystalline quality, surface morphology and the growth mode of the films as a function of growth temperature and the film thickness.

Using Ion Channeling we have determined the thickness and temperature range for which the films are either epitaxial single-crystal, polycrystalline with a preferred orientation or polycrystalline randomly oriented. Even though thin films grown at various temperatures have comparable defect densities we observe that when the substrate temperature is higher the rate of defect annihilation as the film grows is high such that we obtain good films within a thickness of approx. 300 nm.

By comparing the channeling and LEED results we observed that samples for which we observe diffraction patterns can in fact be very poor crystals. This is indicative of the

fact that surface ordering can be achieved for polycrystalline films and that surface diffraction alone cannot be used as an indication of crystallinity.

The epitaxial films are oriented with the c-axis of the film paralleled with the c-axis of the substrate and the planes rotated by 30° with respect to the substrate. The defects density calculated for these films are similar to the ones obtained by other researcher for much thicker films.

Approved:

David C. Ingram

Associate Professor of Physics and Astronomy

To my parents

Acknowledgements

My sincere thanks go to my dissertation advisor Dr. David C. Ingram for his support and guidance. Many thanks go to the members of the dissertation committee: Dr. Allena K. Opper, Dr. Jean J. Heremans, Dr. Daniel A. Gulino, and Dr. David C. Ingram for the careful reading of the manuscript and making important comments and suggestions.

To Don Carter, Dave Sturbois, and Devon Jacobs for keeping the accelerator running and to Roger Smith and Randy Mulford for their help with design and the building of the mechanical parts needed for the experiment to work. To Dr. Daniel A. Gulino for providing me with the high-temperature furnace and the surface profilometer. To our group members Yixiu Kang and Asghar Kayani for the useful discussions.

Special thanks go to my family and close friends.

Financial support of the Department of Physics and Astronomy and the Condensed Matter and Surface Science Program at Ohio University, the W. M. Keck Foundation, and the Office of Naval Research through grant #N00014-96-1-0782 is also acknowledged.

Contents

Abstract	4
Dedication	6
Acknowledgements	7
List of Tables	11
List of Figures	12
List of Abbreviations	19
1 Introduction	21
2 Review of experimental work	26
2.1 Methods of film growth	26
2.2 Epitaxial Growth	30
2.2.1 Choice of substrate	30
2.2.2 Substrate cleaning and preparation	32
2.2.3 Nitridation	32
2.2.4 Buffer Layer	35
2.2.5 Growth Mode and Crystal structure	37
2.2.6 Epitaxial Epilayer Growth	38
2.2.7 Defects	40
2.2.8 Texture, structure, growth mode	41
2.2.9 Surface polarity	42
2.2.10 Parameter choice/optimization	44
2.2.11 GaN surface	46

2.2.12 Ion Beam methods in GaN thin film analysis	47
2.3 Summary	48
3 Experimental Setup for thin film growth by MOCVD	49
3.1 Introduction	49
3.2 UHV Highway Transfer System	49
3.3 Sample Holder	50
3.4 Gas admission and evacuation system	53
3.5 CVD Reactor Chamber Setup	59
3.6 Auxiliary systems: temperature, pressure control	60
3.7 Thin film growth procedure	62
4 Characterization Techniques	63
4.1 Introduction	63
4.2 In-situ characterization techniques	64
4.2.1 Low Energy Electron Diffraction	64
4.2.2 Ion-Beam Techniques (RBS/Channeling)	67
4.2.3 Photoemission and Auger Spectroscopy (XPS/AES)	81
4.3 Ex-situ characterization techniques	86
4.3.1 X-Ray Diffraction (XRD)	86
4.3.2 Scanning Electron Microscopy (SEM)	86
5 GaN thin film growth on sapphire by MOCVD	87
5.1 System baking and contamination	87
5.2 Ex-situ and in-situ preparation and analysis of the sapphire substrates	89
5.3 Nitridation of the sapphire substrate	98
5.4 Optimization of the growth parameters	102
5.4.1 Effect of the geometry flow in the reactor chamber	105
5.4.2 Influence of the gas flow rate on the growth rate uniformity of the film and crystalline quality	106
5.4.3 Influence of carrier gases on the growth rate	109
5.4.4 Growth rate as a function of time	110
5.5 Summary of results	112
6 In-situ characterization of GaN thin films	115

6.1 RBS study of the film growth	115
6.2 Surface structure – LEED	126
6.3 Surface chemistry – XPS	130
6.3.1 Surface composition	130
6.3.2 Surface contamination	134
6.3.3 Angular XPS	135
6.3.4 Etching of GaN film by ion gun sputtering	137
6.4 Crystalline ordering by Ion Channeling	140
6.4.1 Phase identification by Ion Channeling	145
6.4.2 Minimum yield - thickness and temperature dependence	146
6.4.3 Surface peak analysis	148
6.4.4 Defects density	151
6.4.5 Epitaxial relationship of GaN film with respect to the substrate	154
6.4.6 Ion beam damage in GaN	160
6.5 In-situ annealing of the GaN film	163
6.6 Summary of results	166
7 Ex-situ characterization of the GaN film	169
7.1 Analysis by Scanning Electron Microscopy	169
7.2 Analysis by X-Ray Diffraction	176
7.3 Thickness measurements	180
7.4 Summary of results	181
8 Conclusions	182
Bibliography	188
9 Appendix	
9.1 Calculation of the depth resolution scale for RBS spectra	195
9.2 Calculation of the surface peak for sapphire	197

List of Tables

Table 1.1: Physical properties of GaN	24
Table 2.1: Comparison of different epitaxial growth techniques	27
Table 2.2: Lattice parameters, thermal expansion coefficients, and basal planes interplanar distances [22]	31
Table 5.1: Gas flow rates for the two samples	106
Table 5.2: Measured minimum and maximum thicknesses for the samples grown at two different gas flow rates.	107
Table 5.3: Maximum and minimum thickness and growth rate for three deposition times	111
Table 6.1: XPS analysis of the GaN films	132
Table 6.2: Composition of the film as a function of the take-off angle	136
Table 6.3: Surface composition as a function of etch time	137
Table 6.4: Average dislocation density for GaN films	153
Appendix:	
Table 9.1: Stopping cross sections for Al and O	196

List of Figures

Figure 1.1: Bandgap and lattice size of compound semiconductors	22
Figure 1.2: The crystalline phases of GaN: wurtzite (left) and zinc-blende (right)	23
Figure 2.1: Threading dislocations in optoelectronic devices	28
Figure 2.2: c-plane of GaN on c-plane of Al ₂ O ₃ [21]	40
Figure 2.3: The wurtzite crystal structure of GaN, showing the conventions used to discuss its polarity	44
Figure 3.1: W.M. Keck Thin Film Analysis Facility outline	51
Figure 3.2: Sample holders used throughout this work. a) Modified sample holder used for Ion Channeling b) Original goniometer sample holder c) Modified sample holder used for MOCVD growth.	52
Figure 3.3: Schematic of the attachment of the heater to the sample holder (not to scale)	53
Figure 3.4: Vapor pressure of two metalorganic precursors for Ga [89]	54
Figure 3.5: Schematic Setup of one gas delivery line for the MOCVD reactor	56
Figure 3.6: Schematic of the MOCVD deposition system	58
Figure 3.7: MOCVD Reactor chamber (not to scale)	59
Figure 4.1: LEED Principle	65
Figure 4.2: OCI Vacuum Micro-engineering BDL800IR LEED	66
Figure 4.3: LEED Setup	67
Figure 4.4: Energy spectrum of particles scattered from a substrate covered with a film of a higher atomic mass	68
Figure 4.5: Model of lattice atoms viewed along (a) random (b) planar or (c) axial direction [115]	70
Figure 4.6: Schematic of energy spectrum for an aligned and a random beam direction.	70
Figure 4.7: Comparison of experimental values with the “universal” curve of close-encounter probability [92]	74

Figure 4.8: Channeling map for a hexagonal crystal	75
Figure 4.9: RBS Setup (not to scale)	77
Figure 4.10: Electronic setup for ion beam analysis	78
Figure 4.11 Internal setup of the Pile-up Rejection Setup	80
Figure 4.12: Schematic of the XPS process	81
Figure 4.13: a) Axis HIs Electron Spectrometer b) Schematics of a XPS/UPS/AES System	83
Figure 4.14: Schematic of the Auger process	84
Figure 5.1: XPS spectra taken with Al anode of a nitridated sapphire with Fluorine contamination (surface composition: $\text{Al:O:N:C:F} = 36:21:22:19:2$).	88
Figure 5.2: Survey XPS spectra taken with Al anode for the GaN film deposited at 750°C	89
Figure 5.3: Random and Aligned as-received sapphire spectrum	90
Figure 5.4: Aluminum surface before (black) and after background subtraction (red)	91
Figure 5.5: Channeling yield map around $\langle 0001 \rangle$ direction of as-received sapphire for a window of 30 channels below the surface	92
Figure 5.6: a) Yield map of the as-received sapphire for the Al sub-lattice b) Yield map of the as-received sapphire for the Al and O sub-lattices taken together	93
Figure 5.7: Sapphire lattice as viewed from the $\langle 0001 \rangle$ direction, the unit cell is marked orange and the planes : (1-100) is blue, and (11-20) is red (red balls -Al, blue balls -O)	94
Figure 5.8: Sapphire lattice in the plane (11-20) (left) and (1-100) (right)	94
Figure 5.9: SEM images of the as-received sapphire wafers with striations, grooves and features of micron size	95
Figure 5.10: SEM micrograph of the annealed sapphire in air at 1400° C for 30 minutes	96

Figure 5.11: XPS Spectra taken with Al and Mg anode of the as-received sapphire substrate. The composition of the surface is O:Al:C = 53:22:25.	97
Figure 5.12: XPS Spectra using Al anode of the sapphire substrate annealed in air at 1400C for 30 minutes. Composition of the surface is O:Al:C = 56:25:19.	97
Figure 5.13: The effect of nitridation in N ₂ on the surface peak of Al	99
Figure 5.14: The effect of nitridation in NH ₃ on the surface peak of Al	100
Figure 5.15: XPS of nitridated sapphire in N ₂ (blue) and NH ₃ (red) using Mg anode	101
Figure 5.16: LEED patterns of sapphire after nitridation in N ₂ – the beam accelerating voltage is noted next to each picture	102
Figure 5.17: Gas flow geometries	105
Figure 5.18: Channeling yield maps for the HF sample showing small amount of axial channeling ~90% for 50 nm thick film (left), and ~70% for 310 nm thick film (right)	108
Figure 5.19: Channeling yield map for the LF sample showing good axial and planar channeling. The minimum yield is 8.7% ± 2% for a thickness of 135 nm.	108
Figure 5.20: RBS of the film grown with four gases (NH ₃ , N ₂ , H ₂ , TMGa) (black diamonds), and with 2 gases (NH ₃ and TMGa) (red squares). The growth rate is greatly reduced when no precursor gases are used.	110
Figure 6.1: Figure 6.1: The maximum and minimum thickness vs. the growth temperature	117
Figure 6.2 Possible growth mechanism for the two GaN polar orientations	119
Figure 6.3: Arrhenius plot of the maximum growth rate vs. inverse temperature	120
Figure 6.4: Typical thickness variations across the substrate surface	122
Figure 6.5: Sample 450°C random and simulation of a film grown at 450°C with a thickness of 1.5ML	123

Figure 6.6: The random RBS and RUMP simulation for a film grown at 550°C with a thickness of 200 nm and non-uniformity of 25nm (left) and at 610°C with a thickness of 140 nm and non-uniformity of 30 nm (right)	123
Figure 6.7: The random RBS and RUMP simulation for a film grown at 680°C with a thickness of 80 nm and non-uniformity of 40 nm and at 750°C with a thickness of 135 nm and non-uniformity of 50 nm	124
Figure 6.8: Typical RBS spectra and the RUMP simulations for films grown at 850°C	125
Figure 6.9: RBS and simulation for films grown at 950°C with a thickness of 185 ± 5 nm and non-uniformity of 50 nm (left) and with a thickness of 18 nm (right)	125
Figure 6.10: Random RBS and simulation for a GaN film grown at 1050°C with a thickness of 14 nm	126
Figure 6.11: LEED Patterns for film grown at 610°C (left) and 750°C (right)	127
Figure 6.12: LEED Patterns for film grown at 850°C (left) and 950°C (right)	128
Figure 6.13: LEED Patterns for film grown at 1050°C	128
Figure 6.14: Equilibrium phase diagram of the GaN(0001) surface under MOCVD conditions, as obtained from grazing-incidence x-ray scattering [49]	129
Figure 6.15: Typical XPS spectra take with the Al and Mg anode for a GaN film.	131
Figure 6.16: Region of interest in XPS with the main peaks	131
Figure 6.17: Typical peaks for C-1s, O-1s, Ga-3p and N-1s used in quantitative analysis of the GaN films	133
Figure 6.18: XPS for as-deposited and air-exposed sample taken with Al and Mg X-ray source	135
Figure 6.19 Angular XPS, green line corresponds to a 0 degree take-off angle and the blue line corresponds to a 65 degrees take-off angle with respect to the normal to the surface	136

Figure 6.20: Intensity of the XPS signal coming from Ga, N, C, and O during the steps shown in Table 6.3	138
Figure 6.21: XPS survey spectra before etching (green) and after etching for 20 minutes at 1 μ A with Ar ions (blue) with Al and Mg x-ray	139
Figure 6.22: Typical RBS random and channeled spectra fro samples grown at 550°C (a), 610°C (b), and 680°C (c, d)	141
Figure 6.23: Typical RBS random and channeled spectra fro samples grown at 850°C (a, b), 950°C (c, d), 1050°C (e), and 750°C (f)	143
Figure 6.24: Typical minimum yield maps for GaN films grown at 680°C (a), 750°C (b), 850°C (c, d), 950°C (e), and 1050°C (f)	144
Figure 6.25: Stereographic projections for a hexagonal crystal in the <0001> (left) and <10-10> (right) direction. [115]	145
Figure 6.26: Stereographic projections for a cubic GaN crystal in the <111> (left) and <100> (right) direction. [115]	146
Figure 6.27: Minimum dechanneling yield as a function of film thickness and deposition temperature	147
Figure 6.28: Surface peak of the Ga signal for film grown at temperature of 950°C with a thickness of 320 nm (a) and 185 nm (b)	149
Figure 6.29: Surface peak of the Ga signal for substrate temperature 750°C and 135 nm thickness (a) and 680°C and 80 nm thickness (b)	150
Figure 6.30: Proposed cross section for a $(\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstruction (left) and 1×1 structure (right), viewed along [01] surf direction [49]	151
Figure 6.31: Gallium channeling peak for growth temperature of 950°C and thicknesses of 320nm (a) and 180 nm (b)	152
Figure 6.32: Gallium channeling peak for growth temperature of 750°C and thickness 135 nm (a) and temperature of 680°C and thickness of 140nm (b)	153
Figure 6.33 Channeling maps for Ga (left) and Al (right) for the sample grown at 680°C	154
Figure 6.34: Channeling map of Ga (left) and for the Al (right) for film grown at 750°C	155

Figure 6.35: Channeling maps for Ga (left) and Al (right) for the film grown at 950°C	156
Figure 6.36: Perimeter scans for the Ga (left) and Al (right) signal for film grown at 950°C	156
Figure 6.37: Channeling map and perimeter scan for Ga (left) and Al+O signal (right)	157
Figure 6.38: Channeling maps for the GaN channeling plan (11-20)	158
Figure 6.39: Channeling maps for the sapphire substrate in the plan (1-100)	159
Figure 6.40: Ion channeling spectra taken before and after exposing the sample to 10 μ C	161
Figure 6.41: Ion channeling spectra taken before and after exposing the sample to 100 μ C	162
Figure 6.42: Random and aligned RBS spectrum for the sample grown at 610°C and annealed at 950°C for 200 seconds	163
Figure 6.43: LEED patterns for the samples grown at 610°C without annealing (left) and with annealing (right)	164
Figure 6.44: XRD spectra for samples grown at 610°C with and without post-growth annealing	165
Figure 7.1: SEM micrograph of a sample grown at 550°C	170
Figure 7.2: SEM micrograph of a sample grown at 610°C	171
Figure 7.3: SEM micrograph of a sample grown at 680°C	172
Figure 7.4: SEM micrograph of a film grown at 750°C	173
Figure 7.5: SEM micrograph of a sample grown at 850°C	174
Figure 7.6: SEM micrograph of a sample grown at 950°C	175
Figure 7.7: XRD spectra for GaN films on sapphire grown in the temperature range 550°C to 950°C	176
Figure 7.8: XRD Scan and Rocking Curves for sample grown at 950°C	177
Figure 7.9: XRD Scan and Rocking Curves for commercial MOCVD GaN	177
Figure 7.10: FWHM of the Rocking Curves as a function of growth temperature	178
Figure 7.11: XRD spectra for two samples grown at 850°C in similar conditions	179

Figure 7.12 Thickness measurement of GaN on sapphire using stylus
profilometer

180

Appendix:

Figure 9.1: Random RBS and RUMP simulation and aligned channeling
spectrum for sapphire substrate

197

List of Abbreviations

μm	micrometer
ADC	analog to digital converter
AES	Auger electron spectroscopy
ERS	elastic recoil spectroscopy
FET	field effect transistor
FWHM	full width at half maximum
GaN	Gallium Nitride
IC	ion channeling
keV	kilo-electron volt
LD	laser diode
LED	light emitting diode
LEED	low energy electron diffraction
MBE	molecular beam epitaxy
MeV	mega electron volts
MFC	Mass Flow Controller
MOCVD	Metal-Organic Chemical Vapor Deposition
nm	nano-meter
NRA	nuclear reaction analysis
PL	photoluminescence
QMS	quadrupole mass spectrometer
RBS	Rutherford backscattering spectrometry
RF	radio frequency
RUMP	Rutherford backscattering simulation software
sccm	standard cubic centimeters per minute
SEM	scanning electron microscopy
slm	standard liters per minute
TD	threading dislocations
TEM	transmission electron microscopy

TMGa	trimethylgallium
TFT	thin film transistor
UHV	ultra high vacuum
UPS	ultra-violet photoelectron spectroscopy
UV	ultra-violet
WZ	wurtzite
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZB	zincblende

Chapter 1

Introduction

Mobile phones, satellite transmitters, fiber optics systems, and other advanced technologies such as laser and light emitting diodes are rapidly expanding throughout the world, and are transforming our every day lives. All these new consumer products are based on compound semiconductor materials.

The family of III-V nitride materials (GaN, AlN and InN) is one of the most promising materials for optoelectronic and high power/ high temperature electronic device. These materials and their ternary and quaternary alloys are direct bandgap semiconductors and the energy gap covers a large spectral region from red to deep ultraviolet (1.9 – 6.2 eV). A graph illustrating the bandgap and lattice constant of some the most important compound semiconductor materials is presented in Figure 1.1 (direct band-gap materials, useful in optoelectronic applications are marked with a red dot).

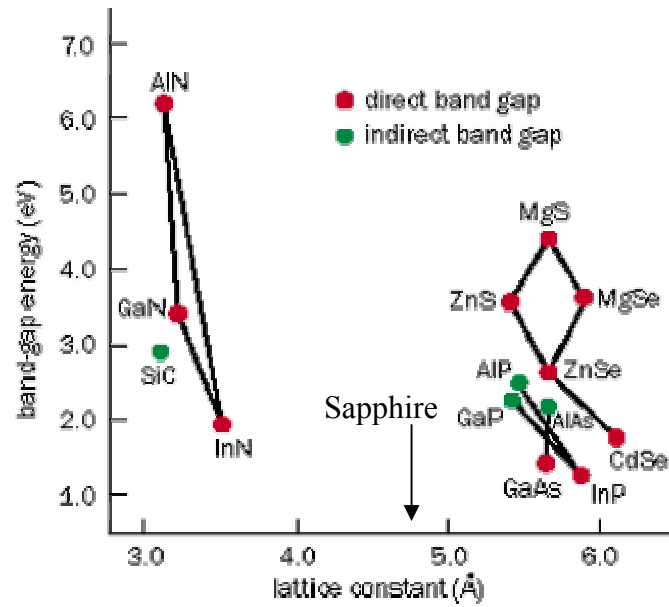


Figure 1.1: Bandgap and lattice size of compound semiconductors

GaN is a material that is synthesized by various methods and it comes in two crystalline phases: wurtzite (WZ) which has hexagonal symmetry and is the thermodynamically equilibrium phase, and zinc-blende (ZB) which is cubic; and a top view of the two is shown in Figure 1.2. In both cases the Ga and N atoms are tetragonally coordinated with 4 atoms of the opposite type.

GaN has a series of physical properties that differentiate itself from other high-bandgap materials and make it are very useful for practical applications:

- wide direct bandgap (3.45eV) useful for both light emitting and detector devices;
- is chemically stable at high temperatures;
- has a good thermal conductivity;
- has a high saturated electron drift velocity (2.7×10^7 cm/sec) and high breakdown electric field ($\sim 5 \times 10^6$ v/cm) which enable superb high frequency operation at high electric fields and in high-temperature environments;
- very sharp band-edge emission in photoluminescence (PL) due to free and impurity-bound excitons observed at low temperature;
- high room-temperature (RT) electron mobilities (~ 1350 cm² /V- sec);
- large piezo-electric constant.

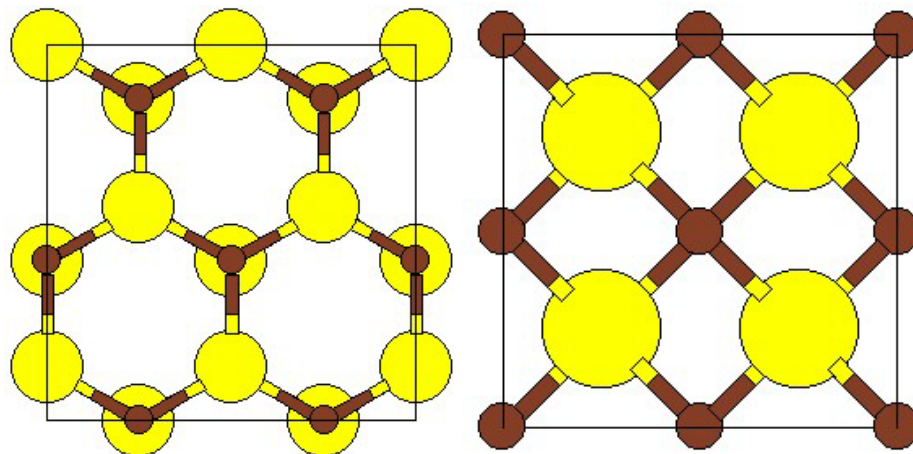


Figure 1.2: The crystalline phases of GaN: wurtzite (left) and zinc-blende (right)

Table 1.1 summarizes the most important physical properties of the GaN material from current references [1,2,3,4,5,6,7,8,9,10].

Commercial applications of GaN present and future run from UV/blue laser diodes (LDs) used in optical data storage, printers, copiers, scanners, blue/green light emitting diodes (LEDs) for large area displays, traffic signs, automotive applications, to public illumination, UV detectors, microwave and high-power/high-speed microelectronic devices that will operate at high temperature (up to 500°C), in space, or other hostile environments.

GaN-based devices are now present on the market, but much work is left in order to expand the application pool and improve the performance and reliability. Major research issues include: choice of substrate, GaN bulk and thin film crystal growth, hetero-epitaxy, buffer layers, doping, contacts, etching, integration with other semiconductors.

Growth of bulk GaN crystals (ingots at least few inches in diameter) is a challenge due to their high melting temperature, low sublimation/decomposition temperature relative to its melting temperature, very high equilibrium nitrogen vapor pressure at moderate temperatures, and low solubility in acids, bases and most other inorganic elements and compounds.

Since no large bulk GaN is available at this time, the future industrialization of these wide bandgap compound materials depends on the development of high-quality hetero-epitaxial growth techniques on various substrates. Due to the need to understand, predict

and optimize the growth process of the GaN films work is needed to understand the heteroepitaxy of GaN.

Table 1.1 Physical properties of GaN

	Wurtzite [1,3,4,5,6,7,8,9]	Zinc-blende [2,6,10]
Density	6.15 g/cm ³	
Band-gap	$E_g(300\text{K})=3.39\text{eV}$ $E_g(1.1\text{K})=3.5\text{eV}$	$E_g(300\text{K}) = 3.2 - 3.45 \text{ eV}$
Lattice Constant	$a = 3.189 \text{ \AA}$ $c = 5.185 \text{ \AA}$	$a = 4.5 - 4.531 \text{ \AA}$
Thermal expansion	$\Delta a/a = 5.59 \times 10^{-6} \text{K}^{-1}$ $\Delta c/c = 3.17 \times 10^{-6} \text{K}^{-1}$	
Thermal conductivity	$\kappa = 1.3 \text{ W/cm K}$ $1000 \text{ cm}^2/\text{V s (bulk)}$	
Electron Mobility	$2000 \text{ cm}^2/\text{V s (2D-gas)}$	
Breakdown field	$> 5 \times 10^6 \text{ V/cm}$	
Melting temperature	$> 1700^\circ \text{ C}$	
Dielectric Constants	$\epsilon_0 = 9.5$	
Index of refraction	$n(1\text{eV}) = 2.33$ $n(3.38\text{eV}) = 2.67$	$n(3.2) = 2.91 \text{ eV}$
Piezoelectric constant	$C_{14} = 0.375 \text{ C/m}^2$	

For this dissertation GaN thin films have been grown on sapphire by the means of metal-organic chemical vapor deposition in a system that has been designed, built and integrated with the analysis facilities via ultra high vacuum transfer lines. In order to investigate the early stages of growth and epitaxy we have analyzed films with thicknesses of 0.5 to 300 nm using a series of techniques, some very surface sensitive, and some able to penetrate deep into the material.

In chapter 2, relevant work related to GaN film growth will be reviewed. Chapter 3 describes the experimental setup that has been designed and built in order to obtain the thin films, as well as the method of integration of the growth chamber into the analysis system for in-situ characterization. Chapter 4 gives a brief introduction to the characterization methods used for investigating the growth and epitaxy. Chapter 5 is dedicated to describing the various procedures developed in order to grow the films and the characterization of the substrate prior to the film growth. In Chapter 6, I list the experimental results of the in-situ analysis and discuss them, and in chapter 7, I discuss the ex-situ results. Chapter 8 summarizes the work and results obtained.

Chapter 2

Review of Experimental Work

2.1 Methods of film growth

Since no traditional method of bulk crystal growth is capable of making large size GaN single crystals researchers have concentrated their efforts on obtaining good quality GaN thin films on various substrates. There are two main methods used for the epitaxial growth of GaN thin films from the vapor phase. Metal-Organic Chemical Vapor Deposition (MOCVD) it operates near atmospheric pressure using metal-organic compounds in the vapor phase. Molecular Beam epitaxy (MBE) operates under High Vacuum conditions and uses solid-evaporation sources; it is the method of choice for high control of interfaces. A summary of the two mentioned methods together with another method of film growth from liquid phase (Liquid Phase Epitaxy) are given in Table 2.1.

Although MBE still has potential advantages over MOCVD for some specific device structures, MOCVD is indisputably the growth method of choice for fabricating devices in commercial settings [11].

For GaN and its alloys the device performance is strongly related to the high density of defects (10^7 - 10^{10}cm^{-2}) (threading dislocation (TD)) formed during the growth of the film. Since there is no economically feasible material with a lattice constant very close to the one of GaN, most of the applications use sapphire inspite of a 14% mismatch in the lattice constant. Other substrates such as SiC are more closely matched but they are too expensive.

Table 2.1: Comparison of different epitaxial growth techniques

	LPE	MOCVD	MBE
Growth Rate (m/min)	0.1-10	0.005-1.5	up to 0.05
Minimal Thickness (nm)	50	2	0.5
Uniformity	good	good	good
Surface Quality	bad	good	good
Interface Sharpness	bad	good	very good
Doping Range (cm^{-3})	10^{14} - 10^{19}	10^{14} - 10^{19}	10^{14} - 10^{19}
Process Yield	low	high	very small
Cost	low	moderate	high

The great success in developing commercial grade devices in the late '90s is based on the two-layer deposition system developed by Amano, Akasaki et al. [12]. Figure 2.1 shows a cross section through a laser diode with a high density of threading dislocations (up to 10^{10}cm^{-2}) formed at the interface between the sapphire substrate and the film.

The dislocations propagate into the active layer and degrade the performance of the optoelectronic device by acting as non-radiative recombination centers.

The use of alternative substrates has been extensively investigated with the premise that the higher manufacturing costs would be offset by the improved performance of the devices due to closer lattice match. High electron mobility transistors (HEMTs) were consistently obtained on SiC due to a better epitaxial GaN material and also better thermal conductivity of SiC [12,14].

The advent of Epitaxial Laterally Overgrowth (ELOG) improved the quality of the films and a decrease of TD density has been reported with this technique [15,16]. The first commercially viable blue laser diodes using GaN-based materials were obtained using this technique [17,18]. It has been shown, by comparing the devices built on dislocated and ELOG GaN that the leakage current has been dramatically reduced for the diodes with less TDs [19]. ELOG involves a processing step and at least one regrowth step, and is therefore not the ultimate solution for the future of commercial GaN devices. This technique shows us what the properties of the bulk GaN substrate would be if available.

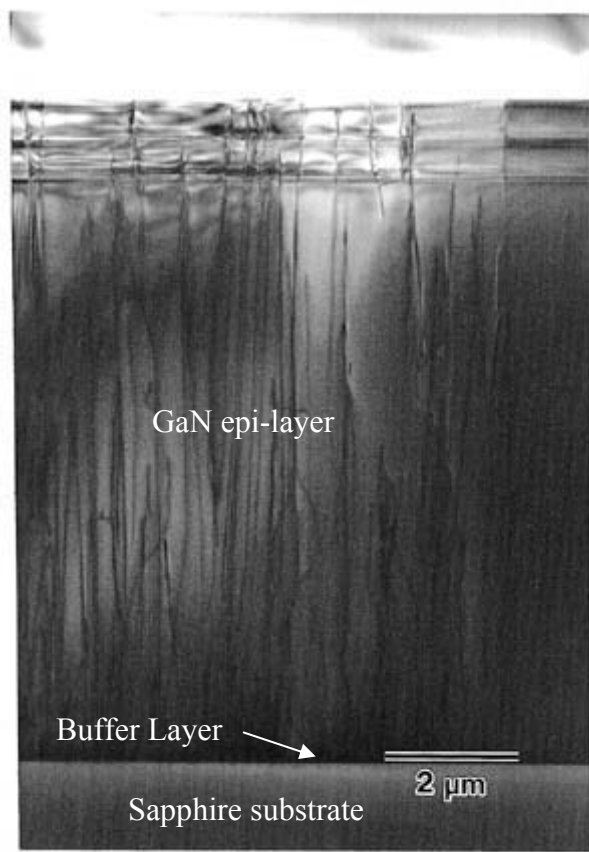


Figure 2.1: Threading dislocations in optoelectronic devices

MOCVD has evolved into the leading technique for production of III-V compound semiconductor optoelectronic devices and electronic devices. For commercial GaN

devices MOCVD has emerged as the leading candidate technique due to the achievement of super-bright blue light emitting diodes (LEDs) [17,20] and also the large scale manufacturing potential of this technique. Understanding the growth of GaN and related alloys (AlN, InN) by MOCVD is of extreme importance in improving the properties of these optoelectronic devices.

MOCVD is a thermodynamically nonequilibrium technique which is based on the transport of the precursors in the form of vapors to the desired substrate. The endothermic chemical reaction between the group II alkyls and group V hydrides is spatially confined due to selective heating of the substrate while the walls of the reactor chamber are kept at a lower temperature. Composition and growth rate are precisely controlled by adjusting the flow rates and relative ratio of the various gases delivered in the reaction chamber. The organometallic group III sources are either solids like trimethylindium (TMIn) or liquids like trimethylgallium (TMGa) and trimethylaluminum (TMAI) at room temperature (RT). Typically the organometallic precursors are stored in bubblers through which carrier gases (hydrogen) flows. Carrier gases will saturate with vapor from the source and transport them to the heated susceptor. In this work a different method was used in which the metalorganic gases were transported directly into the reaction chamber. The control of the amount of gases is achieved by using mass flow controllers (MFCs) calibrated for each individual gas. The group V sources are most commonly gaseous hydrides and in this work we have used ammonia (NH_3).

As well as the issues surrounding the TDs in epitaxial GaN, point defects have been another critical issue, mostly because of the high n-type background concentration and the difficulties in achieving p-doping. Carbon, oxygen and hydrogen are the most common impurities in GaN. While the carbon and hydrogen are contained in the precursor gases themselves there are innumerable ways that oxygen reaches the deposition chamber: contamination of the carrier or precursor gases, leaks in the gas delivery system, and water vapors in the reactor chamber. That is the reason that we have taken measure to limit the oxygen contamination of the system by carefully baking the entire system as well as purging the gas lines with nitrogen.

2.2 Epitaxial Growth

Much work has been devoted to achieving a level of crystalline quality necessary for commercial grade devices. Although certain devices can work with defect densities up to 10^{10} cm^{-2} , a better quality material is needed in order to increase lifetime, decrease temperature effects on electric properties and produce more sensitive devices for high-frequency applications. The method of choice for epitaxial growth involves a multi-step process where the substrate preparation is followed by in-situ nitridation and the growth of a thin “buffer layer” and finally the growth of the epi-layer (Figure 2.2) [12,16].

Although I have tried to review the most relevant work regarding the MOCVD growth most of the available literature is dedicated to the MBE growth of GaN. In this technique the growth occurs at low pressures with to the arrival of the two atomic species at the surface and subsequent condensation, and no chemical reaction is necessary. While this is very different than the MOCVD process, I have included results obtained with it since these results may be general.

2.2.1 Choice of substrate

In spite of the large lattice mismatch sapphire (Al_2O_3) has been the substrate of choice for GaN growth in practical applications due to availability and good physical properties. Sapphire is readily available as a single crystal with diameters up to 10 cm. It is transparent over the spectral range needed to study GaN optically. It is also insulating, thus confining electrical transport to the epilayer grown on it. The 14% lattice mismatch induces biaxial compressive stress in the film. As the film grows this stress is reduced by forming stacking faults and dislocations. It is believed that the dislocations are responsible for the yellow band visible in photoluminescence. Dislocation densities as high as 10^{10} cm^{-2} have been reported and they are undesirable for many applications especially laser diodes where the emission is due to a bound exciton. The exciton emission can be easily broken up by a strong electric field. The potential fluctuations in GaN can easily be greater than 1V and since the material with 10^8 cm^{-2} dislocations has a dislocation every 10^4 cm this means the local electric field is, in average, $\sim 10^4 \text{ V/cm}$. This

magnitude of electric field allows the Franz-Keldysh effect to occur and the break up of the exciton [21].

In the early work GaN was grown on r-plane (1-102) sapphire because this was most readily available and widely used for growing silicon on insulator (SOI) and hence the cheapest. While the electrical quality of the films was good the surface morphology was usually rough with facets. Recent work reports that the GaN grown on r-plane has poorer electrical and crystalline quality than grown on other orientations. Because the rough surface makes device fabrication more difficult, most groups avoid the r-plane for growth of devices.

The c-plane or basal plane of sapphire is by far the most common orientation used for growth of GaN. In this configuration there is a large mismatch between the lattices of the two materials of 14%. The use of c-plane sapphire has been found to produce narrower X-Ray rocking curves compared to r-plane or a-plane as well as a smoother surface and better crystalline and electrical quality. One difficulty with this plane is that there are no cleavage planes suitable for diode laser mirror faces.

Table 2.2: Lattice parameters, thermal expansion coefficients, and basal planes interplanar distances [22]

	a (nm)	c (nm)	a (K⁻¹)	c (K⁻¹)	(10-10)	(11-20)
Al ₂ O ₃	0.4758	1.2991	7.5×10^{-6}	8.5×10^{-6}	0.1374	0.2379
GaN	0.3189	0.5185	5.59×10^{-6}	3.17×10^{-6}	0.276	0.159

Studies of the strain in GaN have found that films as thick as 10-100 μm have a lattice constant larger than the bulk value of GaN [23, 24].

The a-plane (11-20) has been of interest because of the presence of a cleavage plane since the c-plane of GaN grows parallel to the a-plane of the substrate. This configuration produces a lattice mismatch of only 1.7% and 0.5% in the [11-20] and [1-100] directions. The crystalline and electrical quality of these films is in general lower than the ones grown on the basal plane but the films can have a very smooth surface [21].

2.2.2 Substrate cleaning and preparation

Cui, et al. [25] optimized the conditions necessary to eliminate the surface damage of the sapphire substrate for good quality GaN growth. AFM imaging showed that substrates annealed at 1380°C for one hour have flat terrace-like features 0.2 μm wide. The GaN growth by MBE on these prepared surfaces have an improved FWHM of the rocking curve for the [001] direction by a factor of 7 compared to unprepared substrates. Similar results were obtained by Yoshimoto, et al. [26].

The in-situ preconditioning of the sapphire substrates has been investigated by Heinlein et al. [27]. They have found that low temperature (200-300°C) heat treatment in H plasma offers effective removal of the adventitious surface contaminants, in contrast to annealing in vacuum.

2.2.3 Nitridation

It has been experimentally found that in order to improve the film structural morphology and optical properties of GaN on sapphire substrate, the substrate has to be heated and exposed to nitrogen, usually in the form of nitrogen or ammonia. The optimum conditions for nitridation differ over a wide range depending on growth apparatus. The nitridation is done in a very wide range of conditions: sapphire is heated to 500-1300°C in NH_3 or N_2 (3-8 slm) while the total pressure is maintained at 10-760 torr [27,28,29,30,31, 32,33,34,35,36,37,38,39,40,41,42]. It is found that the nitrogen atoms are adsorbed only the surface or they can go deeper into the sapphire.

Two studies of the nitridation process [30,32] concluded that the nitridation process consists of two steps: first, inter-mixing between the nitrogen-related species and sapphire surface occurs forming hydrogenated Al oxynitride with N adsorbed as low as 6 Å [32]; this step does not change the surface morphology significantly. In the second step rough crystalline AlN islands are gradually formed by further exposure to nitrogen of the hydrogenated Al oxynitride.

For high temperature nitridation (1050°C in NH_3) Uchida et al. [31] have found similar results that the nitridation saturates after about 5 minute and a layer of $\text{AlN}_x\text{O}_{1-x}$ is

formed that only is only partially crystalline or amorphous. Shorter nitridation (3 minutes) favored the formation of a flat nitridated layer while extended nitridation (20 minutes) gives rises to a rough surface possibly explained by a method of releasing the stress in the AlN surface layer. It has been found that a flat nitridated surface favors two-dimensional growth while a surface with protrusions favors three-dimensional growth. The quality of the epilayer was controlled by the surface morphology of the nitridated surface.

XPS Analysis of the nitridation has shown that N is significantly incorporated in the surface sapphire layer [41] at temperatures of 800°C and higher. Paek et al. [37] have investigated the low temperature nitridation by using remote-plasma-enhanced- UHV-CVD and analyzing the evolution of the XPS N1s (397.2eV) peak. A thin 6 nm layer of AlN is formed upon nitridation of the sapphire substrate [37] at 400°C which is considerably lower than the temperature used in conventional MOCVD (over 800°C). Two smaller peaks at higher energies suggest that other species are formed in the nitridation layer [37]. Other TEM and XPS depth profiling studies have confirmed that the thickness of AlN is less than 10 nm [31,38].

Using XPS it has been found [27] that nitrides are formed on the surface upon heat treatment in nitrogen plasma and this layer is found to remain stable upon exposure to atmosphere. Similarly sharp (1x1) LEED patterns of sapphire have been obtained after the H cleaning. The clean c-plane sapphire LEED pattern has been observed even after the nitridation step (with a slight distortion of the diffraction spots) but no evidence of surface reconstruction has been found. The paper [27] suggested that this plasma nitridation only produces random adsorption of N with coverage less than 1 mono-layer and no epitaxial crystalline AlN on the surface as seen by RHEED.

Structural characterization by triple axis high resolution x-ray diffraction (HRXRD) rocking curves show that the full width at half-maximum (FWHM) as measured from a symmetric rocking curves is higher for the short process compared to the longer one (269 arcsec and 40 arcsec), while the asymmetric reflection rocking curves (102) that are sensitive to pure edge dislocations are wider for the longer nitridation (740 and 413 arcsec) [29]. Using X-ray reflectivity Kim et al. [42] have concluded data that the

thickness of the nitridated layer depends mainly on the nitridation temperature and that nitridation at 800°C for 15 minute produced the best overlayer in their particular experimental conditions. Grazing incidence diffraction confirmed that the nitridation produces an epitaxial AlN layer with very low mosaicity regardless of the nitridation conditions. Excessive nitridation produced a decrease in lateral domain sizes and increased lateral mosaicity. Hwang et al. [35] has found that the XRD rocking curves have similar values for both nitridated or not samples, but the electron mobility is up to 5 times higher and the [35] nitridated sample.

Nitridation was shown to increase the intensity of optical properties as characterized by the Photoluminescence (PL) line by a factor of 7 [33] or decrease the FWHM of the curves [35,36]. An excessive nitridation above the optimal value led to broader PL lines, indicating poorer layer quality [33,29,34]. The non-nitridated sample has a low PL intensity indicative of high density of non-radiative recombination centers, possibly linked to crystalline defects. PL intensity was also found to be dependent on the crystalline orientation of the film with respect to the substrate [36] but MBE and MOCVD have produces similar values. Optimizing the nitridation from PL emission it was found that 20 sccm of ammonia at 850° C for 10 minutes gives a sharper band-edge emission and a reduced yellow-band intensity for the given experimental conditions [36].

The surface morphology, electrical and optical properties of the epitaxial film are also dependent on the nitridation step by MOCVD. Hwang et all. [34]. While the unnitridated film shows a smooth surface with pits the nitridated films have a rough surface with large hexagonal islands [36].

The effect of nitridation on GaN films deposited on a AlN buffer layer have been investigated by Grandjean et al. [36] by RHEED, TEM and PL in a Gas Source MBE. Two different epitaxial orientations have been observed, one has the c axis of the GaN film parallel with the c axis of the substrate and a second orientation with the c axis at an angle of 19° with respect to the sapphire basal plane. The second orientation is only observed when the substrate is not nitridated. It is believed that the tilted orientation is due to a more favorable lattice matching conditions between sapphire and GaN.

The nitridation of the sapphire in MBE growth has been found to be effective in suppressing of the growth of a rotation domain rotated by 11° from the c-axis [41]. Alternatively the decrease in V/III molar ratio has a similar effect. The FWHM of the rocking curves of the nitridated samples is lower than non-nitridated sample. It is believed that the improvement is due to higher migration of Ga leading to enhanced 2-D growth and suppressing the metastable rotation domain with $[12\bar{3}0]\text{GaN}||[11\bar{2}0]\text{sapphire}$ and $[-1\bar{2}30]\text{GaN}||[11\bar{2}0]\text{Al}_2\text{O}_3$.

Overall three different orientations are observed experimentally when GaN is grown without nitridation by atomic layer epitaxy [35], and just one is observed for the nitridated films [36].

2.2.4 Buffer Layer

A great improvement in the quality of the GaN films has been achieved when the growth started by growing a thin film at low temperature called “buffer layer” (480 to 650°C) [43]. The typical thickness of the buffer layer is tens of nanometers and it is considered to be either amorphous or polycrystalline. Both AlN and GaN can be used as buffer layers [12,18]. The standard procedure is to performed an intentional annealing of the buffer layer at $1000\text{--}1080^\circ\text{C}$ in a mixture of N_2 , H_2 and NH_3 for 5-100 minutes [44,45,46].

The influence of the nitridation time on the buffer layer show that the longer nitridation produce buffer layers that wets the substrate predominantly hexagonal while the shorter nitridation produces a more disordered layer with predominately cubic GaN [29, 47].

The choice of AlN or GaN as a buffer layer (at 530°C) has been investigated by Lorenz et al. [44] by TEM and AFM in a MOCVD system. The authors have suggested that there are different mechanisms responsible for the roughening of the buffer layer surface for GaN and AlN. GaN surface roughens as a result of decomposition from the energetically unstable or highly faulted or strained regions and redeposit of GaN in the high growth rate regions (wurtzite is the phase stable at higher temperatures), while AlN, roughens by developing surface undulations through stress relief. Upon annealing the

GaN buffer layer suffers a series of transformations: first faceting disappears and the islands attain a rounded appearance, second the tilted islands disappear and there are fewer miss-oriented regions, third the density of rounded islands is lower than in the as-grown buffer layer and the rounded islands are connected by a thin interlayer. Features as high as 30 nm are formed upon annealing. Due to the low vapor pressure (about 5 orders of magnitude lower for AlN than GaN at 1000°C) the AlN only develops undulations and maintains the wurtzite structure and the features are only 3-5 nm high. Both buffer layers resulted in similar final products (flat-top islands) although the surface of the as-grown AlN buffer layer is smoother than the surface of the GaN buffer layer. The growth of the epilayer is influenced by the type of buffer layer used. For the AlN buffer layer high temperature GaN nuclei form first followed by the lateral growth of these nuclei into flat-top islands. For GaN buffer layer the growth of the epilayer proceeds by attachment to the existing structure of the buffer layer. Due to this difference it seems that the flat-top islands on AlN would be smaller than on GaN and it is believed that the size of these islands can be somehow related to the crystal quality to a certain extent through the density of threading dislocations. The rocking curve for the best GaN layers grown on the buffer layer was 250 and 460 arcsec for GaN and AlN buffer layer.

The thickness of the buffer layer has an impact on the properties of the film grown on top of it. For thicknesses in the range 10-150 nm the best rocking curves were obtained for the thinnest buffer layer [48].

The recrystallization of the buffer layer can impact on the optical properties of the film [33]. The longer the annealing time of the buffer layer, the poorer the optical properties of the film are as shown by the “yellow luminescence” of GaN around 2.2 eV and the optimal buffer layer is obtained when no additional recrystallization is allowed and the only heat treatment for the buffer layer is the ramping from buffer layer growth temperature to the epilayer growth temperature.

The annealing of the buffer layer it has been found by grazing incidence x-ray to increase the fraction of hexagonal GaN relative to the cubic phase for films grown at 525°C by MOCVD [49].

2.2.5 Growth Mode and Crystal structure

Sitar *et al.* [50] investigated the early stages of growth by MBE for GaN on sapphire at 600°C. Using XPS intensities and position of the peaks from the substrate (Al_{2p} , O_{1s}) and film (Ga_{3d} , N_{1s}) they concluded that the GaN films grows, for the given conditions, in a Stranki-Krastanov mode characterized by 2D growth followed by islands growth on top of the few layers that completely cover the substrate.

Briot *et al.* [33] have found that the GaN buffer layer is amorphous for deposition temperatures bellow 600°C and starts to be polycrystalline above. They have outlined that it is important to have an amorphous buffer layer in order to anneal it and recrystallized by a proper heat treatment and that is why they have used a buffer layer grown at 550°C. They have found an optimal V/III molar ratio of 6000 when TEGa is used. The optimal buffer layer thickness in this work was 25 nm as estimated from the morphology of the surface obtained by optical microscopy.

The growth rate of the buffer layer has an influence on the quality of the epilayer [51]. For MOCVD grown buffer layer 25 nm thick grown at 560°C best films were grown when the growth rate of the buffer layer was set to 18.2 nm/min. Hall mobility, FWHM of rocking curves; PL and dislocation density have been measured in order to find the optimal growth rate.

The initial stages of growth of the buffer layer at 500°C has been investigated by High Energy Electron Microscopy (HREM) by Degave *et al* [52]. At the beginning of the growth hexagonal and triangular shaped 3D islands form on the substrate surface. After 20 seconds of growth the structure appears to be exclusively cubic. After a while both cubic and hexagonal structures are observed with cubic being predominant. Coalescence is taking place and high number of stacking faults and microtwins in islands are formed, meaning that the stress in GaN is relaxed. From calculations is concluded that the strain evolves from a compressive to a tensile character [52].

The GaN properties drastically changed when the buffer layer was introduced in a MBE system [53]. The surface roughness decreased due to the use of the buffer layer, independent of the material (AlN or GaN) or temperature. It is found that for thin epilayers they reproduce the fine-grained surface of the buffer layer and even for 1000

nm thick films the surface features grew laterally only by a factor of 2 or 3 which is a lot less than the extent known for MOCVD. This could be very well since MBE uses growth temperatures 200-300°C lower than MOCVD. Surprisingly the PL of the samples grown without a buffer layer has stronger donor bound exciton emission. The study concludes that the buffer layer introduces non-radiative recombination defects. Simultaneously the electrical resistivity of the samples was 5 orders of magnitude higher for samples on buffer layer. These results are in contradiction to the increase in electrical and optical properties of GaN films grown by MOCVD and is most probably due to the different nature of the films grown by the two different methods.

2.2.6 Epitaxial Epilayer Growth

The final step consists of growing the GaN film on top of the buffer layer at high temperature (typically 1050°C). The quality of the film so deposited is in general better than the ones directly deposited on the substrate. The number of dislocations starting at the interface and propagating into the film is in the range of 10^7 - 10^{10} cm⁻² even for the highest quality films. The fact that devices with such a high concentration of defects work it is still puzzling.

Experimentally it has been found that the films grown on the c-plane sapphire grow with the c-axis aligned with the substrate. Given this constraint two relative orientations are possible for the film with respect to the substrate; one corresponds to the alignment of the corresponding planes in GaN and sapphire ($[1-100]\text{GaN} \parallel [1-100]\text{Al}_2\text{O}_3$) while the second correspond to a rotated film by 30 degrees ($[1-100]\text{GaN} \parallel [11-20]\text{Al}_2\text{O}_3$). In the case of the direct alignment the *d*-spacing mismatch between the film and substrate is -33%, while for the rotated case is 16%. From the point of view of the lattice coincidence in the first case three *d*-spacings of sapphire (11-20) match two *d*-spacings of GaN (10-10) with a misfit of 0.43% and a superperiod of 8.242Å while for the second case it takes six GaN (1-100) *d*-spacings to match seven sapphire (11-20) *d*-spacings with a -0.61% misfit and a superperiod of 16.66Å. The parallel epitaxial relationship gives a better lattice match with a smaller superperiod since a smaller mismatch produces less strain and a shorter superperiod gives more bonding numbers per unit length. Furthermore

considering the thermal expansion (higher for sapphire) during the growth the mismatch in the second case will be even larger.

Experimentally almost all the films grown have the orientation that is not favored by lattice coincidence. Chemical attraction [54] is the only reason that can be used to interpret this result. Since both Al and Ga have similar electronic configurations it is quite natural for the Ga atoms to replace the top Al sites on the sapphire surface or the Ga atoms are attracted by the dangling bonds of the O consequently, an epitaxial film in the GaN(1-100)||Al₂O₃(11-20) relation is formed.

Investigating by TEM films grown by MOCVD and MBE Rouviere et al. [55] have found that the nitridation and buffer layer are essential in releasing the strains, selecting polarity and keeping the crystalline orientation texture of the sapphire. An intermediate AlON cubic phase is formed.

The 2-step deposition technique has been first detailed by Akasaki et al. [43]. This method involves the deposition of a AlN buffer layer at low temperature followed by the growth of the epilayer at high temperature. Using TEM, Hiramatsu et al. [56] has found that the epitaxial relationship between the GaN epilayer the intermediate (600°C) AlN layer and the sapphire substrate grown by MOCVD (this preferential orientation is found by many different studies [35,36]): [0001]GaN || [0001]AlN || [0001]Al₂O₃ and [1-100]GaN || [1-100]AlN || [11-20]Al₂O₃ (Figure 2.2).

This orientation corresponds to an in-plane rotation of 30° of the GaN lattice with respect to the substrate one. They have also found that the orientation of the GaN with respect to sapphire is similar with the one obtained when GaN is grown directly on sapphire[57,58] or with GaN buffer layer[59]. This is also consistent to results obtained by XRD [60].

A different epitaxial orientation has been reported by Sundaravel et al. [61] for MOCVD GaN namely [11-20]||Al₂O₃[11-20] and the authors attribute this orientation to the Mg doping during growth. The films were grown by MOCVD using a 30 nm GaN buffer layer deposited at 550°C, while the epilayer was deposited at 1080°C. By XRD it has been confirmed that a mixture of cubic and wurtzite phase GaN is grown.

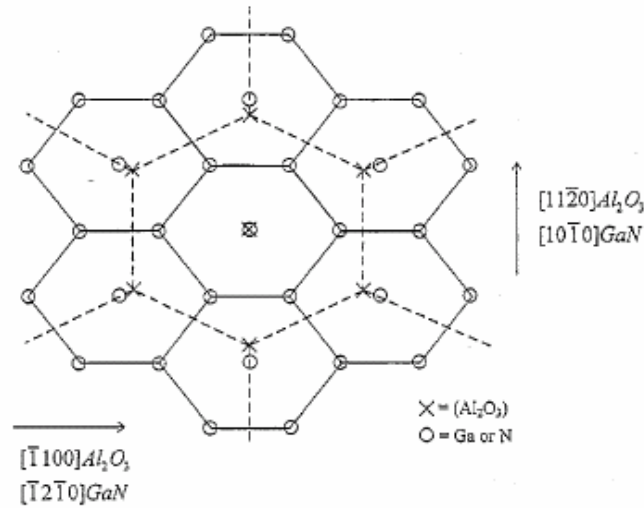


Figure 2.2 c-plane of GaN on c-plane of Al_2O_3 [21]

2.2.7 Defects

The most pervasive crystalline defects present in the GaN films are the threading dislocations (TD) with a density that can be as high as 10^{10} cm^{-2} for a working device. TDs are formed at the film substrate interface and propagate [62] throughout the film (Figure 2.1) reaching the region of the heterojunction. They can act as non-radiative recombination paths [63,64] and diminish the device efficiency, act as scattering centers for charge carriers, or can provide a path for the metal diffusion from contacts or dopants. If the defect density is higher than 10^7 cm^{-2} , light scattering is another unwanted effect [65]. These threading dislocations are most of the time of the type edge or screw, and their characteristics are discussed in chapter 6.

Ning et al. performed a comprehensive study by TEM on the origin of the dislocations in GaN films on sapphire [59] using a low temperature (510°C) GaN buffer layer. The majority of the dislocations are perpendicular to the interface and continue to the film surface. These edge dislocations are thought to occur when different domains that have slight misorientations with respect to one another coalesce, their function being to accommodate the 0.2-0.3 deg rotations around the c-axis between the domains.

They have also found that the film is under bi-axial compression stress due to the large geometrical misfit that is not completely accommodated by dislocations.

Films with different dislocations densities as well as orientation have been grown by altering the deposition conditions of the buffer layer [66]. For some of these MOCVD grown GaN films the orientation of the threading dislocations has an impact on the width of the FWHM of the rocking curves of XRD along various crystallographic directions. The $2 \times 10^{10} \text{ cm}^{-2}$ dislocations in this MOCVD film were all aligned along the growth direction and they were pure edge with Burgers vectors parallel to the film/substrate interface. Due to this arrangement the dislocations do not distort the (002) plane and the FWHM of the curves were very good (40 arcsec) providing misleading results on the quality of the film. For the same film rocking curves in the (102) planes had a FWHM of 740 arcsec.

The influence of the nitridation time on dislocation densities has been investigated [29]: shorter ammonia pre-flow (60 seconds in 3 l/min ammonia) produced films with lower dislocation densities ($2 \times 10^8 \text{ cm}^{-2}$) and higher electron mobilities ($592 \text{ cm}^2/\text{V}$) compared with longer nitridation times (400 seconds).

Another type of defect that is observed in the GaN thin films is called twining and can extend into the epilayer to form domain boundaries. Cheng et al. have shown that most of the domain boundaries arise from the interface between the buffer layer and the epilayer and extend to the top of the film. TEM investigation concluded that during the buffer layer growth cubic twins will be formed and the twin boundaries can extend into the epilayer to form inversion domain boundaries [67]. Inversion domain boundaries is another type of defect that will be discussed in the subsection regarding film polarity.

2.2.8 Texture, structure, growth mode

The structure of the GaN film as studied by TEM by [64] shows three distinct texture regions: closest to the buffer layer is the “faulted zone” about 50 nm thick, above this there is a zone characterized by trapezoidal structures confirmed to be truncated hexagonal pyramidal mesa with a thickness of about 150 nm, and the remaining is a region with smaller amount of defects for thickness more than 300 nm.

The microstructure of GaN epitaxial films deposited by MOCVD on sapphire, using a thin (25-30nm) low temperature buffer layer (600°C) of GaN has been investigated using TEM [70]. The GaN buffer layer exhibited a mixed cubic-hexagonal columnar microstructure with numerous defects to accommodate the misorientations between micrograins and with the cubic phase being stable under the growth conditions. The subsequent annealing at 1050°C produces a drastic change in microstructure: cubic islands remain on top of a film with hexagonal structure but the buffer layer is highly polycrystalline. The structure of the film grown on top of the buffer layer could be separate in two distinct regions based on the defect density with the high dislocation region 500 nm thick. Not the entire misfit is relaxed by misfit dislocations due to the large difference between the thermal expansion coefficients and strain is created during post growth cooling. The author proposed a relaxation mechanism in which the elastic energy due to strain increases with the thickness of the layer and after 7-8 nm is so large that stacking fault nucleation becomes energetically favorable.

One study investigated the strain relaxation mechanism of a GaN film grown on AlN buffer layer [28]. The strain was relaxed through a Stransky-Krastanov growth mode, with 3D islands occurring after a critical thickness of approximately two monolayers. The growth temperature is an important parameter with respect to the transition from 2D growth to 3D growth. A higher temperature accelerates the transition and the growth remains 3D-like even after the islands start to coalesce. A lower temperature increased the critical thickness of the GaN layer, the transition is almost absent and the film remains 2D-like and strained.

2.2.9 Surface polarity

Due to the fact that the GaN crystal does not have centro-symmetric structure and that the growth of the wurtzite phase occurs along a polar direction makes GaN different than other III-V semiconductors. Oftentimes polarity has been overlooked due to being difficult to measure but the control of the polarity is critical in epitaxy as it controls the surface morphology, doping character, and the direction of piezoelectric field.

Figure 2.3 shows the convention used when polarity is mentioned: Ga-face is the $\langle 0001 \rangle$ direction while the N-face is the opposite face. In the picture the size of the spheres indicates the ionic radius, in diagrams which use covalent radii the gallium's radius is bigger than the nitrogen's. Alternative term for polarity is “termination”.

The polarity of the film has been related to the other characteristics of the films such as surface morphology, growth mode and growth rate, surface reconstruction and even though we do not have a direct way to evaluate it we have to take it into consideration. Much work has gone into corroborating the surface polarity with the surface reconstruction [49,69,70,71,72] and we will review here just the results from the standard framework that are relevant to our work [73]: 1) films with hexagonal pyramidal morphology grown on sapphire are N-polarity 2) smooth films on sapphire are usually Ga-polarity 3) Ga-face is chemically more stable 4) while many reconstructions are possible of 2×2 is frequently observed for the Ga-face and 3×3 for the N-face 4) bulk-like 1×1 face is common to both polarities 5) oftentimes both polarities can co-exist on a sample [47,48,74,75,76] 6) the two polarities have growth and evaporation rates that vary with the substrate temperature [47,75] 7) the coexistence of both polarities can be accommodated by inversion domain boundaries (IDB), a type of defect that has very low formation energy [77] (0.41 eV) (IDBs does not induced electronic states in the band-gap and therefore have no influence on the optical quality of the film) 8) IDB are found in all materials and they depend on the growth conditions [78] 9) in general the buffer layer polarity defines the film polarity 10) polarity can be defined as early as the sapphire nitridation and/or buffer layer annealing [48] 11) a GaN buffer layer can have both polarities and the annealing can change the ratio of the two 12) Ga-polarity is laterally growing faster but preferentially re-evaporated upon annealing at 1040°C [79] 12) growth parameters such as the molar ratio V/III can have an influence on the film polarity [79] 13) sometimes conflicting results are reported in the literature that can be due to different/wrong assignment of the polarity.

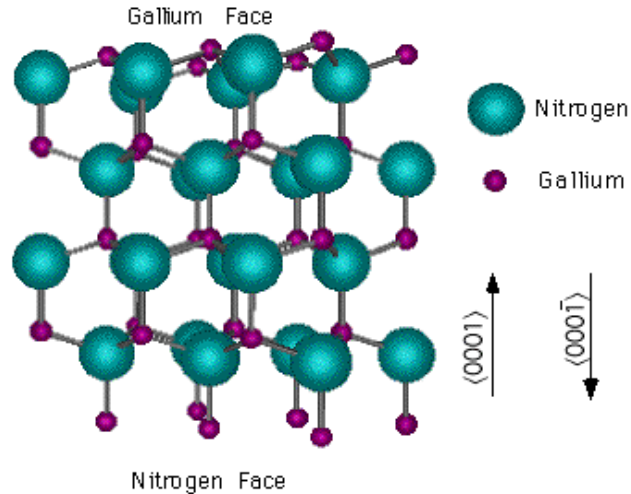


Figure 2.3: The wurtzite crystal structure of GaN, showing the conventions used to discuss its polarity

2.2.10 Parameter choice/optimization

For the two-step process there are in fact many parameters that influence the quality of the film, and they are related to the nitridation as well as buffer layer deposition and epilayer growth. For the nitridation step parameters are: heating temperature and time, ammonia flow, chamber pressure, gas(s) used. For the deposition of the buffer layer the parameters are: growth temperature, precursors flow, the III/V molar ratio, thickness of the layer, geometry of the gas flow. An intermediate recrystallization step can be introduced after the deposition of the buffer layer, and the annealing temperature and time are the parameters. For the growth of the epilayer the parameters are: substrate growth temperature, precursor flow rates, molar ratio of III/V precursors, chamber pressure and geometry.

A study of the optimization of the MOCVD growth of GaN on sapphire using GaN buffer layer has been performed by Briot et al. [33] (using triethylgallium (TEGa)) and they have found that the parameter window leading to high quality material was very narrow. They have investigated the quality of the film by XRD and Photoluminescence and the optimized film shows at low temperature the free-exciton recombination line which is an indication of a high quality GaN film.

It has been shown experimentally that the optical properties of the epilayer are very strongly correlated to the deposition temperature of the film. [33]. The optimal substrate growth temperature for PL free-exciton emission has been found to be 980°C. The temperature window is very small since a 3% change had dramatic effects on the film optical quality.

The V/III molar ratio can play an important role in the growth rate of the film [33]. Providing more ammonia has the effect of decreasing the growth rate even when the decrease in partial pressure of the group V gas is taken into account. This may be related to the chemistry involved in the growth of GaN and a possible strong adsorption of the ammonia on the surface on both Ga and N sites that can slow down or block the growth, this effect can be seen for both buffer layer and epilayer growth. The lower V/III ratio has been found to produce films with larger islands that give rise to fewer defects [80] while in a different study the FWHM of the rocking curves in x-ray increases slowly with higher ratio in 1000-10000 interval [81].

Fischer et al. [82] has found that for MOVPE the crystalline quality of the film increases with higher deposition pressure due to decrease of the growth rate. Besides the reactor pressure, the growth rate strongly depends on the substrate temperature because of surface reactions and altered reaction path-ways. From Arrhenius plot analysis the temperature dependence of the growth rate can be clearly determined. The growth rate at lower temperatures indicates thermally activated deposition kinetics. In the temperature range of 870 – 1020K the GaN film growth is associated with activation energy of 151 ± 5 kJ/mol. The maximum growth rate of 2500 nm/h was obtained in the temperature range of 1020 – 1175K. In this range, the growth rate shows nearly no temperature dependence that means the growth is only controlled by the diffusion of the precursor molecule fragments to the substrate surface. At temperatures over 1175K the growth rate decreases because of desorption and depletion processes consistent with the typical behavior of a CVD process. Different precursors have been used in this study than the ones used by Fischer. Although similar behavior can be expected with respect to the temperature dependence, one can expect a shifting in temperature range and different activation energy.

The growth temperature is a very important parameter in the growth of GaN. In general the growth temperature is about 1050°C for MOCVD. At high temperature, the equilibrium vapor pressure of nitrogen is very high so there is desorption of nitrogen from the film that gives rise to a lot of vacancies that can only be reduced by supplying an excess of the nitrogen precursor. It has also been found that the incorporation of In is decreased at high temperatures due to In desorption rate, and this is important since the actual devices have quantum wells that are made by alloying GaN with InN. Moreover the interfaces in quantum wells degrade when grown at high temperature. As a result it is desirable to decrease the growth temperature to avoid these problems.

2.2.11 GaN surface

While the surface reconstructions of GaN films obtained by MBE have been extensively studied the MOCVD films have received only a limited amount of attention. Extensive work has been done for bare and adsorbate covered plasma assisted MBE grown films [72] and following reconstructions have been found for the N-polar: 1x1, 3x3, 6x6, c(6x12) while for the Ga-polar: 2x2, 5x5, 6x4 and pseudo-1x1. The pseudo-1x1 GaN surface has been observed by Smith et al. [69] and has a temperature dependence. They observe a modulated ring around the first-order spots that change irreversibly as the temperature is increased. These patterns are not correlated with or depend on faceting or periodic steps and they suggest an incommensurate structure that can be caused by Ga rich (0001) surface.

Various techniques have been used to identify the polarity of the surface: surface reconstruction [69,70], chemical etching [75], hemispherically scanned x-ray photoelectron diffraction [75]. The different nature of the reconstruction for the two faces of GaN has been used to identify the polarity of the crystal.

Munkholm *et al.* [49] have found that only two surface reconstructions are observed for the MOCVD grown films kept under ammonia flow at close to atmosphere pressure and temperatures below 1000K after the growth. The two reconstructions observed are 1x1 (bulk-like) and the $\sqrt{3} \times \sqrt{3}$ R 30° that corresponds to a structure with 1/3 of the surface Ga atoms absent.

2.2.12 Ion Beam methods in GaN thin film analysis

Hollander [83] has used RBS/Ion channeling together with TEM to investigate both MBE and MOCVD GaN films on sapphire substrate. Unfortunately the thickness of the films was very different (400 nm for MOCVD and 1550 nm for MBE) and it is known that the defect density tends to decrease as the film thickness increases. For the GS-MBE there seems to be similar number of screw and edge dislocations while for the MOCVD sample the number of edge dislocations is twice that of the screw dislocations. Based on the planar de-channeling results it was concluded that the ion channeling is 4 times more sensitive to the edge than to the screw dislocation. This is explained by the orientation of the dislocation with respect to the channeling direction. The study also found that the two types of crystallographic planes can be distinguished when an angular scan around the c axis is performed with the reservation that the film has to be thicker than about 400 nm. When the films are thinner than 400 nm there is no difference in the planar channeling for the two crystallographic directions and other method is needed to identify the planes.

Sundaravel et al. [61] have made a different assignment compared to Hollander [83], for the planar dips observed when the sample is azimuthally rotated around the c-axis and they obtained a parallel orientation of the GaN crystallographic planes with respect to the sapphire substrate.

The damage in GaN platelets due to the ion bombardment for 2 MeV $^4\text{He}^+$ has been investigated [84] and it has been found that the channeling yield increases a factor of two when the surface is bombarded with a beam fluence of 1×10^{17} ions/cm² (which is about 10 times the dose that is the normal dose used for taking one spectrum). Osipowicz [85] has found no measurable damage when using almost the same dose (7.4×10^{16} He⁺ ions/cm²).

Using ion channeling and convergent beam electron diffraction Daudin et al. [47, 86] have determined that the morphology of the sample can be related to the polarity. Flat samples tend to have Ga-polarity while samples with pyramidal defects on the surface contain inversion domains and have mixed polarity. The difference in sample preparation was the nitridation of the sapphire for the flat films.

Linden et al. [87] have performed ion channeling measurements for thick MOVPE films (1-2 μ m) and he has found that the quality of the film increases towards the surface. Some of his samples with poor quality had constant profile of disorder and he has attributed this to “disturbances in the growth process” rather than the interfacial mismatch with the sapphire.

Ion implantation with both easy (C) and heavy ions (Au) at energies in the range 40keV to 2MeV is shown to produce an amorphisation of the surface followed by loss of the nitrogen visible even in the RBS [88].

2.3 Summary

Due to its unique properties GaN is a material useful for a variety of applications but obtaining good quality films is still a challenge. MOCVD is the main method for epitaxial growth of GaN for mass production and the early stages of growth are decisive for the quality of the film. While extensive work has been devoted to GaN in the last decade, the *in-situ* analysis of MOCVD films has not received the same amount of attention due to experimental difficulties.

Ion beam analysis is a very powerful technique both for bulk and surface analysis that we have used in conjunction with other complementary techniques to look at the early stages of growth of GaN films grown by MOCVD on sapphire substrate. The analysis is performed without taking the sample out of the ultra high vacuum environment.

Chapter 3

Experimental Setup for thin film growth by MOCVD

3.1. Introduction

The investigation of the first stages of the heteroepitaxial growth of GaN requires very well controlled environment as well as measures to reduce the contamination. It is well known that the exposure of the films to atmosphere or other contaminants greatly alter the properties of the surface and further investigation does not reveal the actual structure and composition of the films or interfaces but rather a system altered by the interaction with the ambient gases.

For the purpose of this work a purpose-built MOCVD system has been successfully designed, built, and integrated into a UHV thin film analysis facility.

3.2 UHV Highway Transfer System

The experiments have been designed in such a way to be able to analyze the samples without exposing them to air. They have been conducted in three ultra high vacuum

(UHV) chambers connected via a UHV transfer system (UHV Highway) and known as 'W.M. Keck Thin Film Analysis Facility' (Figure 3.1).

The MOCVD chamber is dedicated to the pretreatment of the substrate and the growth of the film and the two other chambers are equipped for film analysis. The ultra high vacuum (UHV) connection between the chambers is kept at a pressure of approximately 5×10^{-9} torr and allows the transfer of the sample without contamination. One of the chambers is equipped for electron spectroscopy where UPS/XPS/AES/SEM of the surface can be performed using a Kratos XSAM800 electron spectrometer. The second chamber is connected to the accelerator line and is equipped with the LEED system and a six axis goniometer, where experiments in RBS/ERS/NRA and ion channeling have been performed.

3.3 Sample Holder

The heating of the substrate is of utmost importance in the MOCVD film growth to sustain the endothermic reaction and the heating of the substrate. In order to be able to transfer the sample from the MOCVD reactor into the ion channeling/LEED analysis system a sample holder that is compatible with all the three chambers has been designed and built. The new sample holder (Figure 3.2-c) has the layout of the legs and the attachment mechanism of the sample holder of the goniometer (Figure 3.2-b) and incorporates an Advanced Ceramics boraelectric heater. The heater is electrically insulated with ceramic spacers from the all-metallic body of the sample holder and the details of the integration of the heater to the sample holder are shown in Figure 3.3.

The two electrical contacts needed for the resistive heater have been routed through two of the legs of the sample holder that are also insulated with respect to the body of the sample holder. The heater is connected to the sample holder legs by tungsten wires. The sapphire substrate it is held on the ceramic heater by a tungsten wire made into two spring clamps. A metallic screen can be mounted above the substrate by using one of the heater posts if electron suppression is desired in Ion Channeling experiments.

XSAM800 XPS/UPS/AES/SAM

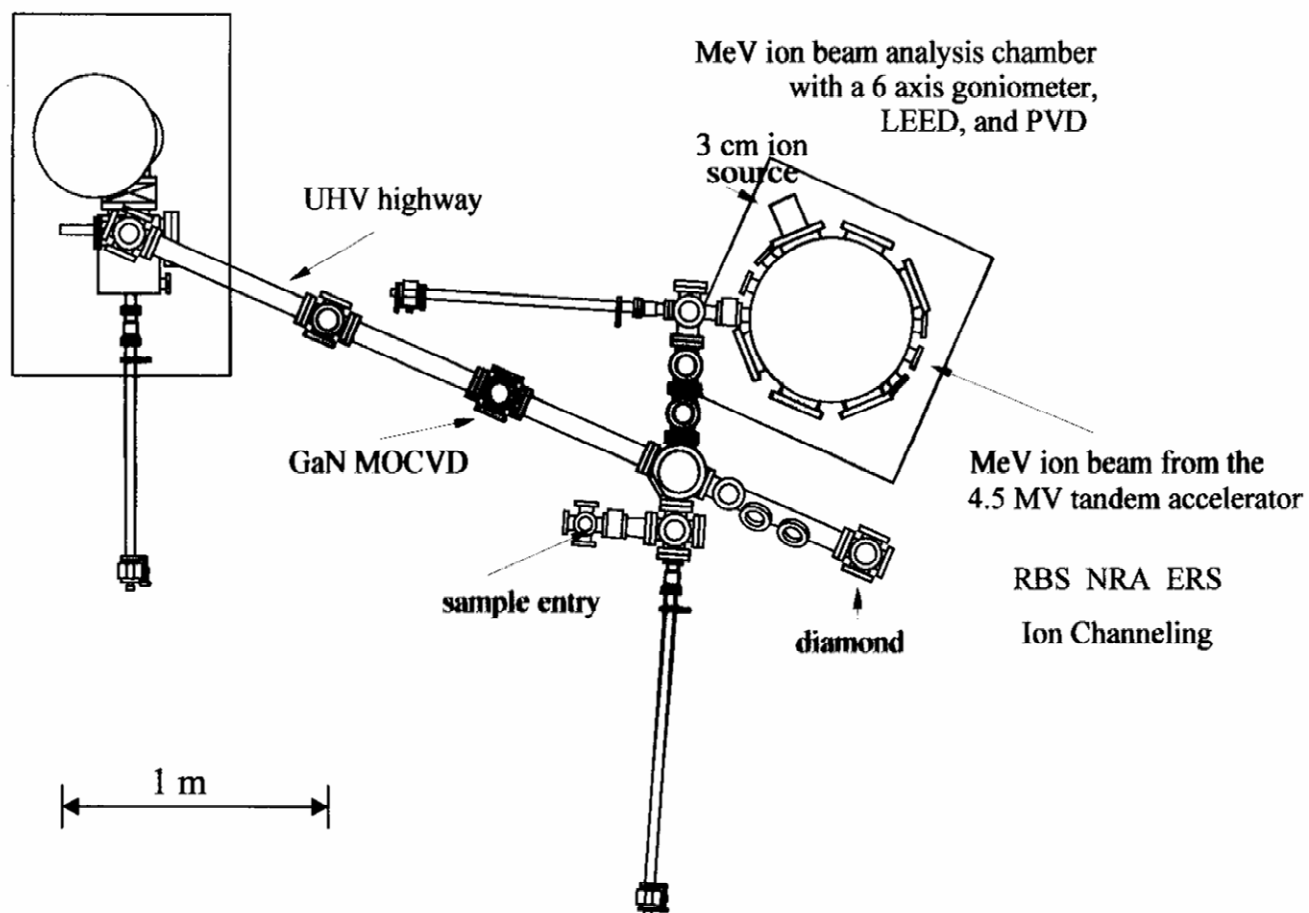


Figure 3.1: W.M. Keck Thin Film Analysis Facility outline

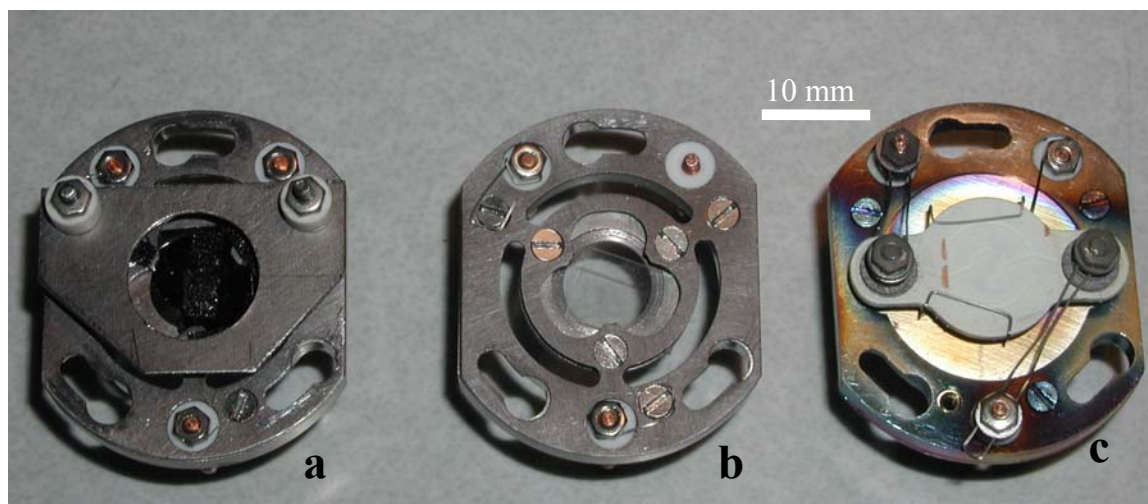


Figure.3.2: Sample holders used throughout this work. a) Modified sample holder used for Ion Channeling b) Original goniometer sample holder c) Modified sample holder used for MOCVD growth.

This modified sample holder is transferable into the six axis goniometer for LEED and ion beam measurements. In order to be able to transfer the GaN thin films grown in the MOCVD system in the XPS/AES/UPS measurement system an adapter has been designed and built. This adapter consists of a triangular metallic piece with 3 orifices for the three legs of the sample holder and one additional orifice for the XPS stub holder.

In addition to the sample holder modified for the MOCVD system another sample holder has been used for Ion Channeling (Fig 3.2-a) that has a circular screen mounted in front of the sample and electrically insulated from the sample holder body. The purpose of this screen is to repel the secondary electrons emitted from the sample during ion beam bombardment. This is useful in the correct measurement of the integrated current when Ion Channeling measurements are performed.

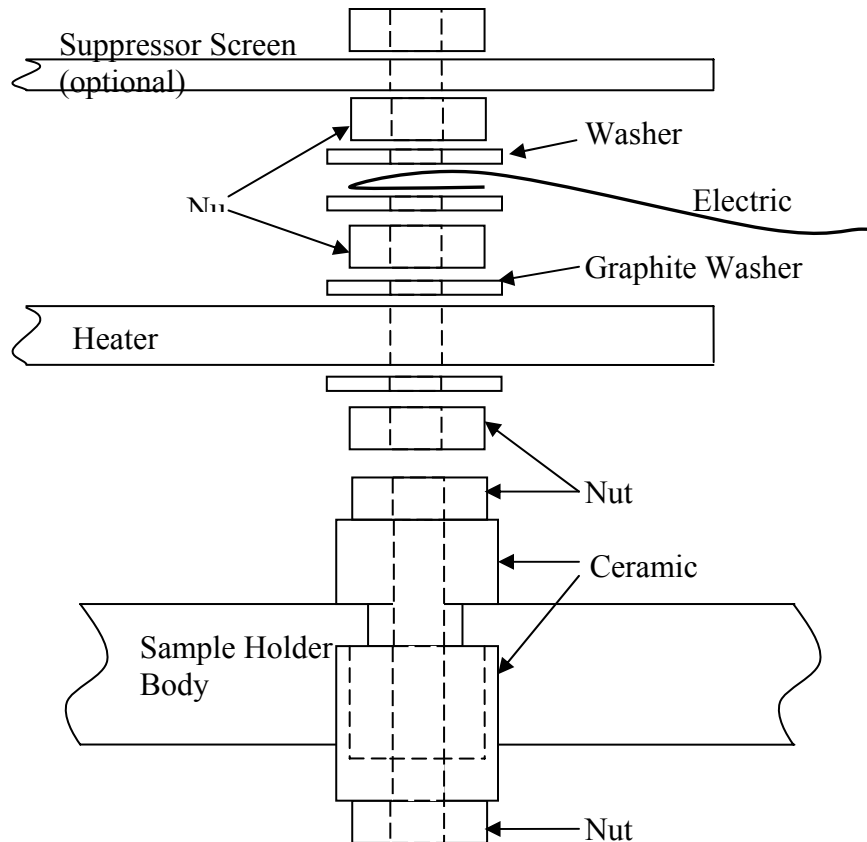


Figure 3.3: Schematic of the attachment of the heater to the sample holder (not to scale)

3.4 Gas admission and evacuation system

The popularity of using metal-organic compounds is partly due to availability of high vapor pressure, pure precursors for a wide variety of elements that are of interest in compound semiconductor deposition. In general they are pyrophoric and react adversely with the moisture. Most precursors have a vapor pressure between 1 and 100 torr around room temperature. Figure 3.4 shows the temperature dependence of the vapor pressure of two metal-organic precursors used extensively for GaN deposition: trimethyl Gallium (TMGa) and triethyl Gallium (TEGa). In this work TMGa has been used due to the higher vapor pressure at room temperature. The boiling point of TMGa at one atmosphere is 55°C and the vapor pressure at 273K is 65.4 torr.

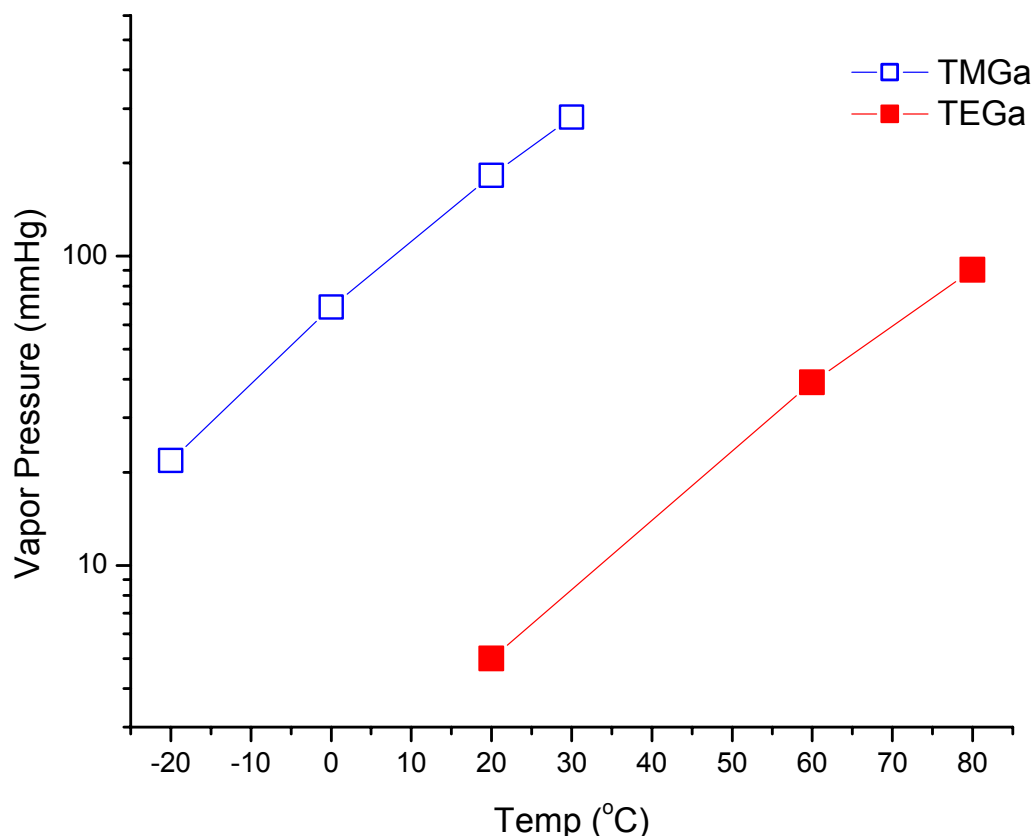
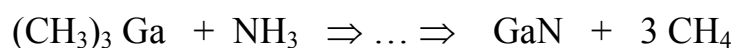


Figure 3.4: Vapor pressure of two metalorganic precursors for Ga [89]

Ignoring intermediate steps, the chemical reaction that takes place can be described as follows if TMGa is used as precursor, and only the initial gases are considered:



Since reaction between gases during transport needs to be prevented, two separate tubes are used to deliver the gases into the chamber. Also nonvolatile reaction products can be prevented by the use of adducts that have lower vapor pressure than either of the gases. In general the sources are kept below the temperature of the tubing to avoid the condensation. If very low vapor pressure gas is used, the gas container, tubes and all the connections can be heated to avoid condensation.

The control of the admission of the gases in the chamber is achieved by using mass flow controllers (MFCs). For each of the five gases that are being used (N_2 , H_2 , NH_3 , TMAI, TMGa) a flow control line has been assembled (Figure 3.5).

The main component for each gas delivery line is the Mass Flow Controller (MFC) that controls the throughput of gas entering that is delivered inside the chamber. The gas lines have incorporated filters to ensure the removal of particles that might be trapped in the bottles or in the tubing. Check valves are incorporated in each line to ensure that no backflow of gas occurs and therefore no cross-contamination of the gas lines from the other gas lines. To control and synchronize the gas admission each gas line is equipped with three pneumatic valves (A1, A2, A3) as well as three hand valves (V1, V2, V3). The hand valve V1 is used as a safety measure in case there are failures in other valves and it stays open during film growth and closed at all other times. Valves V2 is the admission of the purging gas and is only open when purging is performed, and is closed at all other times. The valve V3 is the one controlling the bypass around the Mass Flow Controller and is used during the purging. Nitrogen is used as a purging gas. The valves A1 and A3 are the main controlling valves for gas admission during film growth. Valve A2 is one of the purging valves and connects the gas line to the exhaust line.

Due to the large number of pneumatic valves (15 for all five gas delivery lines, and 2 for linking the reactor chamber to the UHV and vacuum pumping system) that have to be controlled before, during and after growth, and because of the harmful nature of two of the gases used in the process, a special control unit has been designed and built to control the opening of the air controlled valves and to avoid accidental exposure of the operator to dangerous gases, as well as the contamination of the other parts of the system with the gases used in this experiment. The control unit has been built using relay logic and was implemented using a set of rules regarding the opening and closing of the various valves.

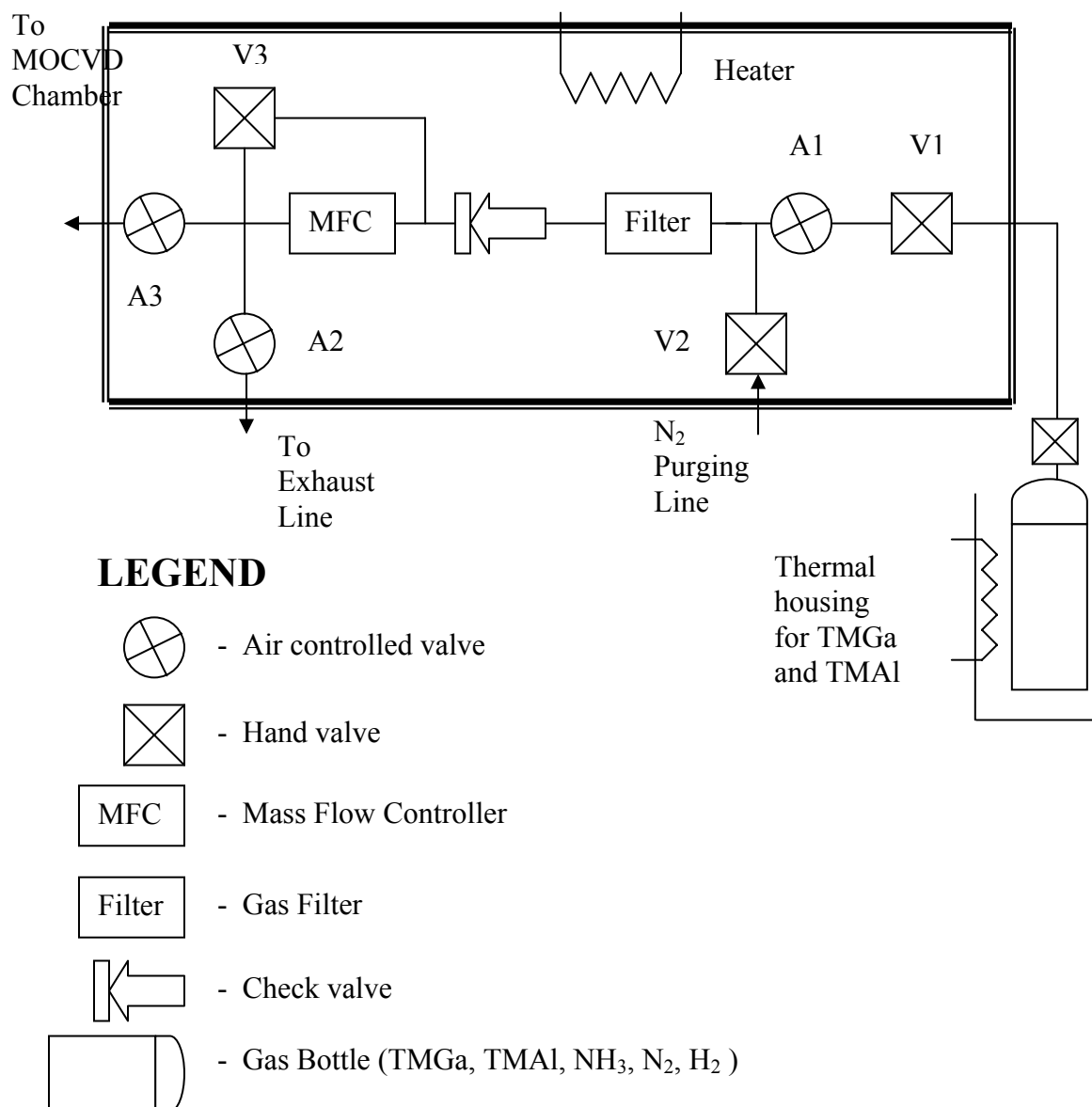


Figure 3.5: Schematic Setup of one gas delivery line for the MOCVD reactor

The five gas delivery lines are all mounted inside a thermally insulated box that can be heated up to 150°C for outgasing and removing the contamination. The schematic of the entire MOCVD reactor system is shown in Figure 3.6.

The rules used in the 'Air Valve Control Unit' for the control of the valves are as follows:

- 1) during film growth of the film (A1, A3 open) the chamber has to be isolated from the transfer line or lower chamber (VG1 and VG2 stay closed);
- 2) during film growth the purging exhaust line has to be closed (all A2 valves has stay closed);
- 3) during purging (A1 and A2 open) no purging gas should enter the reactor chamber (all A3 valves have to stay closed);
- 4) during purging only one of the valves A2 can be open at one time;
- 5) during reactor chamber pumping (GV1 open) no gas can enter chamber (all A3 stay closed);
- 6) during sample transfer (GV1 open) no gas should enter the reactor chamber (all A3 valves stay closed)

Two pumping stations are needed for the system as seen in Figure 3.6. The PS1 pumping system is composed of a turbo-molecular pump backed by a mechanical pump and has the role to pump the reactor chamber before the film growth. If the system is backed the base pressure in the reactor chamber before the film growth is started can be as low as 10^{-8} torr. The PS2 pumping system consist of a mechanical pump connected to the exhaust from the reactor chamber and is used during the film growth to eliminate the used gases from the reaction chamber.

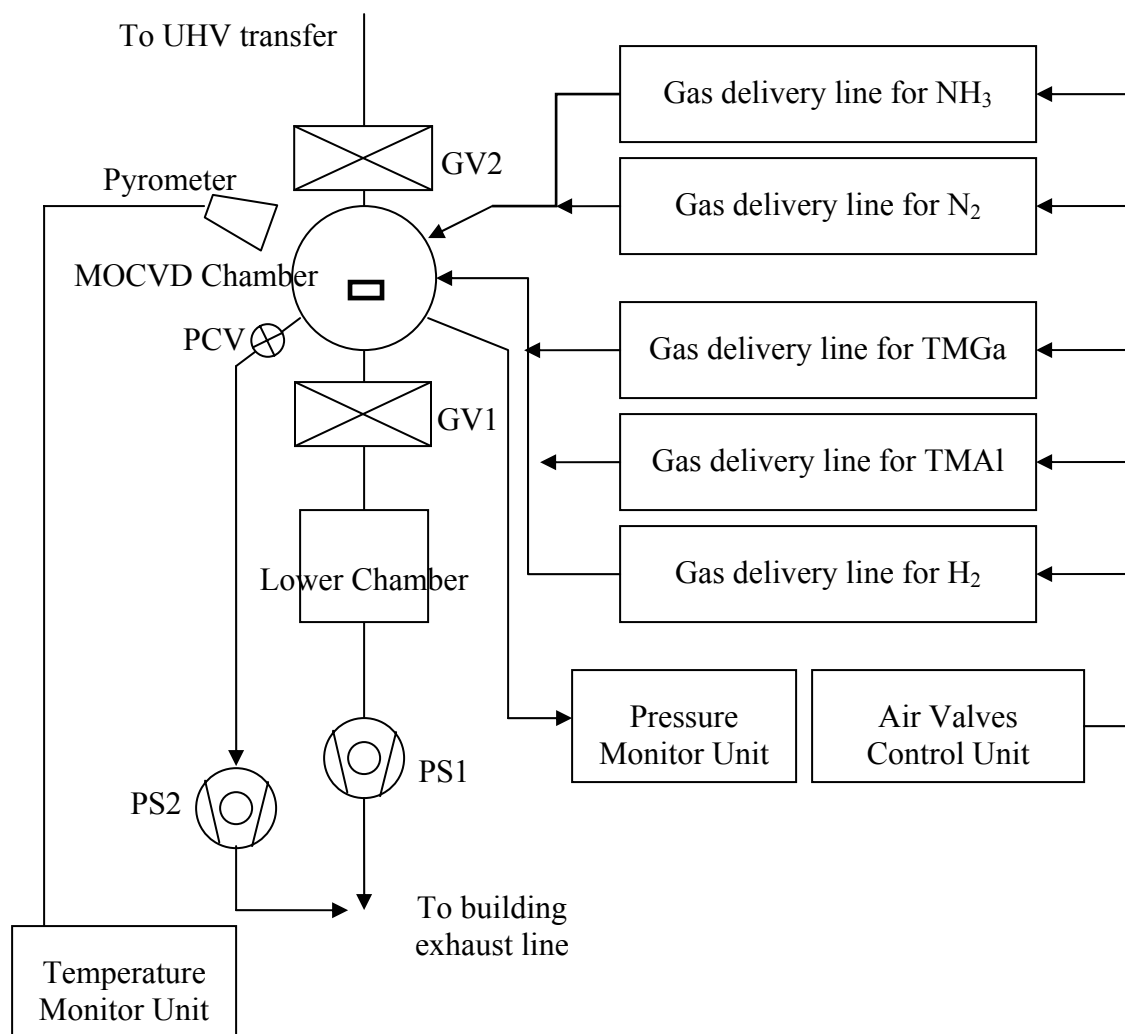


Figure 3.6: Schematic of the MOCVD deposition system

3.5 CVD Reactor Chamber Setup

A diagram of the MOCVD reactor chamber is presented in Figure 3.7. The main reactor chamber is spherical and is connected via gate valves at the top flange to the UHV Highway and at the lower end to a second chamber that is kept under high vacuum conditions. The connection to the Highway allows the easy transfer of the sample holder from the CVD chamber into the UHV Highway and subsequent transfer towards the two analysis chambers. In addition to the two mentioned ports the chamber has the following additional windows: NH_3 and N_2 port entrance; H_2 and TMGa port entrance; gas evacuation port; pressure gauge; leak valve connecting to the lower chamber; glass windows for temperature measurement with optical pyrometers; electrical feedthroughs for the sample holder power.

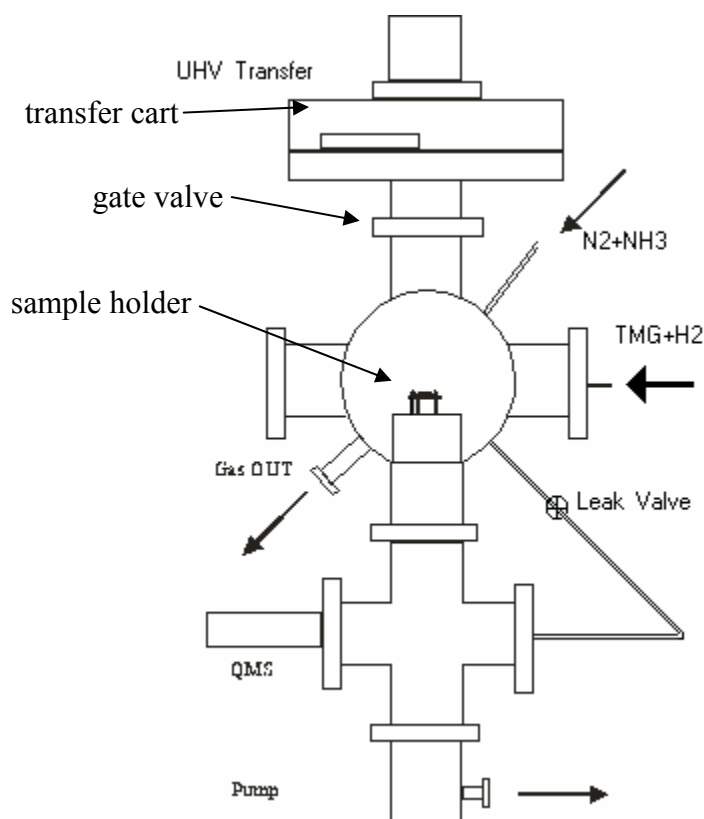


Figure 3.7: MOCVD Reactor chamber (not to scale)

The substrate holder described in a previous section is transferred in the middle of the spherical deposition chamber by a magnetically coupled transfer arm.

The deposition chamber is connected via a very small leak with a lower chamber equipped with a quadrupole mass spectrometer (QMS). The pressure in the lower chamber is 10^{-5} – 10^{-6} torr during the deposition of the film and can be adjusted by opening/closing the leak valve. The arrangement permits the sampling of the gas inside the reactor chamber before and during the deposition for determining its approximate composition.

The gases enter the reaction chamber from two different directions. In order to decrease the probability of reaction between the gases before reaching the substrate, two inlets are used for the delivery of gases. One inlet supplies the TMGa carried by hydrogen, while the second one supplies the mixture of ammonia and nitrogen prior to delivery inside the chamber. The exhaust gas outlet is situated in the opposite position with respect to the inlet port.

In order to be able to bake the entire system to high temperature, only copper gaskets and subassemblies that can withstand the baking temperature (150°C) are used.

3.6 Auxiliary systems: temperature and pressure control

The pressure in the reactor chamber is determined by the total amount of gas delivered and the pumping rate at the output port. The amount of gas delivered can be varied as follows: ammonia 0.1-5 standard liters per minute (slm); hydrogen 0.1-5 slm; TMGa 0.1-2 standard cubic centimeter (sccm), and nitrogen 0.1-5 slm. The gas is evacuated through an outlet situated on the lower side of the chamber and the pumping rate is controlled by one manual valve and one butterfly valve connected in series between the output port of the chamber and the vacuum pump (PCV on Figure 3.6). Since the control of the pressure is done manually, a set of calibration runs have been performed before the actual film deposition in order to obtain the position of the two valves needed for a given pressure and for various gas combinations for the different steps involved in the growth of GaN films.

The pressure in the reactor chamber is measured with a capacitance manometer calibrated to measure pressures in the 1-100 torr range. Additionally, the pressure is monitored in the lower chamber with an ion gauge that measures vacuum better than about 5×10^{-5} torr. On this lower chamber we have connected a quadrupole mass spectrometer (QMS) that monitors the composition of the gas before, during, and after deposition. The adjustable leak valve mounted on the line between the two chambers allows us to sample the gas in the main chamber.

The temperature of the substrate is an important parameter and it is dependent on the electrical power delivered to the heating element, on the pressure in the chamber and the speed of the flow of gases inside the chamber. Since the control of the temperature is manual and done by the operator during the deposition, a series of calibration runs have been performed in order to determine the values of the parameters needed for the desired temperatures during the various steps of the deposition. For the measurement of the temperature, two pyrometers have been used due to the large range of temperatures needed during a run. The range of the two pyrometers is: 300-800°C and 600-1400°C. The pyrometers are connected to two Radio Shack multimeters with computer output and the temperature variation during the entire run is recorded for further reference and check on the accuracy of the temperature control and stability during the growth.

The ratio of nitrogen to gallium (V/III ratio) delivered in the chamber is one of the most important deposition parameters, usually determined empirically for each reactor chamber. The numbers reported in the literature varies widely (500-15000) and they depend on the method used to introduce the TMG and the geometry of the deposition chamber [48,90]. In section 5.4 we discuss the choice for this parameter.

The reactor is operating in a viscous flow regime and the total flow of gas through the chamber is of the order of 1.5 slm. The pressure inside the chamber can be kept in the range of 10-90 torr. It is important to keep the flow of the gas in a laminar regime because the turbulent flow creates cavities of lower pressure which impact negatively on the performance of CVD reactors by creating inhomogenities in the concentration of gas. The residence time of the gas in the chamber calculated from the volume of the chamber and the speed of the gas is of the order of seconds.

3.7 Thin film growth procedure

Before the introduction of the sapphire substrate in the vacuum chamber, the following preparatory operations need to be completed: purging of the gas lines with N₂ and reactor chamber; baking of the valve box while pumping with the mechanical pump; baking of the reactor chamber while pumping with the turbo-molecular pump; pumping of the reactor chamber and gas lines to high vacuum.; heating of the metal-organic gas bottles.

The steps involved in the actual growth of the films are as follows:

- ex-situ: degreasing of the sapphire with acetone, annealing in air at 1400°C for 30 minutes,
- introduction in the UHV environment, flash heating in vacuum of the sapphire substrate at 850°C, flash heating of the sapphire at 1000°C in H₂ flow of 0.5 slm and 50 torr,
- lowering the substrate temperature and introduction of the ammonia at 0.5 slm and 50 torr,
- nitridation of the sapphire at 850°C for 300 seconds in ammonia at 0.5 slm at 50 torr,
- ramping up or lowering down the temperature of the substrate to the growth temperature while simultaneously allowing 0.5 slm NH₃, 0.5 slm N₂ and 0.5 slm H₂ in the reactor chamber,
- when the desired deposition conditions have been stabilized, admission of 0.5 sccm TMGa for 100 seconds,
- terminating the growth by simultaneously decreasing the substrate temperature, shutting off the gases and opening the evacuation valve,
- cooling down to room temperature of the sample at 50 torr in N₂ flow of 0.5 slm.

Due to the inherent human variability in handling the deposition steps we have decided to a minimum step in the growth temperature of 50-70°C.

Chapter 4

Characterization Techniques

4.1 Introduction

In order to understand the initial stages of epitaxy we have used a series of techniques complementary in nature that give information about the composition and structure of the initial surface, surface after exposure to nitrogen and after the first layers are deposited.

The techniques used fall in three categories: ion scattering techniques: Rutherford Backscattering Spectroscopy (RBS) and Ion Channeling; surface spectroscopy techniques: X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES), diffraction techniques that are based on the periodicity of the crystal structure and the surface: Low Energy Electron Diffraction (LEED) and X-ray Diffraction (XRD).

The techniques have their own strengths, and mostly they are complementary. The diffraction techniques are used to determine the structural nature of the sample. The elemental composition could be determined by RBS which gives good quantitative results and does nondestructive depth profiling. AES provides a better sensitivity than RBS and gives also chemical information. Chemical information can be obtained also

using XPS and UPS. Ion Channeling gives information about the quality of the crystal and can help determine the location of the adatoms in relation to the lattice atoms.

Most of the analysis is performed in-situ right after the sample has been prepared: RBS/Ion Channeling, LEED, XPS/AES while more analysis is performed after the sample is taken out of the vacuum environment (XRD, SEM, thickness profilometry)

4.2 In-situ characterization techniques

4.2.1 Low Energy Electron Diffraction (LEED)

This technique is used to determine the surface structure of single crystal surfaces and the structure of ordered adsorbate layers. The principle is illustrated in Fig. 4. A beam of monoenergetic low energy electrons (50-400 eV) falls on a surface and are scattered elastically in all directions. The associated wavelength of the electrons is:

$$\lambda = \frac{h}{\sqrt{2 \cdot m_e \cdot E_k}} \quad (4.1)$$

h -Plank's constant, m_e - mass of the electron, E_k - kinetic energy of the electrons

The scattered electrons will exhibit an interference pattern with constructive interference in directions with:

$$\sin \alpha = \frac{n \cdot \lambda}{a} = \frac{n \cdot h}{a \cdot \sqrt{2 \cdot m_e \cdot E_k}} \quad n = 0, 1, 2, \dots \quad (4.2)$$

α – angle between the scattered electrons and surface normal, n – order of the interference, a – interatomic distances

The scattered electrons are collected on a fluorescent screen and they form a series of dots for a single crystal surface, this LEED pattern has the same form as the reciprocal lattice of the crystal. For films with high degree of disorder on the surface no patterns can be observed.

In the case of adsorbed gases that form an ordered structure, the unit cell of the overlayers can also be determined with LEED, but the exact position of the adsorbate atom with respect to the substrate remains undetermined because the pattern only reflects the periodicity of the layer.

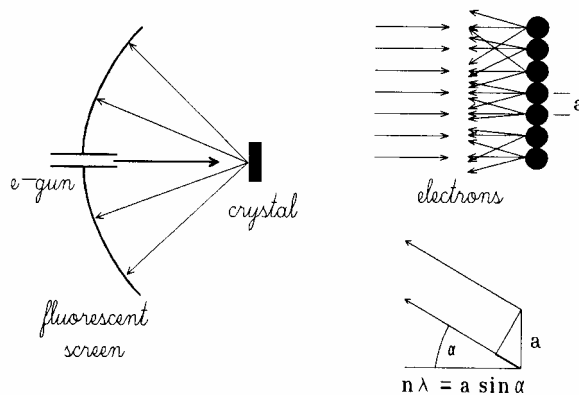


Fig 4.1: LEED Principle

LEED patterns can also give information about the third dimension because electrons can be scattered from the deeper layers. For each layer spacing there are combinations of electron energies and angles of diffraction for which a Bragg condition in the vertical direction is satisfied. In such directions one observes very intense spots. Plots of the spot intensity as a function of the electron energy are called I-V plots. The I-V plots contain in combination with the LEED pattern itself, three dimensional structure information, but the interpretation of data is rather difficult. LEED intensities also depend on the lattice vibrations at the surface of the crystal. A high Debye temperature of the surface results in intense spots [91].

In summary, this method is most often used to verify the structure and quality of single crystal surfaces, to study the structure of ordered adsorbate and to study surface reconstruction.



Figure 4.2: OCI Vacuum Micro-engineering BDL800IR LEED

We have used a LEED setup manufactured by OCI Vacuum Micro-engineering, model BDL800IR, with four grids (Figure 4.2). The LEED assembly has variable length, this making possible to retract it towards the wall of the chamber when not in use. This type was chosen so that it could be kept clear of the six-axis goniometer when that is being used for ion channeling as well as LEED.

The LEED apparatus shown in Figure 4.2 is introduced in a cylinder of μ -material with a high permeability in order to screen from the parasitic magnetic fields of the earth and of other electronic devices. The LEED geometry is of the back-view type, meaning that the phosphorus screen is transparent and observed from the back of the device, in Figure 4.2 the viewing is from the left.

The entire LEED setup is shown in Figure 4.3 and consists of the LEED apparatus, power supply (for the electron gun and screen voltages), video camera, and computer with video capture board and control software. The timing and integration parameters for the recording of the LEED patterns using the video camera are controlled via the software program: the image captured can be the result of integration of up to 2 seconds corresponding to 120 frames. The computer, also connected to the power supply, it controls the accelerating voltage of the incident electron beam.

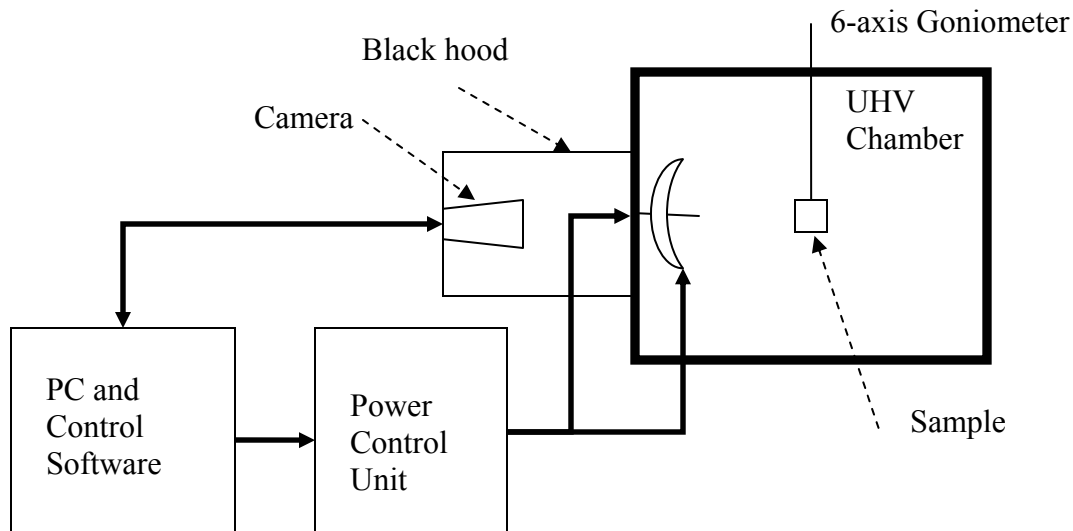


Figure 4.3: LEED Setup

The control of the other parameters of the electron beam (Wehnelt and focus voltages) are directly adjustable from the power supply. The voltages of the LEED grids (screen and suppression) are also controllable using directly the power supply.

4.2.2 Ion-Beam Techniques (RBS/Ion Channeling)

Rutherford back-scattering (RBS) is a surface analysis technique widely used in many branches of surface science and studies of thin films. A beam of energetic ions is directed at the solid under investigation. The ions collide elastically with the atoms within the sample and are scattered back into a suitable detector connected to a high speed data acquisition system that counts the number of scattered particles and measures their energy. The information contained in the scattered particles can be interpreted to give data on the composition of the sample and the sample thickness.

The interaction of the energetic ions with the atoms of the crystal depends on how close the ion approaches the nucleus, in other words, on the impact parameter. For small impact parameters (comparable to the nuclear size) the interaction is with nucleus, with large energy transfers ($\sim 100\text{keV}$) and large angle of scattering. These collisions have relatively smaller cross sections compared to the second type of interactions where the impact parameter is of the order of 0.01 to 0.1 nm. These interactions, which occur with

the electrons, have a cross section of $\sim 10^{-15} \text{ cm}^2$ and are responsible for the gradual energy loss of the ions as it penetrates into the solid. For this case the energy transfer is less than 100 eV and is transferred to the electrons and the scattering angle is very small. Thus the energy of the backscattered particle is determined by the masses of the atoms involved in the process and the depth at which the scattering event took place. The energy spectrum of particles (M_1, Z_1) backscattered from a solid composed of a substrate (M_2, Z_2) and a surface film (M_3, Z_3) with a thickness t is shown in Figure 4.4 for the case where the film atoms have a higher mass than the host atoms [92].

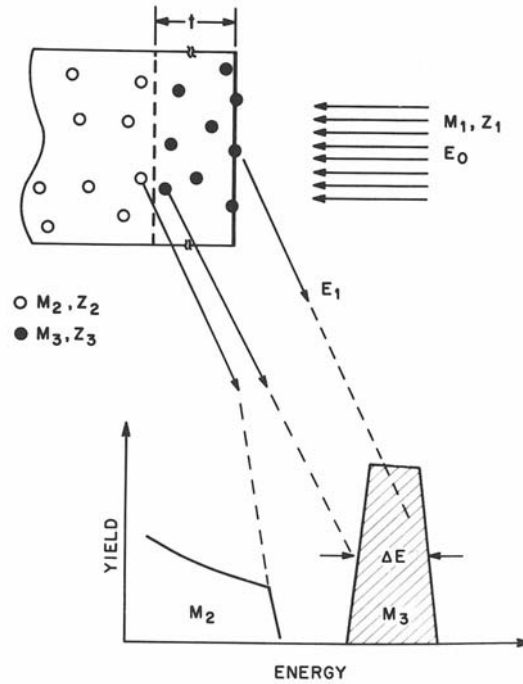


Figure 4.4: Energy spectrum of particles scattered from a substrate covered with a film of a higher atomic mass

The powerful aspect of this analysis technique is that the surface density of the film atoms N_s can be accurately be determined from the equation:

$$Y = N_s \cdot \frac{d\sigma}{d\Omega} \cdot \Delta\Omega \cdot Q \quad (4.3)$$

where Y is the yield of the backscattered particles, $d\sigma/d\Omega$ is the known differential cross section for scattering, $\Delta\Omega$ is the solid angle of the detector, and Q is the number of incident ions.

For pure Rutherford scattering (Coulomb) the scattering cross section is given by:

$$\sigma(E, \theta) = \left(\frac{Z_1 Z_3 e^2}{4E} \right)^2 \times \frac{4 \left[(M_3^2 - M_1^2 \sin^2 \theta)^{1/2} + M_3 \cos \theta \right]^2}{M_3 \sin^4 \theta (M_3^2 - M_1^2 \sin^2 \theta)^{1/2}} \quad (4.4)$$

The film element can be identified from the high energy side of the peak and the equation of the kinematic factor:

$$K = \frac{E_1}{E_0} = \left[\frac{(M_3^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_1 + M_3} \right] \quad (4.5)$$

From the previous analysis we can see that both quantitative and qualitative analysis are possible using the RBS method.

Most solids exist in crystalline form. Although the RBS gives information about the atomic composition of the solids, in ion channeling mode ion beam analysis reveals the crystal structure of the solids. Unlike other tools of crystallography, such as x-ray or neutron diffraction, which are reciprocal space methods, ion channeling is a direct space method. In channeling, due to the preferential orientation of the lattice with respect to the incident ions, the number of backscattered particles can be drastically reduced when the lattice is oriented such that the atoms are lined up with the beam, and a shadowing effect limits the number of interactions. In Figure 4.5 [93] we see such a lattice in three distinctive orientations with the viewing direction: while the position a) is random and expose the maximum number of atoms the positions b) and c) are such that there are less atoms exposed.

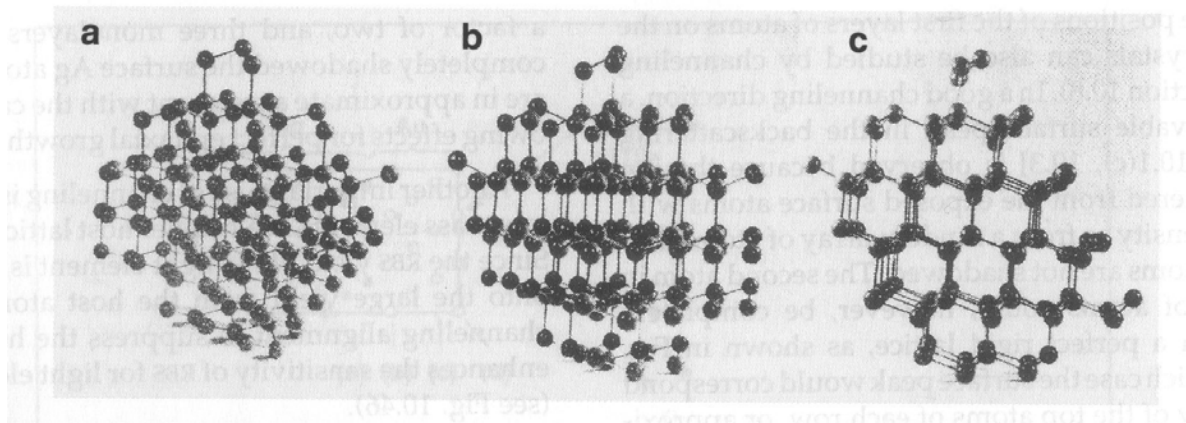


Figure 4.5: Model of lattice atoms viewed along (a) random (b) planar or (c) axial direction [115]

The energy spectrum of the particles scattered from an aligned crystal is dramatically different from that of a non-crystalline solid Figure 4.6 [92].

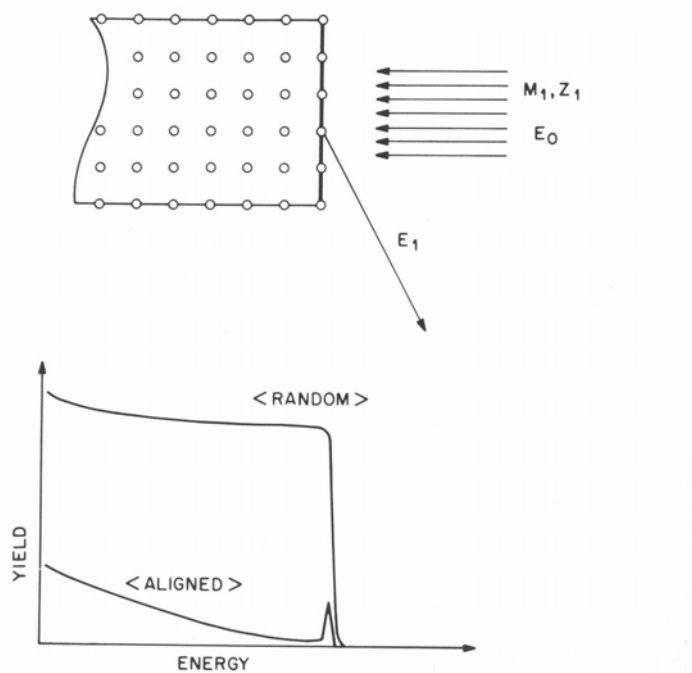


Figure 4.6: Schematic of energy spectrum for an aligned and a random beam direction

Due to the alignment of the rows of atoms the ion beam can penetrate deeper into the crystal and fewer ions are back scattered. An incident ion entering a crystal lattice in a low index direction passes down the open channels of the crystal and does not come sufficiently close to lattice atoms to elastically collide and be back-scattered. The yield of backscattered ions decreases by almost two orders of magnitude for good quality crystals and this decrease in yield is the basis of the channeling applications. The decrease of the yield is quantitatively described by the quantity $\chi_{\min}$ - the “minimum dechanneling level” also called “minimum yield” [92] and is defined as:

$$\chi_{\min} = \frac{\text{Minimum Yield of Aligned Spectra below the Surface Peak}}{\text{Yield of Random Spectra at Surface}} \times 100\% \quad (4.6)$$

In general the minimum value of yield of the aligned spectra is obtained just below the surface. For good quality crystals if the beam is aligned along a low index axis the value of the minimum yield is of the order of a 1 to 2%. For damaged or low quality crystals the value of the minimum yield is higher and it is a direct indication of the amount of defects in the crystal.

The small peak that is observed in Figure 4.6 in the aligned spectrum is due to the surface atoms that are shadowing the underlying atoms. The RBS yield for single crystals therefore depends on the angle between the analyzing beam and the crystal lattice of the target. There is no analytical formula for the minimum dechanneling level for a perfect crystal but an approximation has been derived [94]:

$$\chi_{\min}(\rho) = 3 N d \pi^2 \rho \sqrt{1 + \left(\frac{\psi_c^B d}{1.55 \rho}\right)^2} \quad (4.7)$$

where N is the atomic density, d is the atomic spacing along the row, ρ is the rms vibrational amplitude of the atoms at the surface, and ψ_c^B is the critical half-angle derived from computer simulations by Barrett [94]:

$$\psi_c^B = 0.83 F_{RS} (0.85 \rho / a) \psi_1 \quad (4.8)$$

where F_{RS} is a sum of three modified Bessel functions and $\psi_1 = \sqrt{\frac{2 Z_1 Z_2 e^2}{E d}}$.

The intensity of the surface peak can be measured from the experimental spectrum and from this we can extract the amount of surface atoms that are contributing to the scattering process. This can be compared to the expected number of atoms on the surface and in this way we can determine if any lateral reconstruction of the surface has occurred.

In order to establish the depth scale at the surface and calculate the number of atoms that produce the surface peak we need to use a material constant called the stopping cross section. In Appendix 9.1 we show a sample calculation for the energy loss per unit length for the incident ions and we derive the corresponding stopping cross section factors (ε_0) for sapphire and GaN surfaces (using accepted values for the stopping power). Having determined the stopping cross section factor (ε_0) we can obtain the number of atoms in the surface region from the formula:

$$\frac{A}{H} = \frac{\varepsilon_0 (N t)}{\varepsilon \cos(\theta_{out})} \quad (4.9)$$

where A is the area of the surface peak in the channeling spectrum, H is the height of the random spectrum at the surface edge, ε is the energy per channel in the spectrum, ε_0 is the stopping cross section factor evaluated at the surface, θ_{out} is the exit angle of the backscattered ion, and (Nt) is the surface density of the atoms.

The previous formula has no dependence of the solid state of the detector or the total charge used for the analysis, which makes it easier to use and less prone to errors arising from the correct estimation of the mentioned quantities.

In general, due to the thermal vibration of the atoms in the crystal, more than one atom will interact with an incident ion for each row of atoms perpendicular to the surface. Feldman [92] has shown that the probability of close encounter of the incident beam with a second atom in a row is a measure of the amount of shadowing and depends sensitively on the ratio ρ/R_c , where ρ is the root-mean-square of the thermal vibration of the crystal atoms parallel to the surface and R_c is a quantity called ‘‘Coulomb shadow cone radius’’

representing the radius of a cone in which the atoms are shielded from small angle collisions by the atoms in front of them. The shadow cone radius is defined as:

$$R_c = 2\sqrt{\frac{Z_1 Z_2 e^2 d}{E}} \quad (4.10)$$

where Z_1 , and Z_2 refer to the atomic number of the incident ions and target atoms, d is the distance between the atoms in the row along the direction of the ion beam, E is the energy of the incident ions. Usual values for R_c are of the order of a few tenths of Å. For practical applications R_C must be corrected by using a screened Coulomb potential and the most accurate is the Thomas-Fermi model. One used model is the Molier numerical approximation that can derive an alternate Molier shadow cone radius which is more accurate. In most cases the R_M/R_C ratio is greater than 0.8. This potential is defined on the base of a new parameter called Thomas-Fermi screening distance:

$$a = 0.8853 a_0 \left(Z_1^{1/2} + Z_2^{1/2} \right)^{-\frac{2}{3}} \quad (4.11)$$

where a_0 is the Bohr radius, 0.528Å.

In the Molier model the close encounter probability of the ions with the atoms in the row is calculated from computer simulations and is shown in Figure 4.7 as the solid curve and compared to experimental values. It is found that this curve is “universal” in the way that various materials and orientations produce points that lie along this curve. From the curve we see that the incident ion has a probability to interact with only one atom per row only for small value of the thermal vibration relative to the shadow cone radius ($\rho/R_M < 0.3$) and as the ratio increases the incident ion will interact with more and more atoms from each row and the corresponding size of the surface peak will be higher.

Channeling is sensitive to structural defects in crystal. Each type of defect has a particular influence on the trajectory of the passing particles and can be associated with a dechanneling factor σ_D . The probability of dechanneling per unit depth is given by the product of the defect dechanneling factor and defect density n_D [92]:

$$\frac{dP_D}{dz} = \sigma_D n_D(z) \quad (4.12)$$

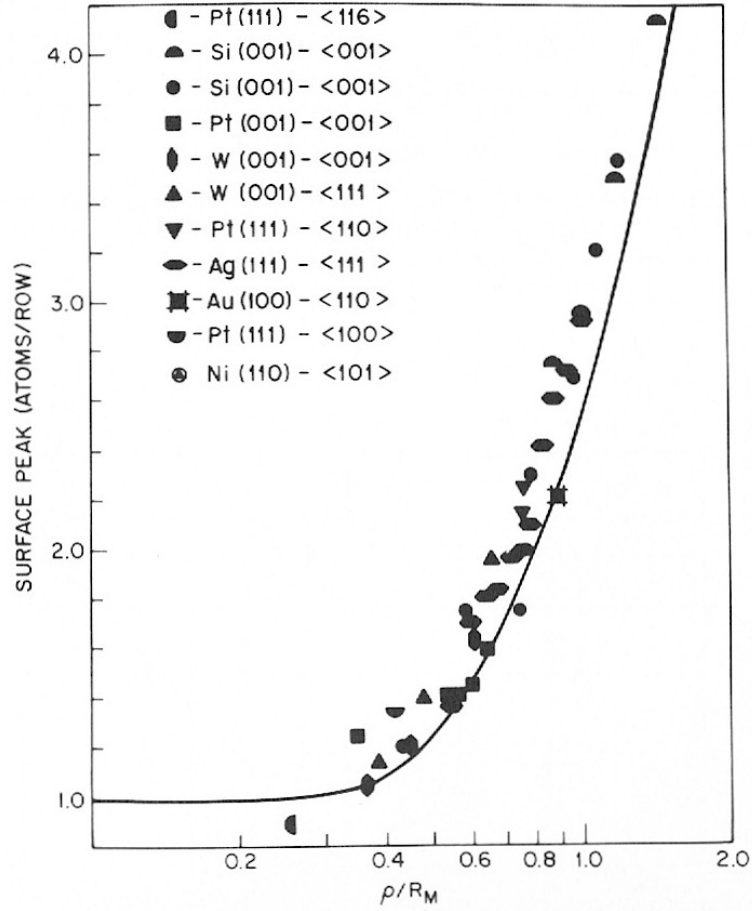


Figure 4.7: Comparison of experimental values with the “universal” curve of close-encounter probability [92]

Dechanneling factors for point, line, area or volumetric defects have different units but the product $\sigma_D n_D$ has always units of cm^{-1} . In GaN the predominating defects are the dislocations. The nature (screw or edge) and the orientation of the dislocations with respect to the ion beam determine the amount of dechanneling they produce. For screw dislocations the dechanneling factor can be written as [92]:

$$\sigma_D = K \frac{\sqrt{a |\mathbf{b}|}}{\psi_1} \quad (4.13)$$

where K is 0.47 for the edge dislocation and 0.4 for the screw dislocation (for axial channeling), a is the Thomas-Fermi screening distance, and $\mathbf{b}$ is the Burger vector of the

dislocation. For dislocations in GaN with a burger vector equal to one lattice spacing and 2.2 MeV the dechanneling factor is $44.4\text{\AA}$ for edge dislocations.

We have taken the channeling technique one step further and we have measured the channeling yield as a function of the crystal orientation in a range of angles around a crystalline direction. Figure 4.8 shows such a channeling map for sapphire. We can see six crystallographic planes crossing into a main crystal axis in the center of the map. From such a measurement we can determine unequivocally the symmetry of the crystal as well as the orientation of the crystal with respect to the direction of growth. This complex map is obtained by measuring the channeling yield just below the surface while we adjust the angle of the crystal with respect to the incident beam. This particular map is formed by taking 30 points in the pan direction times 30 points in the tilt direction for a total of 900 points.

While this map takes a lot of time to acquire the information obtained is reliable, and easier to interpret. The upper part of the graph in Figure 4.8 shows the $(\text{Yield})^{-1}$ which can facilitate identification of the plane directions.

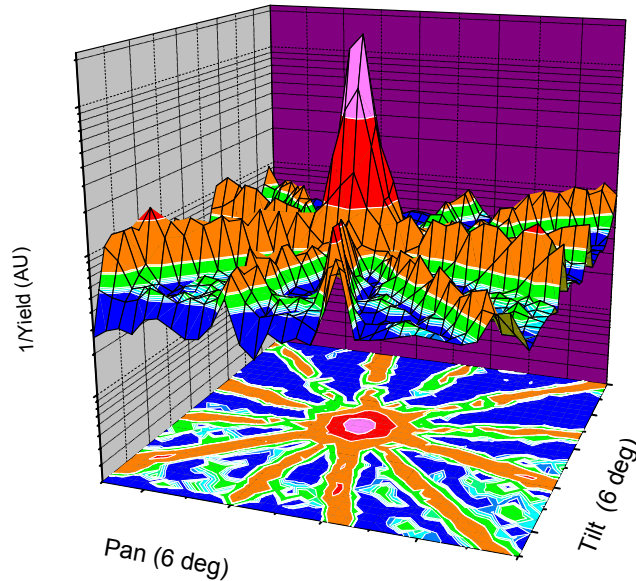


Figure 4.8: Channeling map for a hexagonal crystal

In addition to the application mentioned in the previous paragraph the combination of RBS and channeling has been used to investigate the degree of disorder within a single crystal and the lattice position of impurities within the lattice. Also measurements can be made of the relaxation in position of crystal surface atoms and determine if reconstruction or relaxation occur on crystal surfaces. The RBS/Channeling technique could be used to analyze the damage recovery following ion implantation during different annealing steps and to determine the lattice location of impurities implanted into GaN [95]. The Channeling technique can be used in conjunction with the LEED to make sure that the LEED pattern matches the entire surface. The surface peak from RBS should equal the number of atoms of the surface as seen by the LEED pattern.

A channeling experiment requires three basic components: a source of collimated ions, a detector, and an accurate crystal manipulator (goniometer).

A schematic of the equipment used in RBS/Ion Channeling analysis is shown in Figure 4.9. First we will outline the way in which the ion beam is obtained. A duoplasmatron ion source produces low energy ${}^4\text{He}^{-1}$ ions that are injected in the OU Tandem Accelerator. The negative ion beam is injected at the low energy end of the accelerator that is at ground potential and is accelerated towards the high potential terminal situated in the center of the tank. When the ${}^4\text{He}^{-1}$ beam reaches the terminal the ions are stripped of the negative charge using either thin carbon foils or nitrogen gas and is transformed into ${}^4\text{He}^{+1}$ or ${}^4\text{He}^{+2}$. The efficiency of the charge exchange taking place at the terminal ranges from approximately 0.5 to close to 1 and depends on the cross section of electron transfer for ${}^4\text{He}^{-1}$, ${}^4\text{He}$, and ${}^4\text{He}^{+1}$. These cross sections are energy dependent and in practice the stripping efficiency depends on the quality and thickness of the carbon foils, or the pressure of the stripping gas. The positive beam is now accelerated in the electric field between the positive terminal and the ground potential at the high energy end of the accelerator tank. Depending of the charge of the beam the ions are accelerated once or twice the potential energy of the terminal. Typical Energies typically used in this experiment are from 1 to 3 MeV of ${}^4\text{He}^{+1}$ or ${}^4\text{He}^{+2}$. This corresponds to a terminal energy of approximately 0.5 MeV for 1MeV ${}^4\text{He}^{+1}$, 0.73 MeV for 2.2MeV ${}^4\text{He}^{+2}$ beam and 1 MeV for 3.05 MeV ${}^4\text{He}^{+2}$ beam. The high-energy beam extracted from the accelerator is passed through a magnetic analyzer to filter out ions with slightly different energy and

with un-wanted charge states. The beam is then collimated using first a circular aperture with a diameter of 3 mm; followed by a second aperture 2 meters away with a height of 2 mm and a width of 1 mm (Figure 4.9). The divergence of the ion beam is no larger than 1 mrad. Ions that are back-scattered into a particular solid angle are detected by a silicon solid-state detector placed at an angle of 12 degrees with respect to the incident ion beam in an horizontal plane (IBM geometry). This position corresponds to a backscattering angle of 168 degrees. The detector has a resolution of $\sim 15\text{keV}$. The target is attached to the 6-axis goniometer (Panimore/England) with 3 concentric axis of rotation (pan, tilt, azimuth) and 3 axis for translation (X,Y,Z). The rotation motions are accurate and reproducible to 0.1° in 0.0025° steps.

The choice of energy used for the ion beam is based on few considerations: Coulomb scattering breaks down at low energies (below 0.1MeV) but in our system the minimum achievable energy is 1MeV ; at low accelerating energies the Rutherford cross section is higher, the penetration depth is lower meaning that we have a stronger signal and a low mass resolution, with a beam current of $1\text{-}7\text{ nA}$; at higher accelerating energies the analysis depth is higher, the mass resolution is increased with the cost of a lower cross section and implicitly a lower signal (and the need of a higher beam intensity and/or analysis time), with a beam current of $10\text{-}40\text{ nA}$;

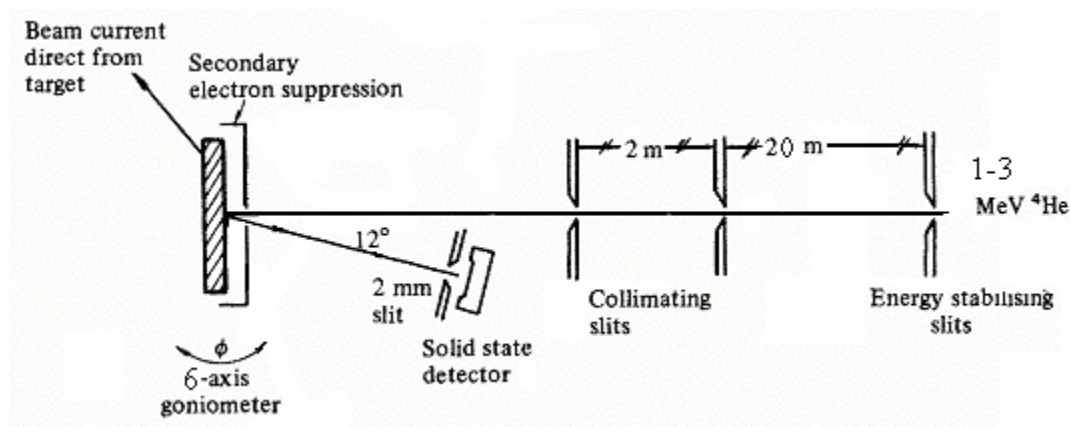


Figure 4.9: RBS Setup (not to scale)

Certain beam energies can be used to provide increased non-Rutherford cross section for certain elements for the trace detection, e.g. for oxygen a resonant energy is 3.05 MeV. Block diagram of the electronics of the RBS/Channeling system is shown in Figure 4.10. The backscattered alpha particles are detected in a solid state barrier detector with an active area of about 25 mm² and active depth of 100 μm. The energy and timing information of the particles striking the detector is passed to the Pile-Up Rejection System. After the rejection of the pile-up pulses the true pulses are feeded into the fast Analog to Digital Converter (ADC) hardware.

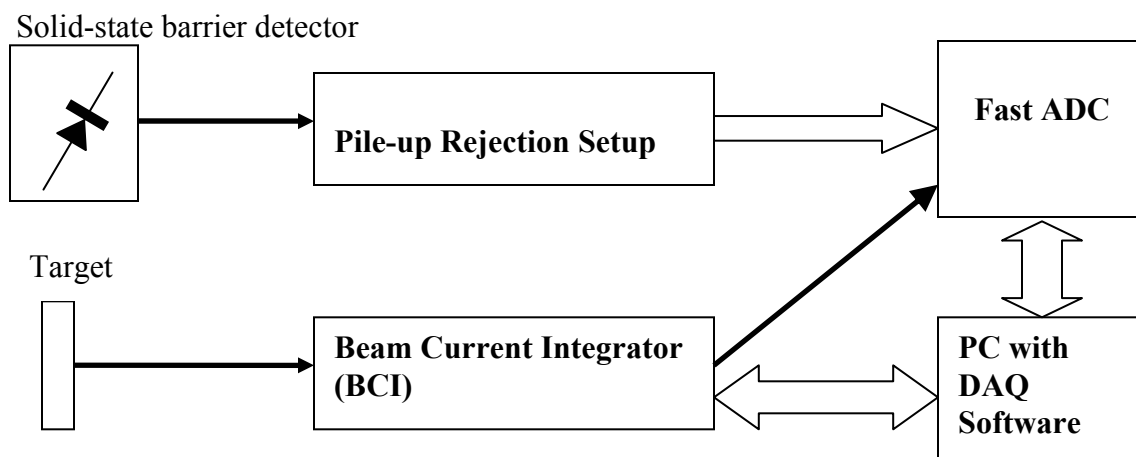


Figure 4.10: Electronic setup for ion beam analysis

The target is connected to a “Beam Current Integrator” unit. This module measures the ion current incident on the target and integrates the total charge. The accuracy of this device is crucial for Ion Channeling measurements where the charge used for the two spectra (random and aligned) has to be identical. The system allows for the BCI unit to control the acquisition of the pulses in the ADC such that data is taken only when the intensity of the beam current is within a preset range. A personal computer running the Data Acquisition Software “DAQ” developed at Ohio University (Linux or Windows operating system) is controlling the ADC and BCI units and its storing and displaying the data as well as converting it into RUMP format for further analysis [96]. The ADC and BCI units are two units that have been designed and built at Ohio University and tested

and used extensively during the last 30 years. The DAQ Software has been designed and written at Ohio University and runs under Windows or Linux Operating Systems.

The beam current measured during the experiments performed ranged from 1 nA to 30 nA. While higher beam current is desired in order to acquire faster the RBS spectra the high intensity beam can give rise to complications such as crystalline damage of the sample and as well as measurement complications due to pile-up and dead time.

Three complications arise in these measurements: one is the secondary electron emission from the sample, the second one is the dead time of the detector and ADC Hardware, and the third one is the “pile-up” of pulses. The secondary electron emission from the sample has the effect of creating a electron current leaking from the target towards the ground. This current would be in addition to the positive ion current due to the ion beam impinging on the target. Since the target current has to be accurately measured the secondary electron current has to be either minimized or accurately measured and taken into account. The magnitude of secondary electron emission can be as high as 300% and depends on the nature of the target and ion beam. In order to minimize the electron emission we have employed a suppression screen placed in front of the target. This screen is biased negatively -300V with respect to the target and has the role of repelling back the low energy secondary electrons that result from the ion bombardment.

The dead-time of the detector and ADC Hardware is dynamically determined by the Data Acquisition Hardware and Software and it has been found to be less than 3%. The magnitude of the dead time is also ion beam intensity dependent.

The pile-up of pulses has the effect of increasing the background in the high energy region of the RBS spectra by creating a “ghost” of the spectra at the high energy side of the spectrum. This effect is especially unwanted when a low intensity signal is measured, as for example, in measurements of low concentration of high-Z material doping or for very thin films of high Z materials on top of lower Z substrate (for example the case of a few monolayers of GaN on sapphire). The pile-up occurs by the superposition of two pulses that are counted as one pulse with a higher energy by the electronic measurement system. This is due to the two pulses time separation being shorter than the length of the

pulses. The “pile-up” is usually noticed when the counting rate is very high in other words when the ion beam is very intense and from high mass elements. In practice we have observed pile-up when the ion beam is more than about 8 nA for a 4He^{+2} ion beam incident on gallium. The solution for pile-up is a more complicated measurement system that is able to determine when a pile-up occurred and rejects it from the counting system. The electronic setup for the Pile-up Rejection System shown in Figure 4.10 as a box is detailed in Figure 4.11.

The backscattered ions are detected by the solid state detector and the output of the detector is run into a preamplifier. To reduce the possibility of two alpha particles that arrive almost simultaneously and causing a false signal, or pile-up, to occur, both a timing and an energy signal are taken from the preamplifier attached to the detector. The energy signal is input to a spectroscopy amplifier with a $1\ \mu\text{s}$ integration time, and then delayed before proceeding to the analog to digital converter (ADC) and being stored as data. The timing signal from the preamplifier is amplified by a timing amplifier before passing into the pile up detector. If a second alpha particle is detected within $7\ \mu\text{s}$ then an anticoincidence signal to send to the ADC to stop it accepting the first pulse, which is presumed to have been adversely affected by the second.

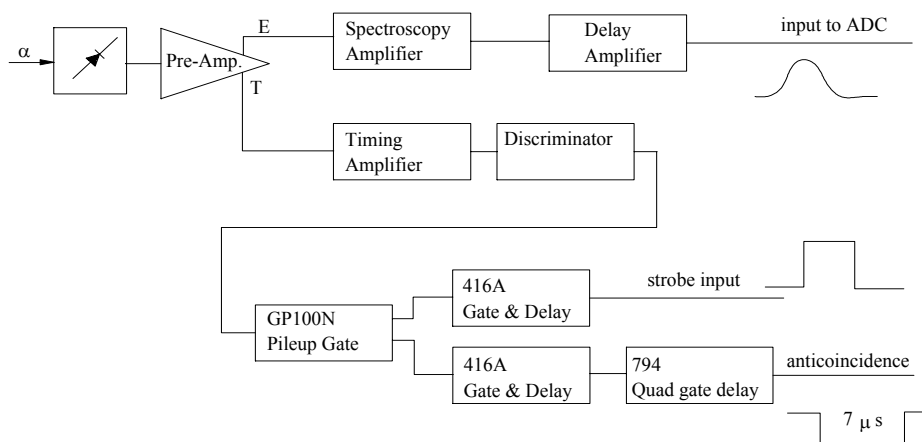


Figure 4.11 Internal setup of the Pile-up Rejection Setup

A pulser (not shown in the diagram) is routed into the preamplifier and has the role to provide a reference signal for monitoring if any change in calibration of the setup has occurred during the data acquisition.

4.2.3 Photoemission and Auger Spectroscopy (XPS/AES)

Photoemission spectroscopy is based on the photoelectric effect. A sample that is irradiated with light of sufficiently small wavelength emits electrons. The number of the photoelectrons depends on the intensity of the light/x-ray source and their energy on the wavelength of the light.

A diagram of the XPS process is shown in Figure 4.12 and consists of the emission of a core electron when an x-ray photon is absorbed by the atom. The energy of the electron is such that the electron becomes free and can even be emitted from the solid.

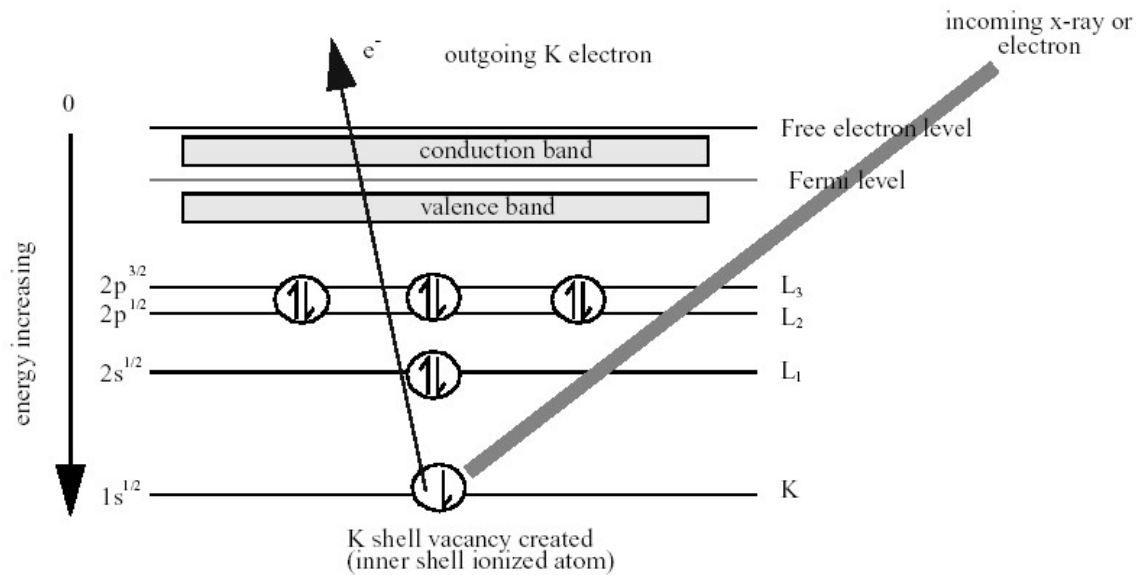


Figure 4.12: Schematic of the XPS process [97]

The kinetic energy of an ejected electron is given by:

$$KE = h \cdot \nu - BE \quad (4.14)$$

where BE is the binding energy of the electron to the atom and ν is the frequency of the incident photon.

The binding energy is specific to the atom concerned, thereby identifying the atom. All elements could be specified from their core-level electrons except H and He for which the binding energy is so low that their peaks are mixed in with the valence electrons from the other elements present in the sample. Quantitative analysis requires the measurement of the peak intensities, combined with knowledge of the interaction cross section σ , plus any experimental artifacts that affect intensities. In general relative differences in composition of closely related samples can be determined with much greater accuracy than absolute compositions.

Information about the chemical state of the atoms in the sample can be inferred from the small shifts in the binding energies of the atoms. The interpretation of the spectra can be quite difficult due to a series of factors: broadening of the lines, spin-orbit splitting, unpaired electron spins, shake-up satellites in the spectrum, Auger effects, etc. but is aided by various resources such as handbooks of spectra for all the elements.

XPS is a very sensitive surface analysis technique due to the small mean free path of the electrons in solids (1-5 nm): only the electrons escaping from the atoms near the surface will reach the detector. It has developed into a very useful surface sensitive technique, being routinely applied for elemental and chemical state analysis. Its main limitations are the lack of high spatial resolution and relatively poor absolute sensitivity (not a trace element analysis technique, $<0.1\%$) and the impossibility to detect hydrogen.

Figure 4.13-a) shows the electron paths through a typical electron analyzer of a XPS system. A 3 channeltron multi-detector is used to record the spectrum. The spectra are collected from an area of the order of 1 mm^2 that can be reduced by introducing an aperture between the analyzer and the sample. The analyzer is operated with a fixed entrance slot in place and at a fixed pass energy (from 5eV to 160eV), giving the choice of a range of sensitivity and energy resolution for a particular analysis area. Voltages are applied to the two hemispheres shown to disperse and focus the photoelectrons. Figure 4.13-b shows the entire XPS system comprised of the electron spectrometer, pulse counting electronics, lens electronics and control software.

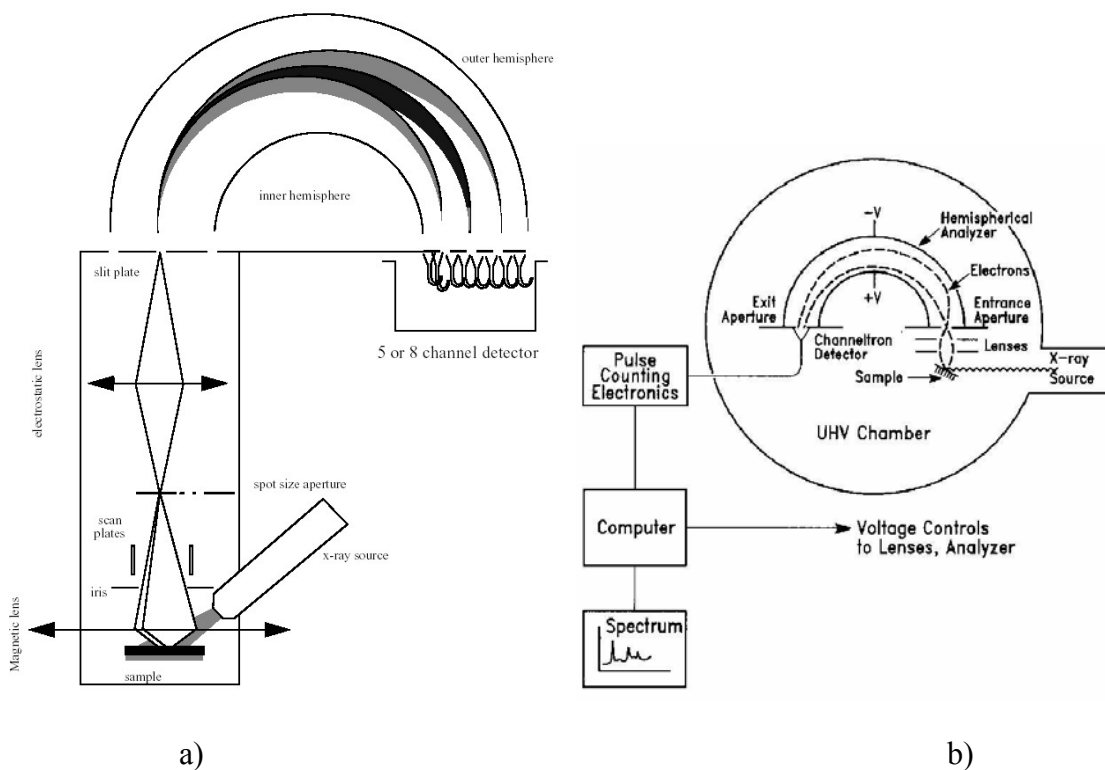


Figure 4.13: a) Axis HIs Electron Spectrometer [98] b) Schematics of a XPS/UPS/AES System [97]

In addition to the detecting the photoelectrons produced by the process shown in Figure 4.12, the electron spectrometer will detect electrons emitted from the solids by other processes. One of the important electron emission phenomena is the Auger process. Figure 4.14 shows a schematic of this emission process. The Auger process is more complex and the kinetic energy of the emitted electron is determined by the three levels involved in the process:

$$KE = E_1 - (E_2 + E_3) \quad (4.15)$$

where E_1 is the lowest energy level and E_2 and E_3 are the upper energy levels.

We notice the interesting fact that the energy of the emitted electron does not depend on the x-ray photon energy. This makes the Auger electrons easy to identify since they have the same kinetic energy no matter what excitation source is used in the experiment.

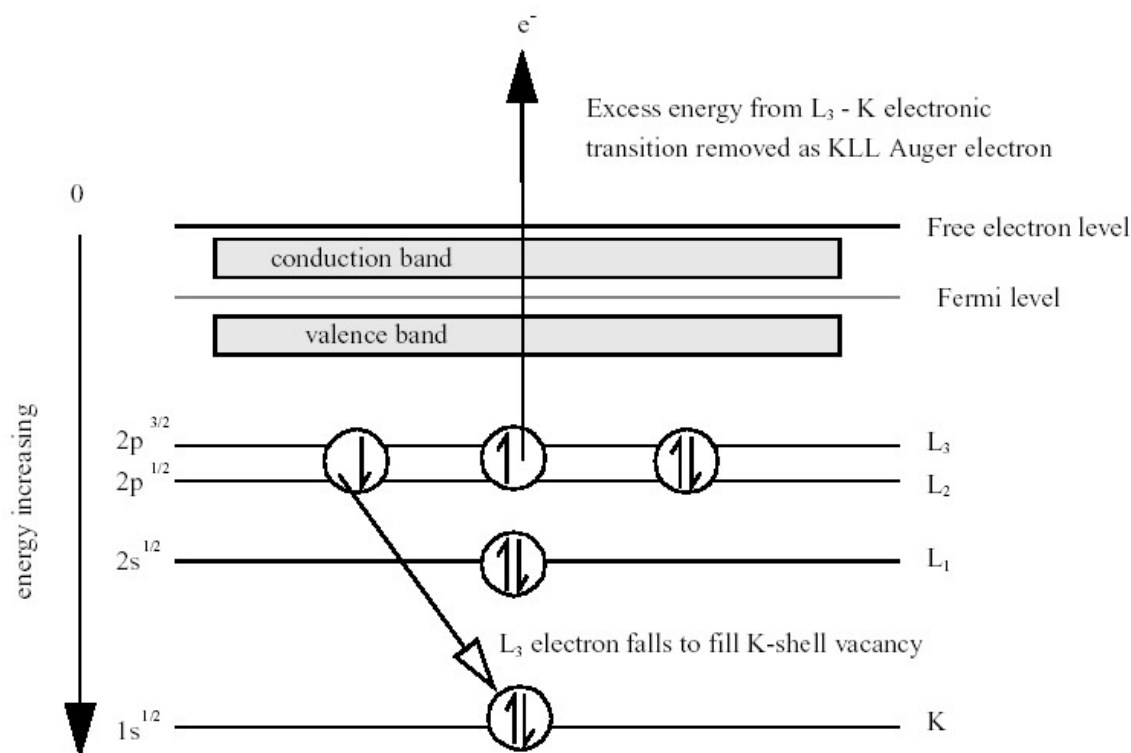


Figure 4.14: Schematic of the Auger process [97]

As a stand-alone technique Auger electron spectroscopy (AES) uses high energy electron beams (5keV) as an excitation source. Advantages of Auger spectroscopy are: it has surface specificity—a sampling depth that varies between 5 and 100 Å depending upon the energy of the Auger electrons measured and the signal-to-noise ratio in the spectrum; it has good lateral spatial resolution, which can be as low as 300 Å, depending on the electron gun used and the sample material. Used in conjunction with an ion beam that sputters the surface it has very good depth resolution, as low as 20 Å depending on the characteristics of the ion beam, and it can produce a three-dimensional map of the composition and chemistry of a volume of a sample that is tens of μm thick and hundreds of μm on a side using ion beam sputtering.

AES cannot detect H or He, and it does not do nondestructive depth profiling. The electron beam can be destructive to some samples. It also requires the sample to be put into and to be compatible with ultra high vacuum. Some nonconducting samples charge under electron beam probing and cannot be easily analyzed. The sputtering process can

alter the surface composition and thereby give misleading results, it also adds to the destructive nature of the technique.

While we have not used extensively Auger Spectroscopy in this study the Auger peaks can be observed in the XPS spectra and are used to help identify the XPS peaks.

The Kratos XPS system is equipped with a dual anode X-ray gun that produces Mg K α X-ray with line energy 1253.6eV and approximate FWHM of 0.7eV and Al K α 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 K α X-ray with approximate FWHM of 0.2-0.3eV. At pass energy of 10eV and using the monochromatic X-ray source, the spectrometer has a resolution of 0.5eV. The accuracy with which peak energy may be measured is better than 0.1eV. We have used spectra from sputter-cleaned samples of Au, Ag and Cu to calibrate the energy scale of the spectrometer.

The XPS/AES spectra were taken and processed on an XSAM 800 XPS/UPS/AES/SAM unit with the VISION2 control and information handling system (software) by Kratos Analytical Ltd.

4.3 Ex-situ characterization techniques

4.3.1 X-Ray Diffraction (XRD)

In general the XRD technique is an good nondestructive method for identifying phases and characterizing the structural properties of crystals. From the measurement of the peak position in specular scans, plane spacing could be determined and possibly stress in the films could be inferred. The average size of the micro-crystallites could be inferred from the width of the diffraction peaks. The rocking curves could be used to estimate the dislocation density in the buffer layer and the overgrown film.

The method cannot distinguish between single crystal and polycrystalline films and the diffraction pattern is obtained over a large volume of crystal. Also, this technique is not surface sensitive and it needs a film of a few hundred nanometers to be usable. We have complemented the results obtained by ion channeling with the ones obtained from the XRD 2-theta and rocking curves.

For this analysis we have used a powder X-ray diffractometer (Rigaku Geigerflex DMAX-B) with Cu K α line (1.542Å) as X-ray source. The original device has been improved by adding a 3-axis rotatable sample holder permitting to perform rocking scans for the measurements of FWHMs.

4.3.2 Scanning Electron Microscopy (SEM)

The morphology of the surface of the films has been analyzed by Scanning Electron Microscopy (SEM) using a JOEL JSM-5300 Scanning Microscope with electron energy of 30keV and magnification in the range 10 to 15,000 times.

Chapter V

GaN thin film growth on sapphire by MOCVD

This section describes the individual steps needed for the growth of GaN thin films starting from the ex-situ and in-situ cleaning and preparation of the substrates to nitridation and film growth as well as the choice of parameters and the optimization process for obtaining good single crystal GaN films.

5.1 System baking and contamination

The cleanliness of a system is absolute necessity when one needs to grow good quality thin films and with low impurity concentration. It is important to determine how clean a surface is, the possible sources of contamination and how to reduce or completely remove the contamination sources.

The deposition chamber and the gas lines have been baked (after each venting) to 120-150°C before the film growth in order to remove the water vapors and other possible contaminants. By heating the system at temperatures higher than 120°C the water adsorbed in the walls of the system is released and can be pumped out. After such a heat

treatment the vapor pressure of water in the system can be decreased one order of magnitude or more, depending on the heating temperature and length of time.

The adventitious carbon is always present on the surface of the substrates that have been just introduced in vacuum. The concentration does decrease a few percent after flashing the substrate in vacuum and in H_2 . We did not try to remove it by ion sputtering since this would destroy the surface stoichiometry and chemistry.

One contaminant that we have found to be present in the system is fluorine (F). We have found in the XPS analysis that fluorine was present on the surface of the sample in a percentage of 1-2%. We have traced the fluorine to the oil used in the fore-vacuum pumps used to pump out the gases during, and after the various steps in the film growth. Figure 5.1 shows the XPS spectra obtained using an Al radiation of a substrate that has been nitridated and has been contaminated by fluorine of 2%. All the present peaks in spectra are identified.

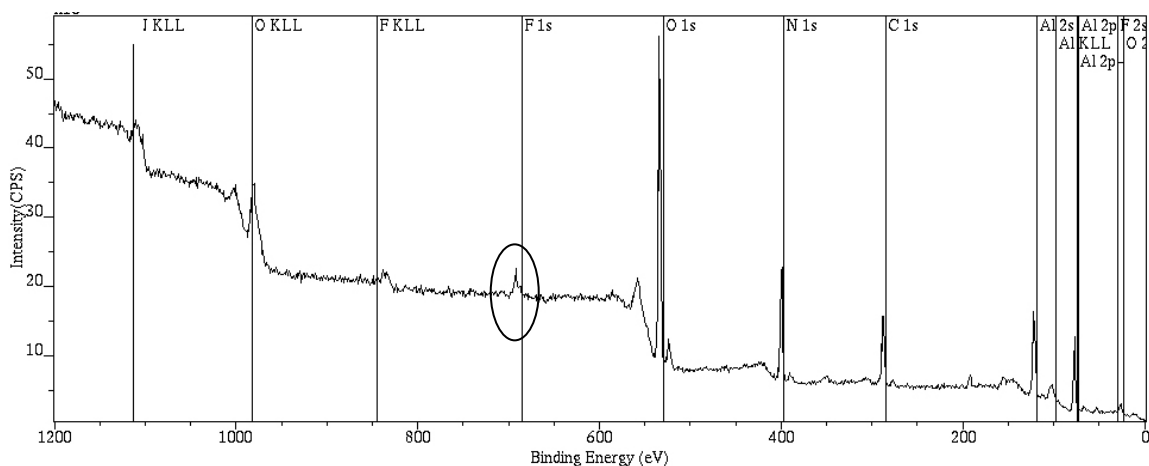


Figure 5.1: XPS spectra taken with Al anode of a nitridated sapphire with Fluorine contamination (surface composition: Al:O:N:C:F = 36:21:22:19:2)

In order to decrease the chance of fluorine compounds back-streaming into the deposition system we have implemented a continuous high pressure (50 Torr) flow of gases throughout the system including the cooling down phase. By using this method we have been able to completely eliminate the fluorine peak from the film. Figure 5.2 shows a GaN film with no fluorine contamination.

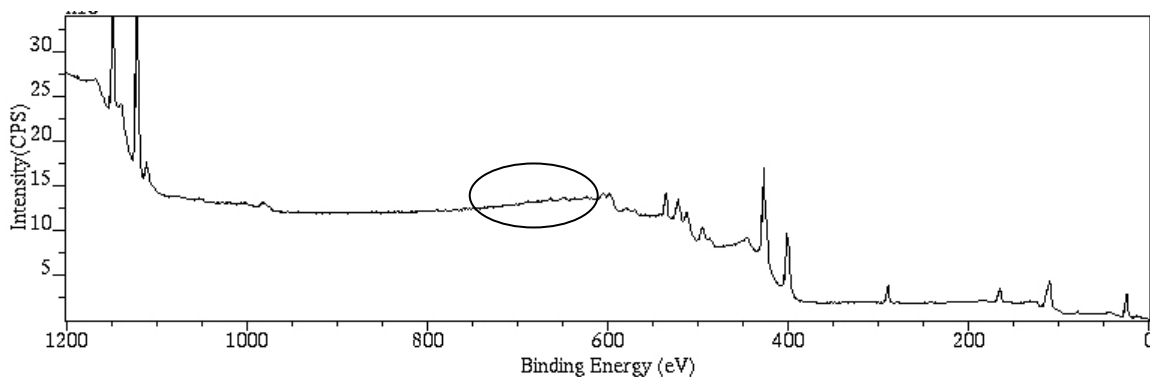


Figure 5.2: Survey XPS spectra taken with Al anode for the GaN film deposited at 750°C

5.2 Ex-situ and in-situ preparation and analysis of the sapphire substrates

Special attention has been dedicated in the literature to the sapphire surface. It has been found that the surface preparation plays an important role in the quality, morphology, and growth mode and defect density of GaN. The crystalline quality of the sapphire substrate used has been investigated by Ion Channeling and XRD and it has been found to be a good single crystal material. The RBS spectra random and aligned are depicted in Figure 5.3.

From the ratio of the yield in the aligned case to the yield in the random case we have determined the minimum yield to be of the order of $1.5\% \pm 0.12\%$ which is a typical value for good single crystals. The size of the surface peak is a good measure of the surface disorder.

In order to correctly estimate the area of the surface peak we have performed a background subtraction of 2nd order as shown in Figure 5.4. In this case the background accounted for 38% of the signal. As shown in Appendix 9.1 for sapphire we have obtained a stopping cross section factor for scattering on aluminum of $3.4 \times 10^{-13} \text{ eV cm}^2$. That gives rise to a measured energy of the backscattered particles of 792 eV/Å for scattering on aluminum at the surface of the sapphire crystal. We are primarily interested in the scattering on aluminum since this is the surface peak that we are able to observe in this measurement.

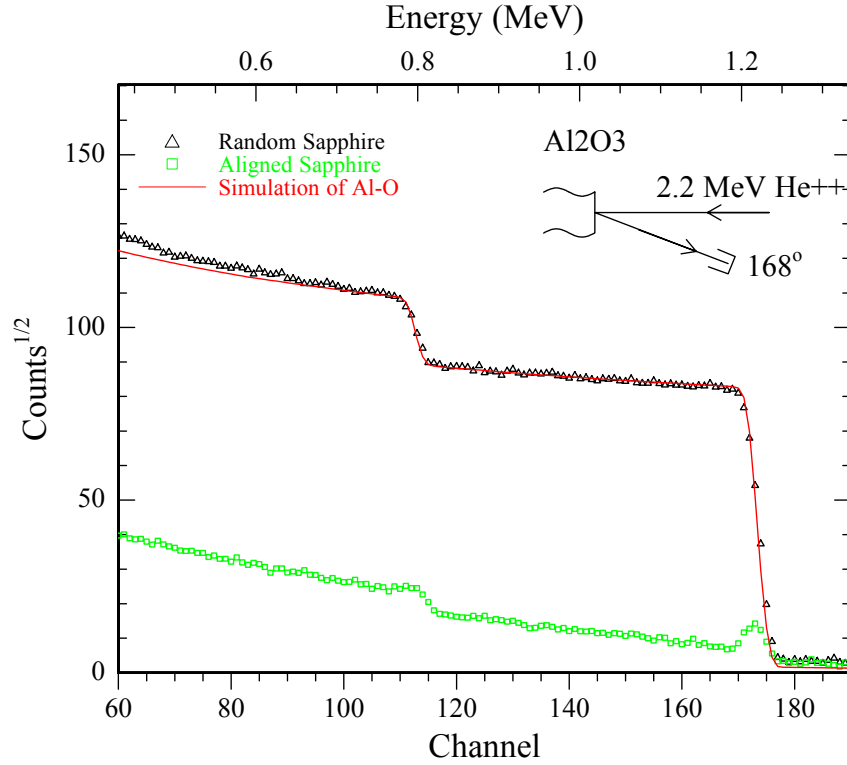


Figure 5.3: Random and Aligned as-received sapphire spectrum

The surface peak is due to a surface density of 8.1×10^{15} atoms/cm² (Appendix 9.2) of aluminum atoms. Since the surface density of the clean unreconstructed sapphire surface has a density of 1.3×10^{15} atoms/cm² we deduce that the ion beam “sees” 6.2 times more atoms than expected if only one atom contributes for each row.

The surface peak is due to a surface density of 8.1×10^{15} atoms/cm² of aluminum atoms. Since the surface density of the clean unreconstructed sapphire surface has a density of 1.3×10^{15} atoms/cm² we deduce that the ion beam “sees” 6.2 times more atoms than expected if only one atom contributes for each row. (Appendix 9.2)

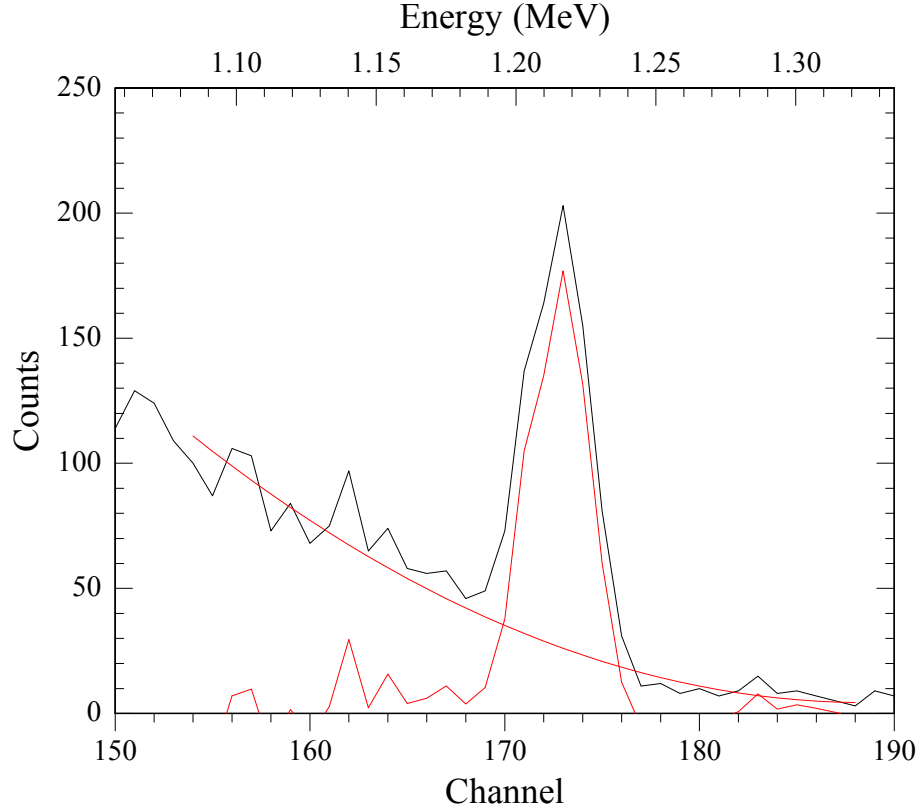


Figure 5.4: Aluminum surface before (black) and after background subtraction (red)

The number of atoms contributing for each row depends on the amplitude of the thermal vibrations and the radius of the shadowing cone for the specific crystal and plane. For sapphire it has been found [99] that the root mean square of the Al atoms in sapphire is $0.12\text{\AA}$. At 2.2MeV the shadow cone radius is $R_m = 0.0412\text{\AA}$. Due to the large vibration amplitude compared to the shadow cone radius more than one atom per row will give non-zero close encounter probability. Using the “universal” curve shown in chapter 4 we have obtained a value of 6.71 atoms per row. By comparing with the experimental result of 6.2 atoms/row we estimate that in fact the sapphire surface is very close to the expected value for a bulk-like termination without lateral reconstruction.

We have imaged the channeling yield map around the $\langle 0001 \rangle$ direction (Figure 5.5) and the hexagonal symmetry of the sapphire is visible from the crossing of the 6 planes. The 6 planes are of two symmetry types ($(11\text{-}20)$ and $(1\text{-}100)$), but just from looking at the Al yield we cannot distinguish between the two types of planes.

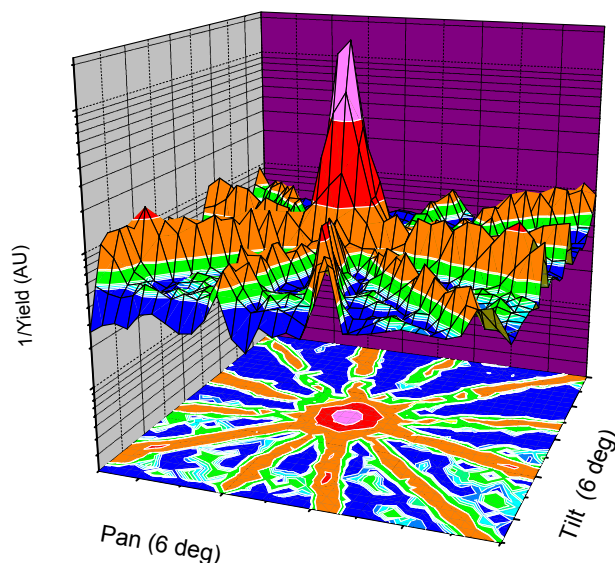


Figure 5.5: Channeling yield map around $\langle 0001 \rangle$ direction of as-received sapphire for a window of 30 channels below the surface

Using the asymmetry in Al and O atoms of the sapphire crystal structure we have been able to identify the crystallographic planes. In the following two channeling yield maps are presented (Figure 5.6) for the same as-received sapphire wafer with the difference that we have chosen a different integration window. The position of the integration window determines the sublattice that we are probe: choosing the integration window just below the Al surface (channels 118 to 168 in Figure 5.3) allows us to monitor the Al sub-lattice, while selecting the integration window below the O surface allows us to look at both Al and O sub-lattices together contribute (channels 33 to 111). This analysis of the data is performed after the entire data has been collected. Thus, the data shown in Figure 5.5 were taken from 900 points of individual spectra taken at 0.2° apart in either tilt or pan direction.

In the Al sub-lattice we observe 6 planes intersecting in the c-axis as we expect from the ball and stick model of the sapphire shown in Figure 5.7. In the second case one can see that three of the planes are no longer visible in the map. This can be explained by the position of the O atoms sitting in the Al planes in such a way that they do not allow channeling to occur.

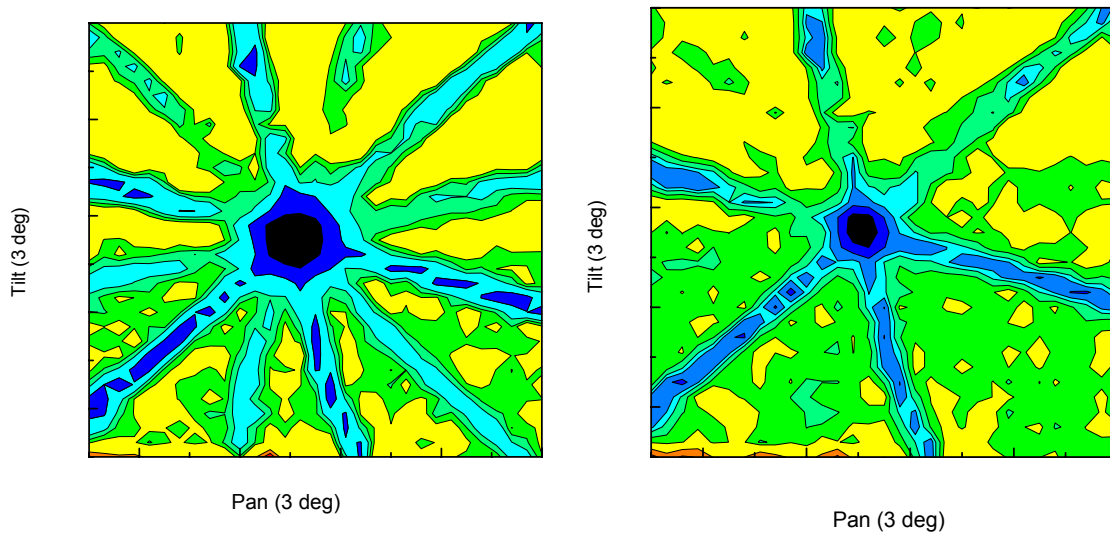


Figure 5.6: a) Yield map of the as-received sapphire for the Al sub-lattice b) Yield map of the as-received sapphire for the Al and O sub-lattices taken together

Figure 5.7 shows a $3 \times 3 \times 1$ unit cells for sapphire as viewed from the $\langle 0001 \rangle$ direction. The two crystallographic planes are shown by red and blue lines and the unit cell is the orange parallelogram. One can see that one of the planes consist of layers of O and Al atoms (red) while the other plane consist of mixed rows of Al and O. When the crystal is tilted along one of these planes the difference in composition of the planes has an impact on the channeling yield. Figure 5.8 shows the two planes as the lattice is tilted few degrees from the $\langle 0001 \rangle$ direction. When both sub-lattices are probed by the ion channeling the plane (1-100) will still exhibit a decrease in yield while the plane (11-20) will give no channeling yield decrease.

The asymmetry of the sapphire lattice which is reflected in the different behavior of the crystallographic planes permits the easy identification of the sapphire planes. This comes in handy when we want to determine the relative orientation of the film to the substrate.

The SEM analysis can give an insight on the large scale structure and morphology of the sapphire surface. As-received sapphire wafers have been cut into pieces and we have looked at the surface morphology of the as-received optically polished sapphire. We can see from the SEM micrograph that the as-received sapphire wafers have a lot of

striations, grooves, pits and dimples due to the mechanical and chemical polishing needed for wafer preparation even though these wafers were rated as epitaxial finish. Figure 5.9 shows representative SEM images where long striations, pits, and micron size features are visible.

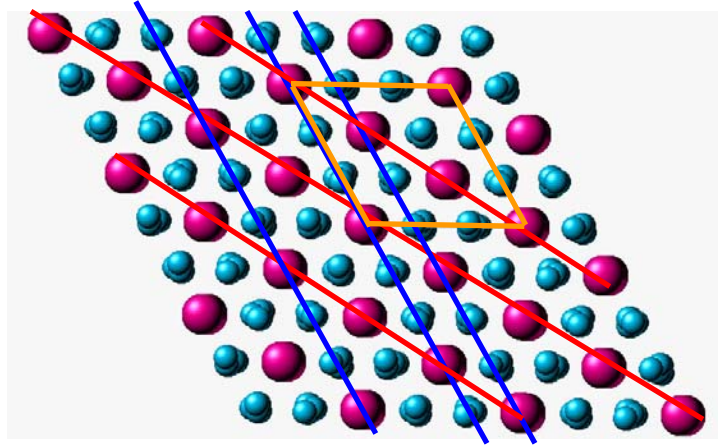


Figure 5.7: Sapphire lattice as viewed from the $\langle 0001 \rangle$ direction, the unit cell is marked orange and the planes: (1-100) is blue, and (11-20) is red (red balls-Al, blue balls-O)

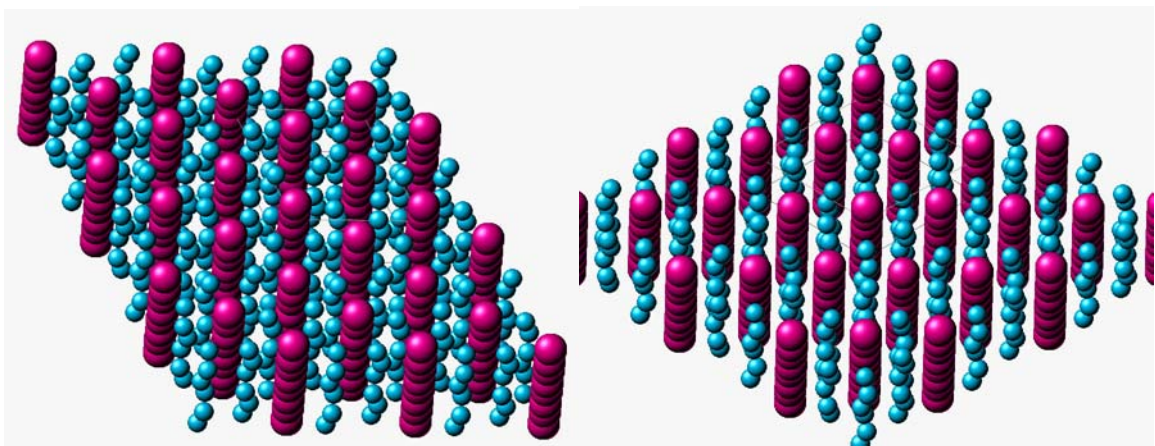


Figure 5.8: Sapphire lattice in the plane (11-20) (left) and (1-100) (right)

The SEM images in Figure 5.9 are not very sharp due to the electrostatic charging effect of the insulating sapphire.

Studies [25,26,100] have shown that pre-treating the sapphire in air can improve the quality of the surface. It has been found that using too high a temperature or a very long time can give rise to increased roughness of the surface. We have chosen to anneal the sapphire in air at a temperature of 1400° C for 30 minutes. We have decided to anneal in air due to studies that shows that using vacuum or a different gas can produce a loss of oxygen from the surface [100]. The heating-up time is approximately 30 minutes and the cooling down time is 90 minutes. For annealing, square pieces of sapphire wafer have been placed on larger, lower quality sapphire discs in order to avoid direct contact with the oven's walls.

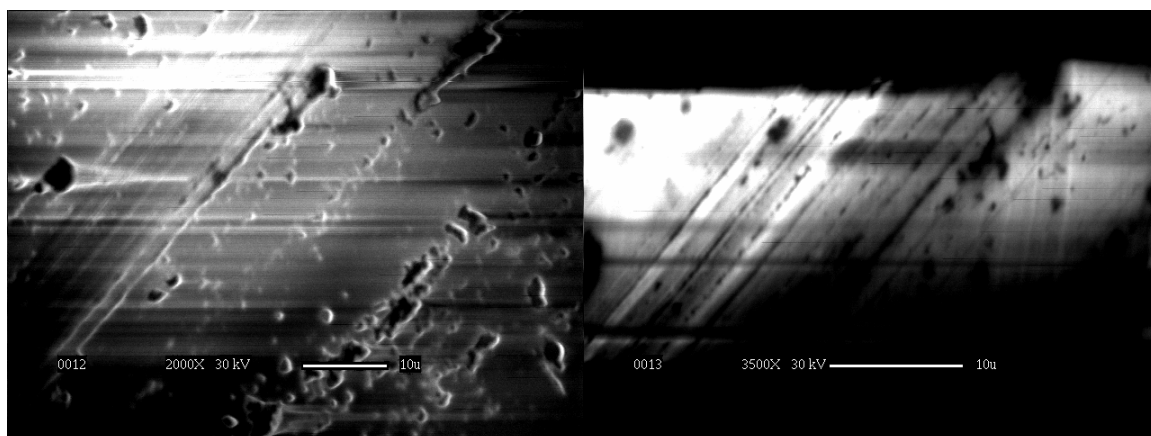


Figure 5.9: SEM images of the as-received sapphire wafers with striations, grooves and features of micron size

After this procedure we have re-analyzed the sapphire substrates. The ion-channeling produced a minimum yield of $1.33\% \pm 0.12\%$ which is very close to the pre-annealing value. Similarly no change is observed in the symmetry of the sapphire.

The SEM image of the annealed sapphire is shown in Figure 5.10. The feature size for this sample is decreased and also the size of the steps seems to be decreased from the lower contrast of the image. Striations and pits are still visible and the sample is strongly charging up making it difficult to analyze by SEM.

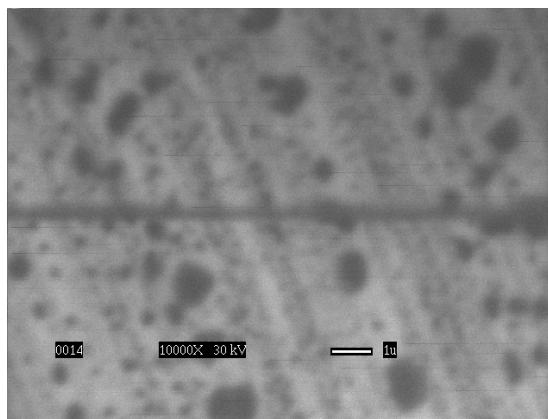


Figure 5.10: SEM micrograph of the annealed sapphire in air at 1400° C for 30 minutes

The surface structure of sapphire has been investigated by LEED. We have not been able to obtain diffraction patterns from as-received sapphire substrates due to the high degree of disorder of the surface as seen by the SEM pictures. In addition the charging of the samples can make it more difficult to obtain LEED patterns.

The XPS spectra of as received sapphire substrate are shown in Figure 5.11. The surface shows the Al and O peaks as well as the adventitious carbon peak. Both Al and Mg x-ray sources have been used in order to better identify the XPS and Auger peaks.

We have taken more XPS spectra after the annealing in air of the sapphire for better surface re-crystallization (Figure 5.12). The annealing process does not remove the adventitious carbon from the surface but we observe a decrease of a few percent in the surface concentration. This form of carbon is found on all materials exposed to air and can only be removed completely by ion beam sputtering in the XPS analysis chamber. Ion sputtering can destroy the chemical information on the surface of the sample. Thus, the adventitious carbon is often left on the sample because it may be used to establish the binding energy scale for samples that charge up during analysis, such as these ones.

After the annealing in air the sapphire substrates are introduced in the vacuum system

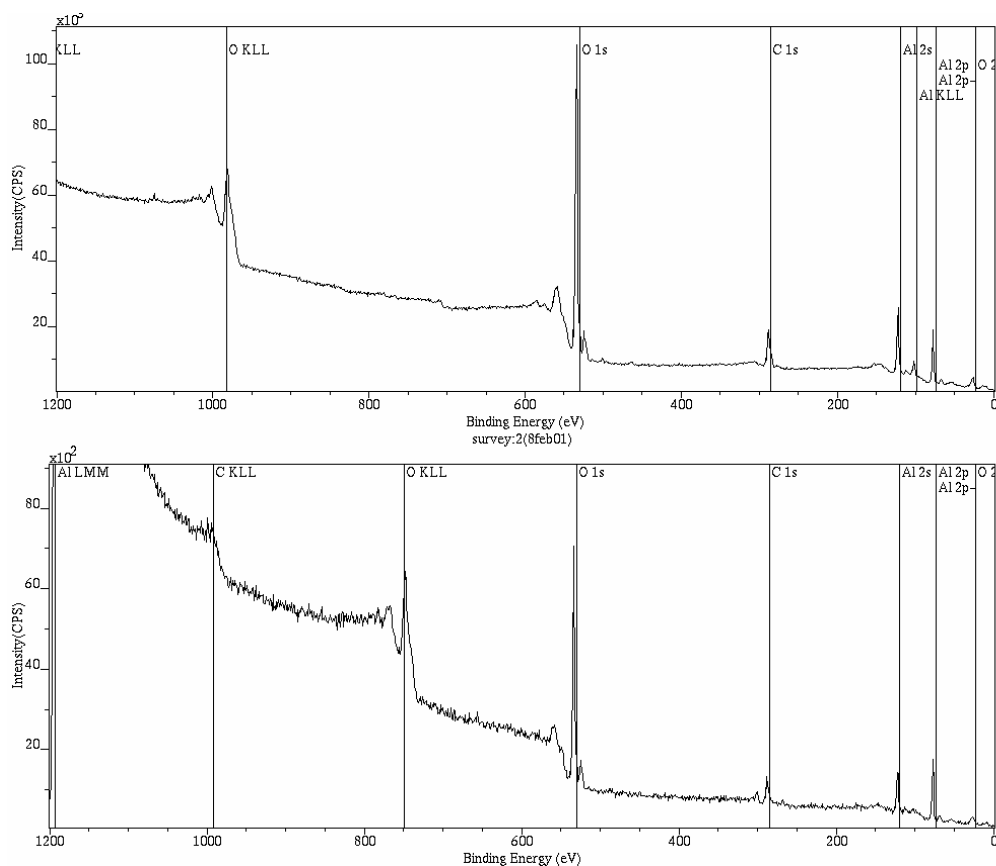


Figure 5.11: XPS Spectra taken with Al and Mg anode of the as-received sapphire substrate. The composition of the surface is O:Al:C = 53:22:25.

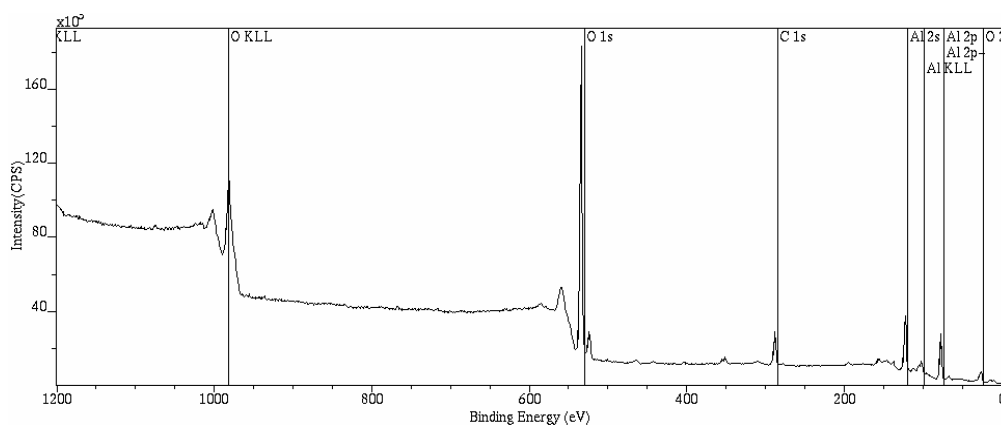


Figure 5.12: XPS Spectra using Al anode of the sapphire substrate annealed in air at 1400C for 30 minutes. Composition of the surface is O:Al:C = 56:25:19.

5.3 Nitridation of the sapphire substrate

Numerous studies [28,29,30,31,32,33,34,41] have shown that the nitridation step is an important and definitive step in the growth of GaN. In this process nitrogen atoms are adsorbed on the sapphire surface and it is believed that a thin AlN film is formed. It has been found that the nitridation has role in establishing the epitaxial relationship between sapphire and GaN [36,41]. A common finding between studies is that there is an optimal amount of nitridation and neither too much nor too little nitridation is good for the quality of the final film. Due to the large number of parameters (mentioned in a previous section) involved in the nitridation we have not tried to do an extensive study of nitridation. We have limited our investigation to studying the effect of nitridation gas with the analysis techniques available to us. The procedure was to use identical nitridation conditions with the only difference of the nitridation gas that was either N_2 or NH_3 . The sapphire substrate was prepared as described in the previous sections and introduced in the vacuum system. The nitridation period was 300 seconds at $850^\circ C$. This is a rather low degree of nitridation taking into account the low dissociation rate of N_2 and NH_3 at $850^\circ C$. This low intensity nitridation has been used in order to investigate the early aspects of nitridation (some authors have performed nitridation as high as $1200^\circ C$). After the nitridation the sapphire substrate were transferred in the analysis chamber and XPS, LEED and RBS/Channeling has been performed.

The effect of the nitridation can be seen in the channeling of the sapphire. Figure 5.13 shows the aligned RBS spectrum for the clean sapphire sample (black) and for the nitridated sample in N_2 at $850^\circ C$ for 300 seconds (red).

The effect of the nitridation is an increase of the surface peak of Al and O and an increase in the dechanneling level deeper in the crystal. The change in area of the surface peak for Al (channel range 175-182) is $6\% \pm 2\%$ and is only due to change in surface peak height while the width stays constant. The value of the minimum yield it is not changed indicating that the overall quality of the substrate has not been affected by the nitridation. These observations are consistent with a reconstruction of the sapphire surface that involves lateral movement of the first few atomic layers. We believed that the nitridation did not penetrate appreciably in the sapphire since no increase in the width

of the Al surface peak is observed. Both oxygen and aluminum surface atoms are affected since both surface peaks are increased in height.

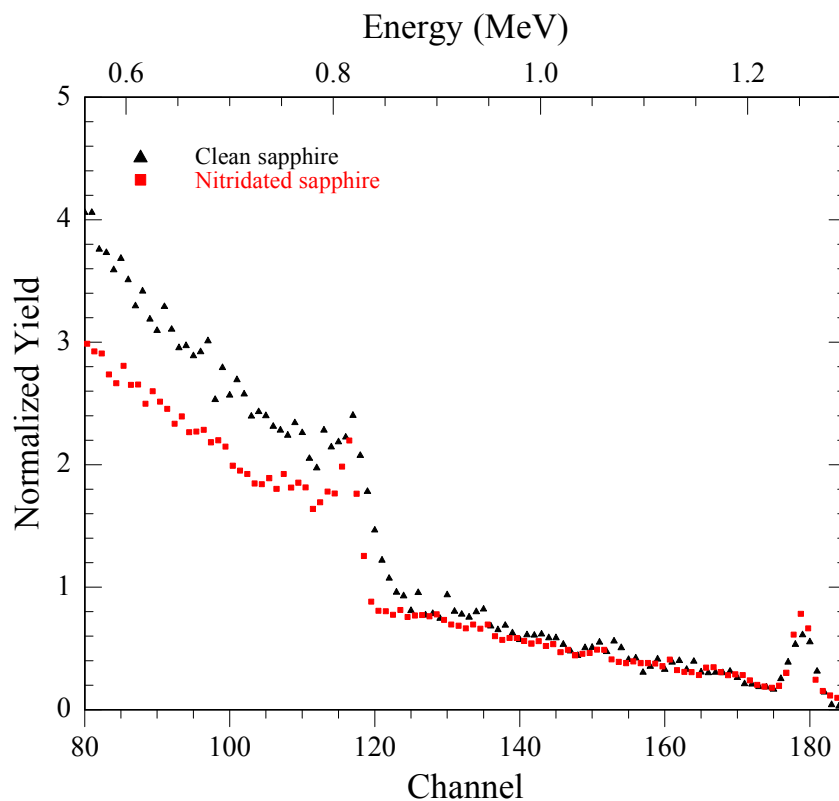


Figure 5.13: The effect of nitridation in N_2 on the surface peak of Al

When similar nitridation conditions are used but the nitridation as is changed to NH_3 we observe again an increase in Al surface peak (Figure 5.14) but this time it more than doubled in size (106%). In this case the surface peak expands not only in height but also in width. The 2 channel width increase corresponds to 16.75keV in energy scale and this translates to 170 Å increase in depth scale (in the surface approximation). (See Appendix 9.1)

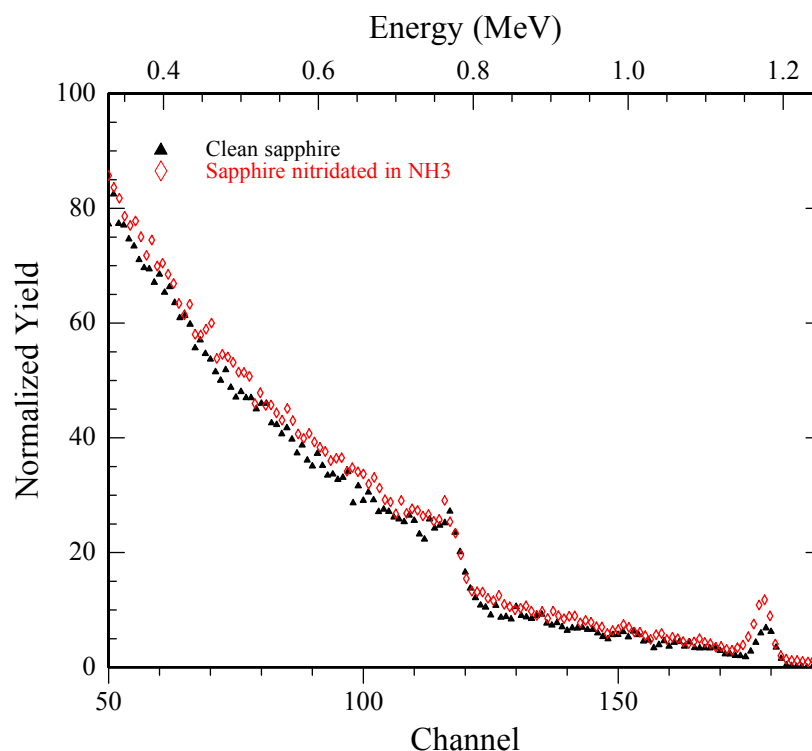


Figure 5.14: The effect of nitridation in NH_3 on the surface peak of Al

These RBS/Channeling results are indirect in the sense that we are seeing the effect of nitridation on the aluminum and oxygen atoms at the surface of the sapphire. To directly investigate the presence of nitrogen atoms on the surface we have used XPS. The Figure 5.15 shows the XPS spectra for the sapphire after nitridation in the two different gases. We have determined that the nitridation using NH_3 give rise to a higher nitrogen concentration adsorbed on the sapphire substrate when using the same nitridation conditions (exposure time, gas flow, chamber pressure, and substrate temperature). Using XPS we have determined the percentage of nitrogen atoms in the surface region of sapphire for nitridation in N_2 and in NH_3 for 300 seconds and 850°C . The N 1s peak at 396.7 eV represents only 4.5% of the surface atoms in the case of N_2 nitridation but 14.2% in the case of nitridation using NH_3 .

For investigating the structure and ordering of the surface we have used electron diffraction before and after nitridation. Before nitridation, the sapphire substrate does not show any LEED pattern. This can be both due to the nature of the surface that can be

damaged from the mechanical polishing as well as due to the charging effect due to the insulating properties of the sapphire.

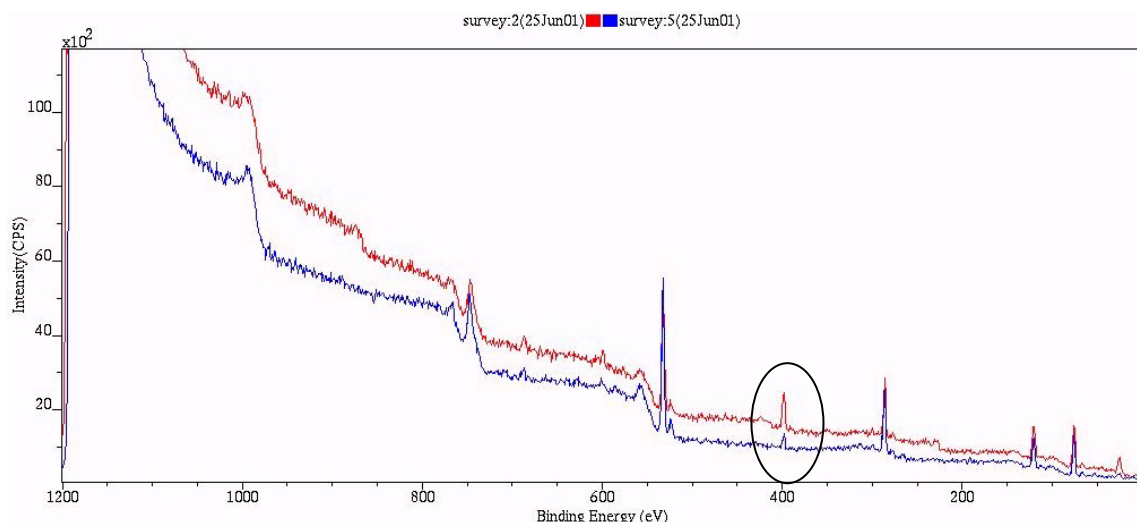


Figure 5.15: XPS of nitridated sapphire in N_2 (blue) and NH_3 (red) using Mg anode

After the nitridation step we have been able to obtain diffraction patterns for the sample nitridated in N_2 but no diffraction patterns for the sample nitridated in ammonia (Figure 5.16). The LEED diffraction patterns obtained after nitridation in N_2 are complicated and point towards a reconstruction and/or preferential adsorption of N on the surface in some lower symmetry positions. We have also measured Intensity-Voltage curves for this surface (I-V Curves). The interpretation of this patterns and of the I-V curves is complicated and usually involves the construction of a model of the surface and the simulation of the I-V curves using the model followed by the comparison of the simulated I-V with the real curves and adjusting of the parameters until a satisfactory match is obtained.

The LEED patterns obtained have the hexagonal symmetry expected for a clean, unreconstructed surface but the intensities of the diffraction peaks are modulated with the electron beam voltage leading to the conclusion that the adsorbed N on the sapphire surface does have preferred site but it is more complicated than the simple 1×1 position.

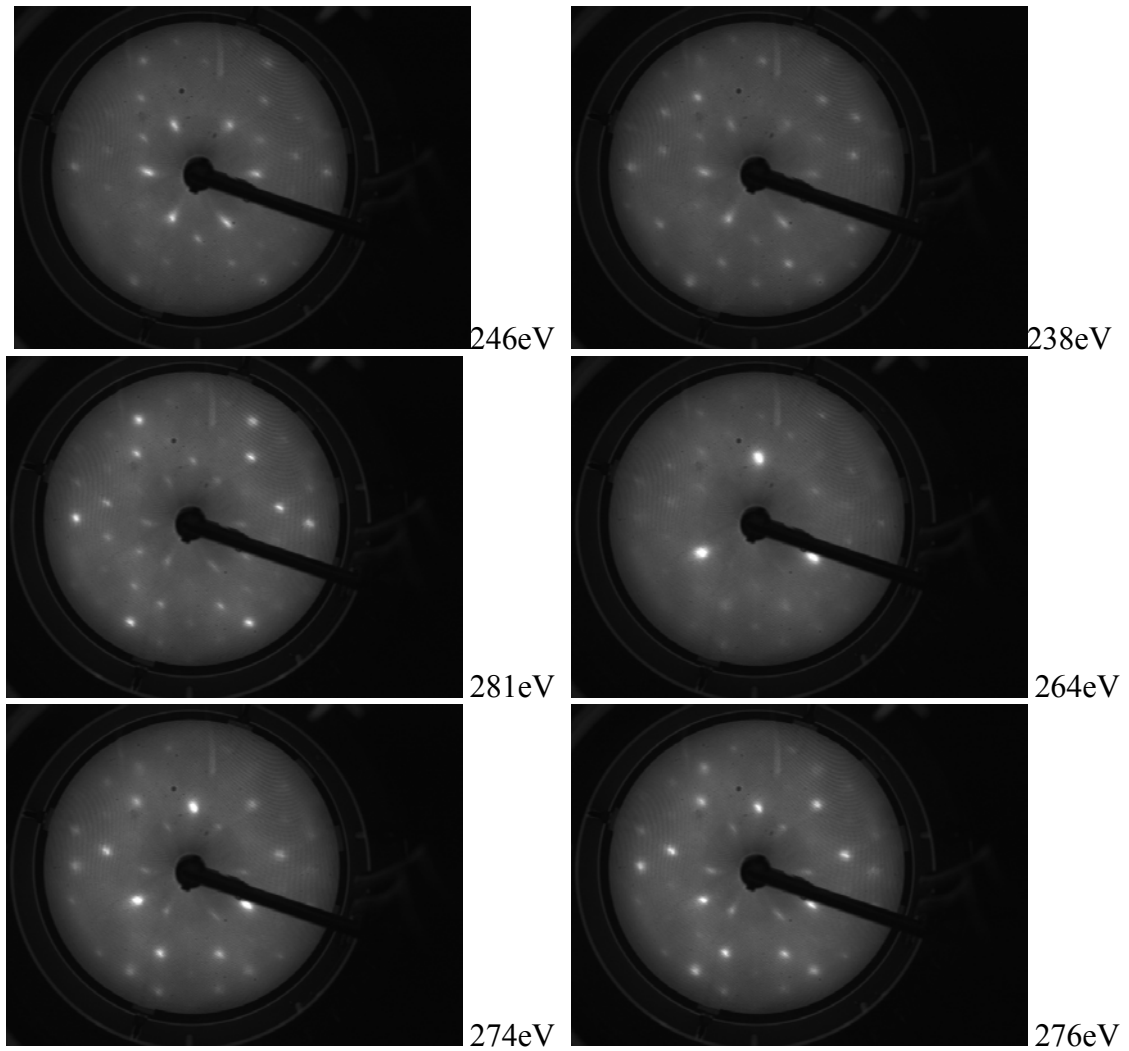


Figure 5.16: LEED patterns of sapphire after nitridation in N_2 – the beam accelerating voltage is noted next to each picture

Complicated reconstruction for sapphire has been observed [32] and has been categorized by $(\sqrt{31} \times \sqrt{31}) R \pm 9^\circ$. It has been also observed that a short nitridation can produce a adsorption of N on the surface as thin as $6\text{\AA}$ while a longer one can create an AlN relaxed layer on top of the sapphire [32,101,102].

5.4 Optimization of the growth parameters

There are a multitude of deposition parameters to be taken into account when considering the deposition of GaN thin film. Since the process involves preparatory steps

that have an impact on the quality of the film, all the parameters related to this steps are to be taken into account and optimized as much as possible.

In the following I will list the relevant parameters to be considered for each of the steps involved in the deposition for the MOCVD system that we have used in this work:

- pretreatment of the substrate: cleaning mixture of chemicals, cleaning temperature and time, heat treatment of the sapphire before introduction inside the vacuum system, ramping rate up and down to/from the peak temperature.
- in-situ cleaning/preparation of the sapphire substrate (flash heating in vacuum and H_2): temperature and time of the heating in vacuum, temperature and time of heating in H_2 , pressure and gas speed of the H_2 during the flash heating, ramping rate up and down to/from the peak temperature.
- nitridation: choice of gas used for nitridation (usually H_2 , NH_3 , or mixture ratio), nitridation temperature, nitridation time, ramping rate up and down to the nitridation temperature.
- actual thin film growth: substrate temperature, geometry of the gas flow in the chamber, mixture of gases used, pressure in the reactor chamber, molar ratio between the group V and group III precursors, gas flow for the four gases introduced in the reactor chamber, ramping rate from the nitridation temperature to the deposition temperature, rate of cooling down after the film deposition, pressure and gas used during cooling down.

Due to the large numbers of parameters listed it was not possible for us to fully explore the phase space given by all possible combinations. We have started by using values found in the literature and optimize by adjusting some of the parameters for our deposition system. As a merit function we have used one or more of the following: the minimum channeling yield (χ_{min}), RUMP simulations of stoichiometric GaN, ratio of Ga to N from XPS analysis, impurities concentration (C and O) from XPS analysis, FWHM of the XRD peaks, the physical aspect of the film and fraction of GaN covered area of the substrate.

Due to the fact that the adjustment of pressure and temperature was controlled manually and the repeatability is difficult, the temperature ramping up/down rate has not

been considered for optimization/change. We have keep it constant, within the operator's abilities, to about 200°C/minute. It is important for this ramping to not be very fast otherwise the cracking of the substrate will occur, too long a ramping time between nitridation and growth can extend the nitridation time and produce a different starting surface.

The following parameters have been changed during the optimization procedure within limits suggested by the literature: [18,27,28,29,30,31,32,33,34,36,37,38,39,40,41,42,48,51,80]: gas flow geometry, nitridation gas, temperature, and time, gas mixtures used for the two precursors during the GaN film growth, gas flow in the deposition chamber for the four gasses used during film growth.

List of parameters that have been kept constant or only changed within small limits: all ex-situ cleaning procedures (used chemicals similar to the literature), all parameters for in-situ flash heating of the substrate in vacuum and hydrogen were similar to the most used values in the literature; molar ratio V/III was fixed to 1000 – motivation for this value due to a report that a lower ratio give rise to less defective film [80], and also the FWHM of the rocking curves increases slowly with higher ratio in 1000-10000 interval [81]; pressure in the reactor during nitridation and deposition: 50 torr which is less than the vapor pressure of TMGa at room temperature; nitridation temperature, time, and gas have been set at 850°C for 300 seconds in NH₃ as higher temperatures (850-1000°C) gave rise to larger FWHM in the rocking curves [48]; the choice of deposition time is explained in section 5.4.4; substrate temperature ramp up/down rate of about 200°C/minute has to be slow enough to avoid the cracking of the film; gas and pressure used during cool down phase: 50 torr is high enough to ensure the cooling down of the sample within 30 to 60 minutes from the end of the deposition,

One characteristic of the films that we have grown is that there is a certain degree of non-uniform of the thickness across the surface. The magnitude of this non-uniformity is dependent on the deposition temperature and the thickness distribution can gives us information about the importance of the various parameters on the growth rate and surface morphology. Further discussion on the non-uniformity of the thickness will be delayed until Chapter VI.

5.4.1 Effect of the geometry flow in the reactor chamber

We have determined that the geometry of the gas flow in the reactor plays an important role in the growth pattern on the substrate. We have tried two geometries as shown in Figure 5.17.

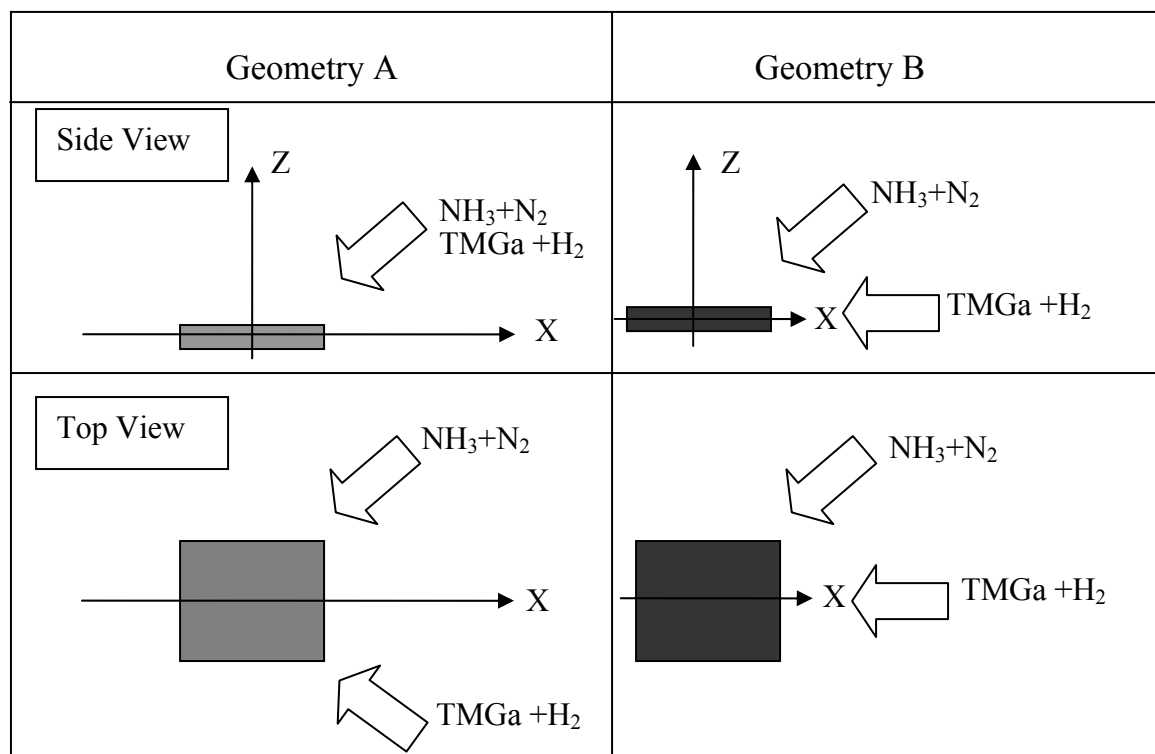


Figure 5.17: Gas flow geometries

In both cases the gas flow of NH_3 and N_2 is oriented in the same direction: 45° away from the horizontal (OX) and vertical (OZ) directions. The gas flow of TMGa and H_2 is oriented at 45° from the vertical (OZ) and -45° from the horizontal (OX) for Geometry A and is oriented along the horizontal direction (OX) for Geometry B. While the Geometry B is the one that is mostly used in commercial reactors and is close to the original geometry developed by Nakamura [18] in our particular case the Geometry A has provided more uniform films. The thickness variation for Geometry A was -35% from the maximum while for Geometry B it was -56%.

5.4.2 Influence of the gas flow rate on the growth rate, uniformity of the film and crystalline quality

In order to determine the importance of the magnitude of the gas flow upon the growth rate we have grown two samples with similar parameters with the only difference that the gas flow for all four gases has been doubled from one sample to the next one. The common parameters used are as follows: growth temperature (750°C), growth pressure (50 torr), gases used (NH₃+N₂ and TMGa+H₂), similar substrate cleaning and preparation conditions (degreasing, air annealing), similar nitridation conditions (300 seconds at 850° C in NH₃). The different gas flows for the two samples are given in Table 5.1 together with the measured thickness. The residence time is calculated from the total gas flow speed and the volume of the reactor chamber (2800 cm³) and since the total flow speed is doubled between the two samples the residence time of the gases in the reactor chamber for sample LF is double compared to Sample NF.

Table 5.1 Gas flow rates for the two samples

	N ₂ (slm)	NH ₃ (slm)	H ₂ (slm)	TMGa (sccm)	Total Flow (slm)	Gas residence time (s)
Low Flow (LF)	0.5	0.5	0.5	0.25	1.5	1.87
High Flow (HF)	1	1	1	0.5	3	0.93

The film thickness has been determined using RBS assuming a constant density across the surface equal to the bulk density of GaN. For both samples we have found that the films have non-uniform thickness across the substrate and the data is shown in Table 5.2. By looking at the numbers in Table 5.2: we can see that the sample LF has a better uniformity as measured by the ratio of maximum to minimum thickness of 1.9 while the for the sample HF the ratio is approximately 6. The maximum thickness for the HF sample is approximately 2.6 times larger than for the LF sample, while the minimum thickness for both samples has similar value. Using just these numbers the amount of GaN deposited is about twice as much for the sample HF than the sample LF, we are

probably in a regime where the growth rate scales linearly with the total flow rate of the gas. Since the uniformity is better for the LF sample and a reasonable value of the uniformity of 5%/mm is desired for the RBS/Channeling analysis the LF growth conditions are more appropriate.

Table 5.2: Measured minimum and maximum thicknesses for the samples grown at two different gas flow rates

Sample	Maximum thickness (nm)	Minimum thickness (nm)	Variation (%/mm)
LF	280	150	4.6
HF	750	125	8.3

The reason for the better uniformity could be attributed to the longer residence time that can give rise to a more uniform dissociation of the precursor gases.

We have measured the crystalline quality of the two samples been estimated by Ion Channeling in conjunction with the RBS measurements. By performing channeling yield maps around the film normal we are able not only to measure the minimum yield but also to determine if crystalline planes are visible and what is the symmetry of the crystal. Figure 5.18 shows two channeling maps for two thicknesses of the film. While dechanneling level is visible the amount is very large (90%), especially for the sample 50 nm thin. Some improvement in crystal quality is observed for the 310 nm thick region with a dechanneling level of 70%.

Both maps show no sign of channeling planes and the channeling axes are very broad signaling that the film is polycrystalline with a distribution of the domains having a crystallographic axis oriented close the growth direction. We cannot determine if the polycrystallites have a hexagonal or cubic nature from these measurements. Overall this is an indication of low crystalline quality film. Figure 5.19 shows the channeling yield map for the LF sample. We have measured an improved channeling level (8.7% for 135 nm thick film) and in addition channeling planes are clearly visible. The film has hexagonal symmetry that corresponds to the wurtzite phase of GaN.

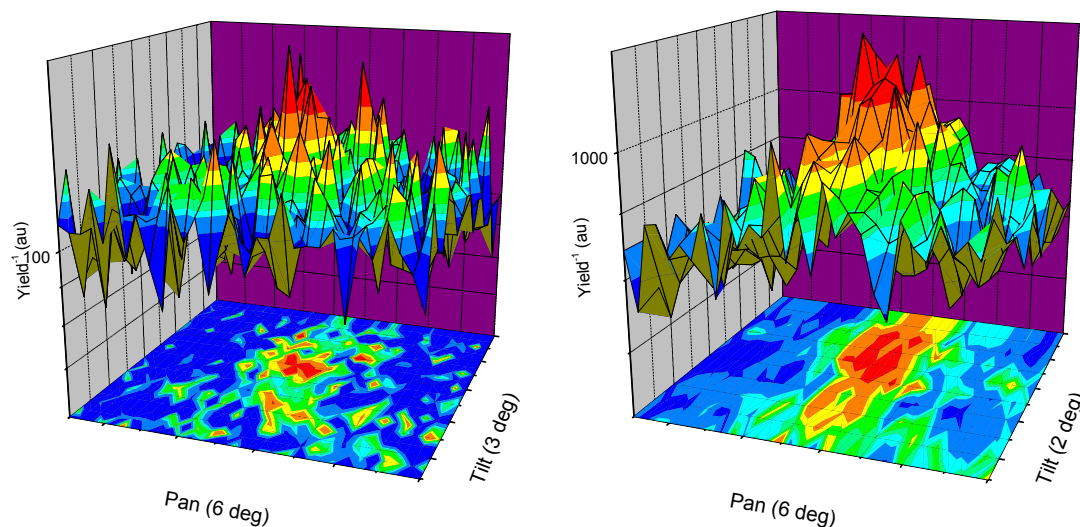


Figure 5.18: Channeling yield maps for the HF sample showing small amount of axial channeling $\sim 90\%$ for 50 nm thick film (left), and $\sim 70\%$ for 310 nm thick film (right)

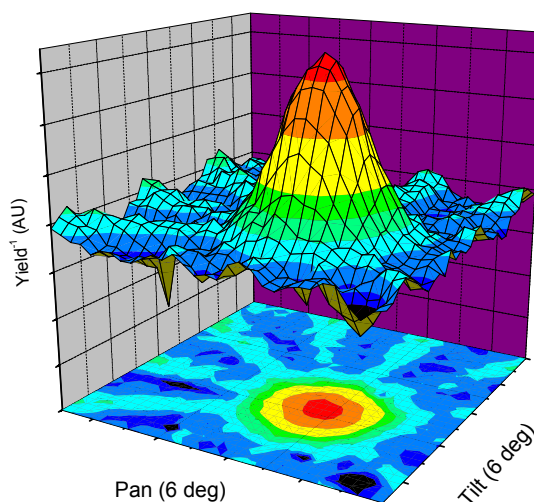


Figure 5.19: Channeling yield map for the LF sample showing good axial and planar channeling. The minimum yield is $8.7\% \pm 2\%$ for a thickness of 135 nm.

Based on the results of these experiments we have decided to use a lower flow speed for the film growth and the conditions used for the sample LF (Table 5.1) have been adopted and used throughout the remaining of the work. Due to the higher error associated with running the MFCs at lower gas rates than 10% of the full scale we have

not deposited films using flow rates lower than 0.5 slm. If lower rates are desired MFCs calibrated for lower rates would be needed.

5.4.3 Influence of the use of carrier gases on the growth rate

For GaN growth we have used in addition to the two precursor gases (NH_3 and TMGa) two carrier gases (H_2 and N_2). We have verified the catalytic nature of the gases used for the growth by growing films in similar conditions with the only difference that just the two precursor gases have been used with no carriers. Checking the thickness of the deposited films using the in-situ techniques, we have measured only minute amounts of GaN. This confirms the finding that the carrier gases play an important role in the chemistry of the growth. This effect can be seen in Figure 5.20 where two samples are shown, one is grown using the four gases (2 precursors and 2 carrier gases) while for the second one only the two precursors are used.

The samples are grown at 750°C and 50 torr for 100 seconds, using a flow of 1 slm for N_2 , NH_3 , H_2 , and 0.5 sccm TMGa and 1 slm NH_3 and 0.5 sccm TMGa respectively. The sample grown in four gases has a maximum thickness of 750 nm while the one grown with precursors only has a maximum thickness of 8 nm. The carrier gases have a critical role in the chemistry involved in the formation of GaN. Based on this result both precursor gases and carriers have been used for the deposition of GaN.

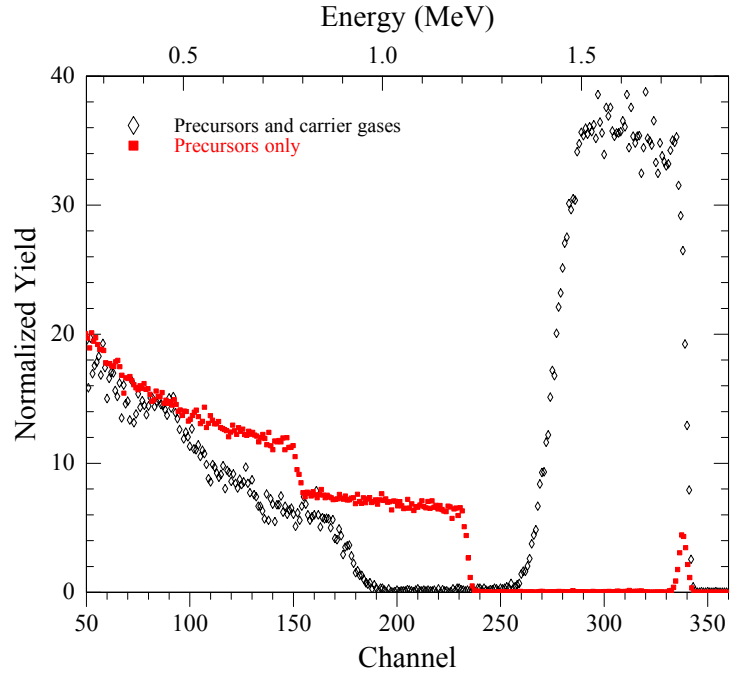


Figure 5.20: RBS of the film grown with four gases (NH_3 , N_2 , H_2 , TMGa) (black diamonds), and with 2 gases (NH_3 and TMGa) (red squares). The growth rate is greatly reduced when no precursor gases are used.

5.4.4 Growth rate as a function of time

For this experiment three films have been deposited in similar conditions with the exception of the growth time that has been chosen to have the following values: 10 seconds, 100 seconds, and 1800 seconds. The substrate temperature has been set to 750°C and the flow of gas set to 1 slm for NH_3 , N_2 , and H_2 , and 0.5 sccm for TMGa. The standard in-situ cleaning steps and nitridation have been performed. After film growth the thickness of the film has been measured and the results are summarized in Table 5.3.

From these measurements we can see that the growth rate at the very beginning of the growth stage is lower than the growth rate after the growth has been initiated. This is due to the nucleation process that requires some time for the GaN nuclei to form, stabilize and grow. This initial stage of the growth is of the order of few tens of seconds for this substrate temperature. For the MO-MBE technique Woll et al. [32] have measured that the growth rate is highly non-linear at the beginning of the growth with a delay of about 10 seconds before the growth started.

Table 5.3: Maximum and minimum thickness and growth rate for three deposition times.

Growth Time (s)	Minimum Thickness (nm)	Min Growth Rate (nm/s)	Maximum Thickness (nm)	Max Growth Rate (nm/s)
10	0	0	20	2
100	110	1.1	750	7.5
1800	580	0.32	12000	6.67

This result establishes the time scale of the nucleation process and gives a limit on the growth time of the film. We have decided to look at films that are grown for 100 seconds since these films pass the nucleation phase and have a complete coverage of the substrate. Based on the work presented in this chapter we have assembled the following recipe for growing a series of films with the same deposition parameters but a different substrate temperature.

- ex-situ preparation of the sapphire substrate: alcohol degreasing of the sapphire, and heating in air of sapphire at 1400°C for 30 minutes, with a ramping up time of 60 minutes, and a cooling down time of 120 minutes,
- in-situ flash heating in High Vacuum (10^{-5} torr) to 850°C for about 5 minutes total time followed by cooling down in vacuum for 5 minutes;
- introduction of H_2 gas at 0.5 slm flow rate and 50 torr pressure and stabilization of the pressure (5 minutes) followed by flash heating to 1050°C with a ramp-up time of 5 minutes and followed by cooling down in 5 minutes.;
- introduction of NH_3 gas at 0.5 slm flow rate and 50 torr pressure and stabilization of the pressure (5 minutes);
- ramp up the substrate temperature to 850°C (3 minutes) followed by nitridation for 300 seconds;
- cool down of sapphire while simultaneously admitting N_2 , NH_3 and H_2 in the reactor chamber and stabilizing the pressure at 50 torr;
- ramp-up the temperature to the desired deposition temperature (3-10 minutes depending on the final temperature);

- introduction of the TMGa in the chamber at 0.5 sccm for 100 seconds;
- end the deposition time by: interrupting the admission of TMGa, NH_3 , and H_2 , and cooling under continuous N_2 flow at 50 Torr for one hour;
- terminating the flow of N_2 and pumping to high vacuum for sample transfer.

5.5 Summary of results

We have successfully eliminated fluorine contamination by using a continuous flow of gas throughout the all steps of the process.

The as-received sapphire substrate used is a good crystal as measured by Ion Channeling had a considerable amount of surface damage as seen in the SEM images. The analysis of the surface peak after in-air annealing reveals that the surface has bulk-like termination. We have identified the crystallographic planes of the sapphire using the asymmetry in the ion channeling yield map and knowledge on the crystalline structure of the sapphire structure. This is relevant to finding the orientation of the GaN film with respect to the substrate. The air annealing of the sapphire did not produce major change in the XPS spectra. The surface morphology shows some improvements in SEM but no LEED patterns are visible.

We discuss the various growth parameters available at our disposal and the range of values found in the literature. We have investigated the effects of some of the parameters such as reactor flow geometry, total flow rate, use of carrier gases, and growth time on the growth rate, film uniformity, and crystalline quality.

The geometry of the flow of gas in the reactor chamber has an impact on the uniformity of the film. We have found that the standard geometry produces less uniform films for our reactor chamber.

We have investigated the influence of the gas flow rate on the film growth rate and uniformity of the film and found that lower flow rates produce a more uniform film but less amounts of GaN are deposited. The crystalline quality of the lower gas flow sample is improved comparatively to the higher flow sample. These points to the existence of an optimal gas flow rate at intermediate values. We have found that, for the gas flow geometry and reactor pressure in our system, consistent results are obtained with a flow

rate of 0.5 slm for MFCs with a maximum flow rate of 5slm. This represents 10% of the maximum value and is towards the lower limit where we can reliably use the MFCs.

The role of the carrier gases is important for the chemical reaction to take place. Even though it is assumed that the N_2 and H_2 are not directly participating their presence is enhancing the deposition process by orders of magnitude.

We have also found that at the beginning the growth process the growth rate is decreased relative to the growth rate later on in the growth process. This is an indication that in the early stages of growth the formation of the GaN nuclei requires extra time. We estimate that the nucleation phase takes a few tens of seconds.

We have obtained films with variable thickness across the substrate. In general the maximum thickness is obtained towards the geometrical direction where the combination of gases NH_3 and N_2 enters the reactor chamber. We attribute the film non-uniformity to the reactor geometry that give rise to different reactant arrivals rate to the various places across the sample due to a boundary layer with variable thickness across the substrate. There can also be an effect due to non-uniform substrate temperature but this effect must be small due to the fact that the observed non-uniformity does not follow the symmetry of the heating element.

We have investigated the nitridation process using both surface sensitive techniques (LEED, XPS) and bulk techniques (RBS/Ion Channeling). We have compared the results for N_2 and NH_3 nitridation when similar nitridation conditions are used. The results of the nitridation study using the methods mentioned are as follows: more N is adsorbed on the surface when ammonia is used for nitridation than when nitrogen gas is used; one indirect effect of N adsorption is to shift, displace the Al surface atoms; for the nitridation in N_2 the effect seems to be on the surface only while for ammonia the shifting seems to occur also below the surface; complicated LEED patterns for N_2 nitridation point towards a preferential adsorption of the nitrogen into sites with certain symmetry; for ammonia nitridation no patterns can be seen indicating a more irregular, random adsorption or a defective surface.

Based on these investigations and the data published in literature we have decided on the recipe for GaN film growth that best suits the studies on the early stages of growth to be presented in the next chapter.

Chapter 6

In-situ characterization of GaN thin films

In this section I will present the results of the characterization techniques we have used to investigate the GaN thin films grown using the procedures detailed in Chapter 3 and the “recipe” obtained after the optimization work presented in Chapter 5.

6.1 RBS study of the film growth

The use of RBS techniques permits us to analyze the composition of the thin films as a function of depth as well as the thickness. The technique is non destructive and it has an accuracy of up to 1% for relative composition.

The common characteristics of the films are:

- they all have variable thickness across the substrate,
- the maximum thickness is towards the direction where the mixture of NH_3 and N_2 enters the reactor chamber,

The magnitude of this non-uniformity is dependent on the deposition temperature and can give us a clue on the importance of the other parameters on the growth rate. We

attribute the non-uniformity to the following factors that are specific to our reactor chamber:

- the gas flow in the chamber is not symmetric, this gives rise to exposure of some regions of the substrate to higher concentrations of reactants than other regions (mass transport limitation);
- substrate temperature may not have been the same due to the fact that the edges of the substrate are probably cooler than the center of the sample (this is not detectable by optical pyrometry – therefore less than 10°C),
- convection currents may create a boundary layer with non-uniform thickness above the substrate that the chemical species need to diffuse through in order to reach the growth area (mass transport limitation),
- the presence of electrical posts (that get hot during the growth) nearby the edge of the sample can give rise to higher concentration of reacting elements in those regions and consequently a higher growth rate (due to the endothermic nature of the chemical reaction involved),

The visual appearance of the sample depends on the deposition temperature. The lower temperature samples have a yellow/brownish color while the higher temperature ones tend to be white or transparent. The transition is gradual and it happens in the 650°C to 750°C temperature range. The samples deposited at the two extremes temperature (450°C and 1050°C) are completely transparent due to the low thickness of the film.

A series of samples have been deposited in similar condition with the exception of the substrate temperature that has been changed from 450°C to 1050°C. After the deposition the samples have been analyzed in-situ by RBS/Channeling, LEED and XPS. In this section I will present the results of the RBS analysis obtained after fitting the experimental curves with the RUMP simulation software [103]. Due to the fact that the samples have non-uniform thickness RBS spectra have been taken at different positions on the film in order to determine the film thickness distribution across the substrate. We have taken RBS spectra across the entire surface with a step size of 2-4 mm. The results of the thickness measurements for the films grown in the entire range of temperatures investigated are summarized in Figure 6.1. The thickness of the film is determined

assuming the standard bulk density of GaN. We have checked this assumption by independently measuring the thickness using a stylus profilometer and the two measurements agree within 10%.

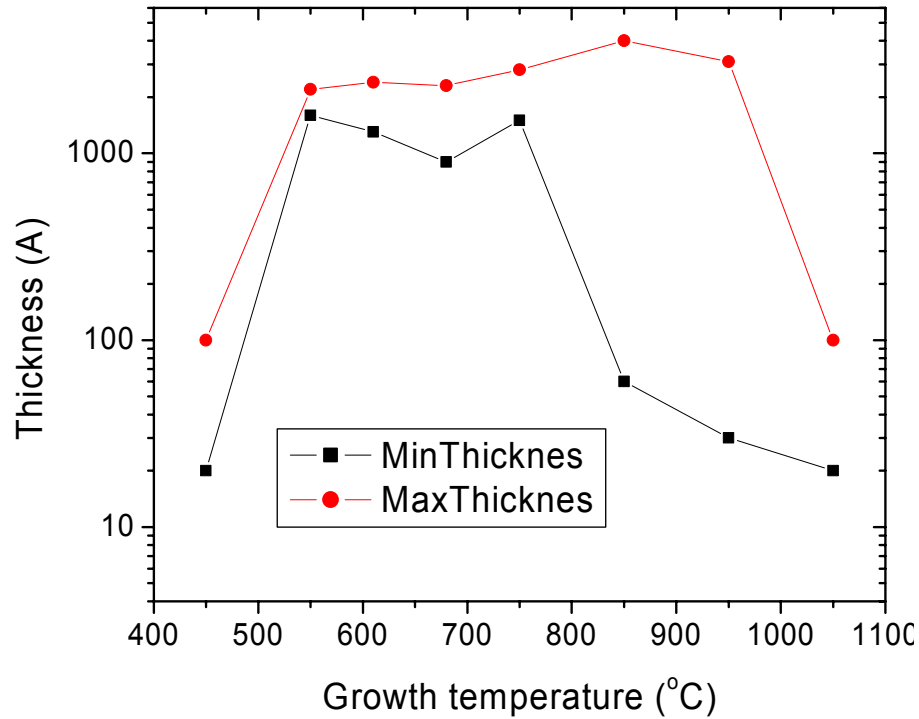


Figure 6.1: The maximum and minimum thickness vs. the growth temperature

The maximum growth rate corresponds to the sample grown at 850°C, with a maximum thickness of 750nm. This corresponds to a growth rate of about 20 $\mu\text{m/hr}$. At this temperature the film does not cover completely the surface as we will see from the RBS measurements. Another observation looking at Figure 6.1, is that the non-uniformity in the thickness across the substrate for the films grown at 850°C and 950°C is a lot higher than the non uniformity for films grown at lower temperatures. Also the morphology of the surface changes between the films grown at 500-750°C and the ones at higher temperatures 850-950°C.

A transformation of structure at 750°C has been observed by Lin et al. [30] for films grown on a low temperature buffer layer and has been attributed to the change from cubic phase to hexagonal phase. We do not believe this to be the case here case since no cubic

phase is detected in Ion channeling, LEED or XRD. A different explanation can be a temperature dependent growth rate for the N-polar and Ga-polar faces. It has been established that in the case of MOCVD both polarities can be obtained in the early stages of growth [48,74,76,105] and they have different growth and evaporation rates as a function of temperature [44,76]. The same result has been obtained for thicker films grown on low temperature buffer layer [47,75,104] and in addition the surface morphology has been correlated with polarity: smooth surfaces tend to be Ga-polar while rough pyramidal samples contain tiny columnar inversion domains (Ga-polar) embedded in a N-polar matrix [47,75]. Furthermore it has been shown that one polarity can laterally overgrow the other such that 20 nm GaN films are covered with Ga-polar film while below there is a mixture of both faces. [48, 105, 106]. The presence of the two polarities together with inversion domains was shown [78], and from calculations only a low energy of formation is needed (0.41eV) [77] and it is presumed that is triggered by a sapphire surface that contains steps and inhomogeneities. The density of domains depends on the growth technique and the substrate pretreatment prior to the growth and could be as high as 50% of the total area [78,105]. The two polarities have different properties and morphologies for example the annealing in H₂ preferably remove the Ga-polarity, and etching in KOH removes the N-face [48]. Based on the above observations a possible mechanism that can explain the observed change in the morphology of our films, schematically shown in Figure 6.2, can be that at low temperatures the Ga-polar face is favored due to the higher lateral growth rate while for higher temperatures the N-polar phase takes over and the film has a rougher morphology. This assignment is supported by the work of Sumiya [79] that observed that using a molar ratio of 2000 and lower (we have used 1000 for these films) mostly the Ga-face film is observed for 600°C films. Also for films grown at 770°C and higher N-polarity film have been obtained in MBE [107, 108 (770 and 900°C with BL by MBE), 109 (810°C by MBE, no BL)] and no results have been published for MOCVD. The surface morphology of the GaN film grown with and without buffer layer observed by Nakamura [18] is consistent with this possible explanation.

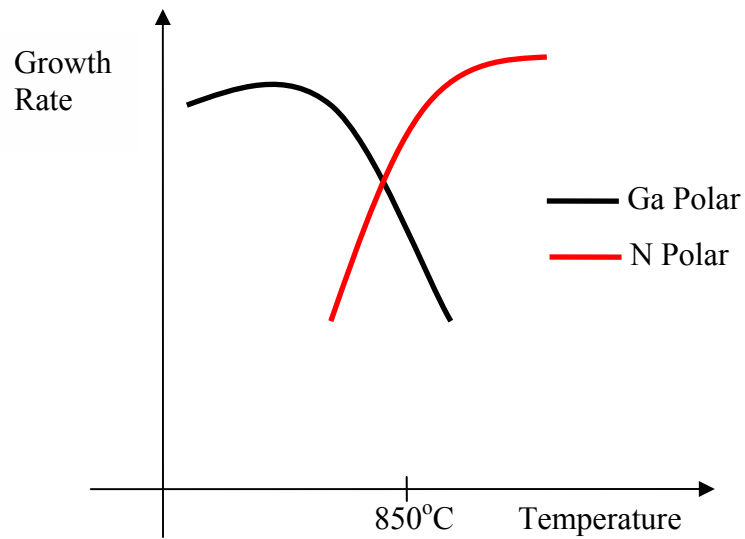


Figure 6.2 Possible growth mechanisms for the two GaN polar orientations

This can explain the different growth mode observed at low temperatures (2D) and high temperatures (2D+3D) due to the different interface chemistry specific to the two polar systems [105]. The fact that the film grown at 850°C is incomplete can be due to the lower diffusion length of the Ga atoms when the growth is N-polar.

If we look at the maximum growth rate we observe that the highest growth rate for a complete film is about 10 $\mu\text{m/hr}$ and corresponds to a temperature of 750°C. The minimum thickness is obtained for a growth temperature of 450°C with a maximum thickness of 102 nm corresponding to a growth rate of 0.36 $\mu\text{m/hr}$. The growth rate at 1050°C the highest temperature investigated is 0.43 $\mu\text{m/hr}$. For intermediate temperatures 550°C to 950°C the growth rate does not have strong temperature dependence and has a value of approx 10 $\mu\text{m/hr}$. If we draw the maximum growth rate as a function of the reciprocal temperature we obtain an Arrhenius plot shown in figure 6.3 that shows the three main regimes for the CVD process.

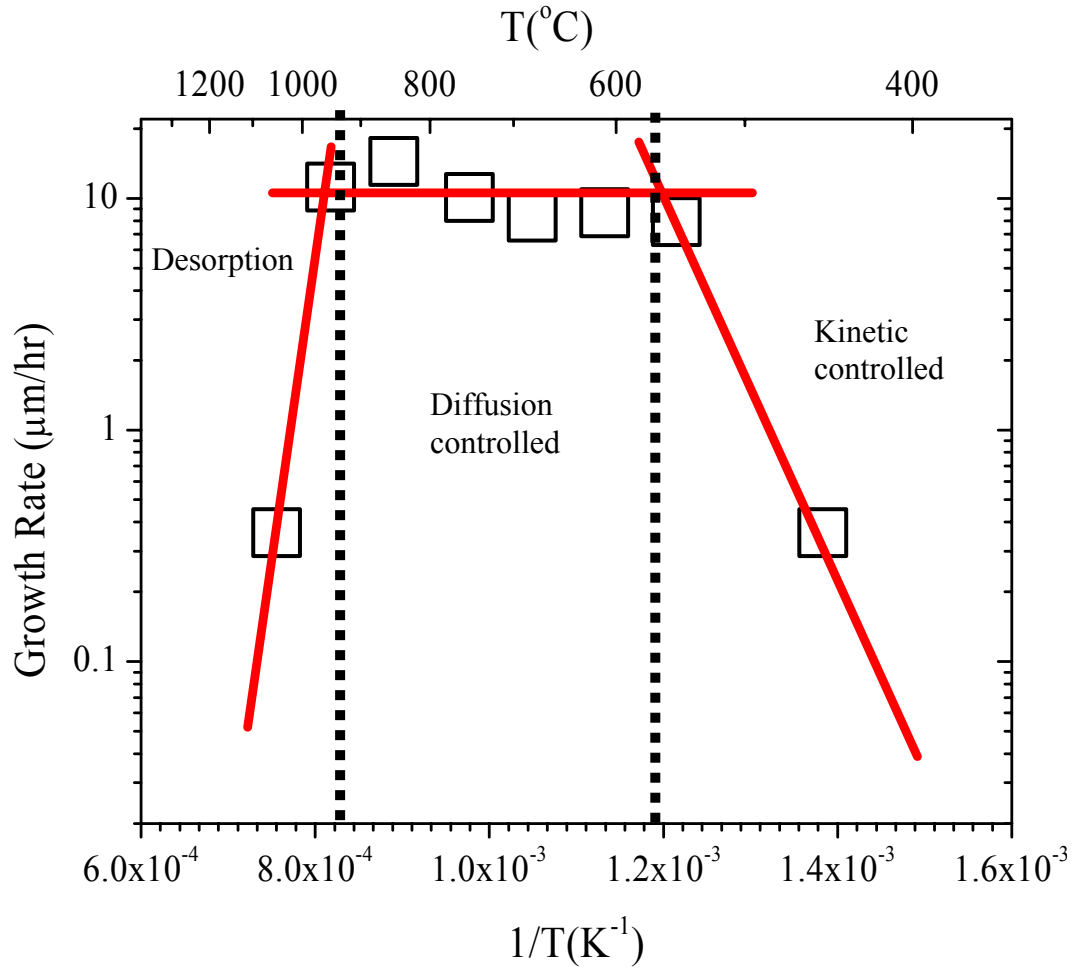


Figure 6.3: Arrhenius plot of the maximum growth rate vs. inverse temperature

From Figure 6.2 the low growth rate at low temperatures indicates thermally activated deposition chemistry kinetics. To determine the activation energy (E_a) for the right side portion of the graph we have used the Arrhenius equation $G = A \exp(-E_a / RT)$ where G is the growth rate, A is the Arrhenius pre-exponential factor, $R = 8.314 \text{ J/mol K}$, and E_a the activation energy that is the rate limiting process under the given conditions. In the temperature range 720 – 820K the activation energy is 169 kJ/mol (or 1.75eV) which is close to other value [82] but higher than 1.1eV obtained for a standard CVD reactor [110]. In the temperature interval 820-1220K the growth rate show almost no temperature dependence that mean the growth is determined by the diffusion of the precursor molecule fragments to the substrate through the boundary layer. At the high temperatures over 1220K the growth rate decreases because of the

desorption and depletion processes consistent with the typical behavior of a CVD process. For intermediate temperatures another study has found a linear dependence [33] of the growth rate with temperature contrasting with the results found in this work. A possible reason can be a lower activation energy for that particular reactor chamber that will extend the kinematic regime to higher temperatures. An argument in favor of this hypothesis is the large non-uniformity in thickness for the samples grown at higher temperatures (850°C and 950°C). The significance of large activation energy is that it indicates that the Ga and N precursor fragments do not carry sufficient energy for the reaction to occur and the hot substrate is absolutely necessary for the chemical reaction and deposition.

Two types of typical thickness variation distributions across the substrate surface have been observed and they are shown in Figure 6.4 for samples grown at 750°C (a) and 950°C (b). In both cases the maximum thickness is obtained for the corner of the sample pointing towards the direction from where the precursor gases are introduced in the chamber. The minimum thickness is obtained in the center of the substrate for samples grown at temperatures lower or equal to 750°C and for samples at higher temperatures the minimum thickness is observed in the corners opposite to the precursor gas entrance as seen for the sample grown at 950°C. The samples grown at higher temperature have a higher overall non-uniformity in thickness (up to -10%/mm) as seen in Figure 6.4.

We attribute this different behavior to the difference in the gas flow patterns in the reactor chamber when different substrate temperature affect the amount of convection currents above the substrate and consequently changes the thickness of the boundary layer that the chemicals have to diffuse through in order to reach the substrata and react. The laminar flow of the precursor gases is perturbed by the upward convection currents created by the heated substrate and this creates a different boundary layer thickness configuration and consequently a different thickness of material is deposited. In general the thicker the boundary layer the longer it takes for the precursor gases to diffuse through it and the smaller the thickness of the film.

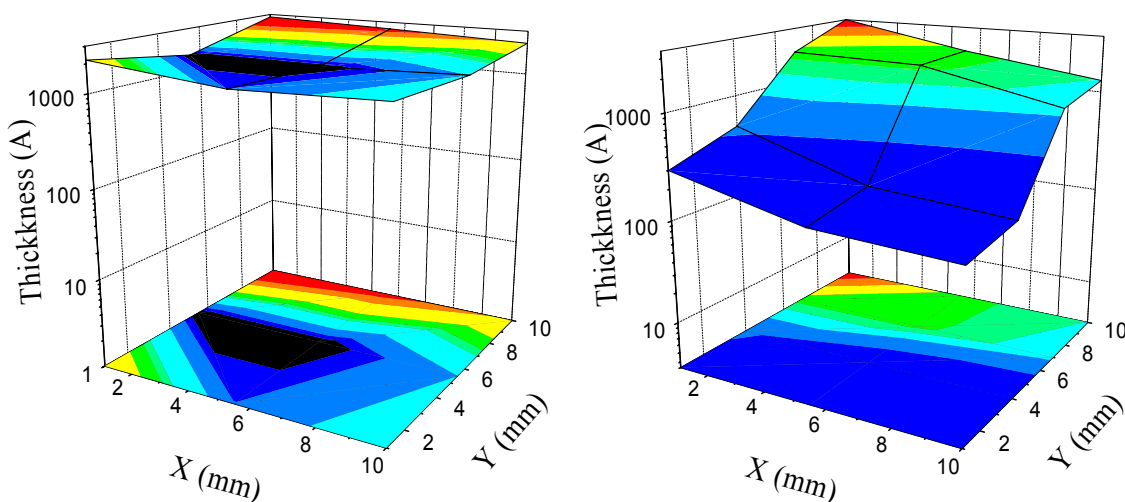


Figure 6.4: Typical thickness variations across the substrate surface

In the following I will present the RBS results for the entire set of samples that have been used for these graphs. Using this analysis technique we have obtained information on the composition of the film, stoichiometry, possible impurities and contaminants incorporated in the film, thickness variation and non-uniformity of the film across the surface of the substrate, and even coverage fraction for films that are not completely coating the substrate.

One limitation of this method is the macroscopic size of the area probed by the ion beam. Due to this and the non-uniform thickness of the films we cannot determine very precisely the thickness but rather the maximum thickness and the magnitude of the non-uniformity for the area analyzed.

The films grown at 450°C are very thin, Figure 6.5 shows the RBS spectra and RUMP simulation for such a film that has a thickness of ~ 2 ML. Due to the small thickness the technique cannot detect the nitrogen signal but using XPS we confirmed the deposition of GaN.

As the substrate temperature is increased to 550°C the thickness of the film increases as seen in the RBS spectrum. At this temperature the film has the highest thickness uniformity of approximately 50% across the 10 mmx10 mm substrate.

The films grown in the temperatures range of 550°C to 750°C have similar thickness variation across the surface. The films are completely covering the surface with a thickness variation in the range of 100 nm to 300 nm. Typical RBS spectra for the films grown at temperatures from 550 to 750°C are shown in Figure 6.6-7.

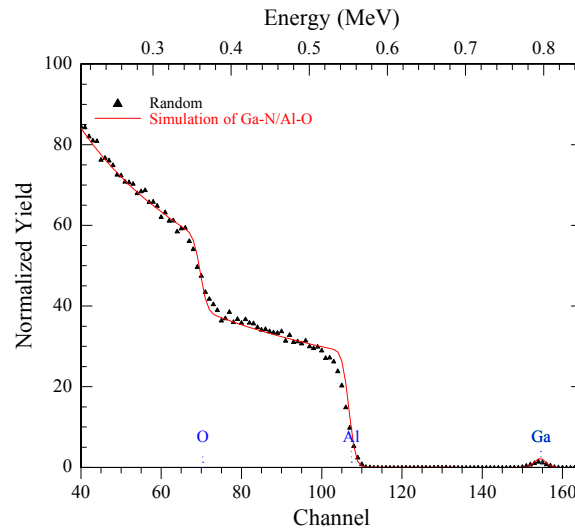


Figure 6.5: Sample 450°C random and RUMP simulation of a film grown at 450°C with a thickness of 1.5ML

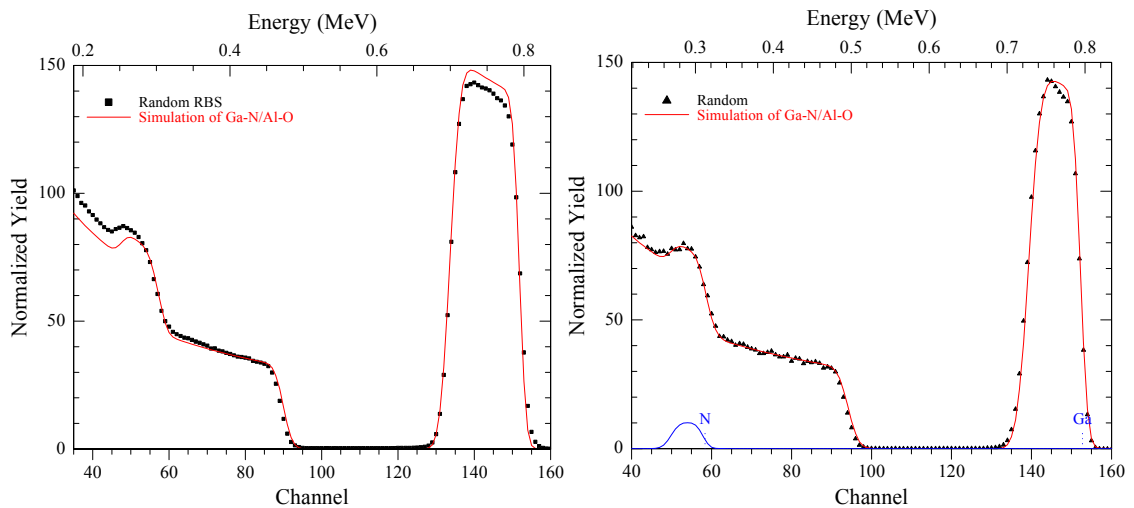


Figure 6.6: The random RBS and RUMP simulation for a film grown at 550°C with a thickness of 200 nm and non-uniformity of 25nm (left) and at 610°C with a thickness of 140 nm and non-uniformity of 30 nm (right)

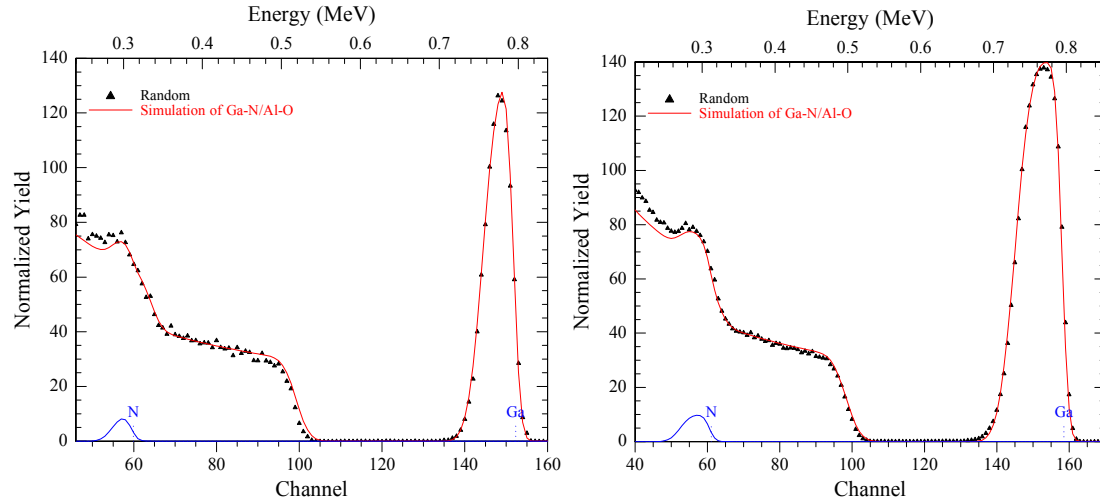


Figure 6.7: The random RBS and RUMP simulation for a film grown at 680°C with a thickness of 80 nm and non-uniformity of 40 nm and at 750°C with a thickness of 135 nm and non-uniformity of 50 nm

The film grown at a substrate temperature of 850°C is significantly different than the ones obtained for lower temperatures. The film shows a higher degree of thickness non-uniformity (50-450 nm) and from the RBS signal one can determine that the film is not covering the entire substrate. This was also confirmed from the XPS analysis where the substrate signal is visible and from the electron microscopy (Chapter 7). The films grow in the form of islands with a tall aspect ratio. The amount of coverage is not constant across the substrate but follows similar trend as the thickness of the islands: where the islands are taller they also cover more than in the regions where islands are shorter. In addition to the island-like film, in some regions the islands are sitting on top of a thin continuous 8 nm GaN layer. For the regions with a low amount of material deposited the nucleation density can be determined from the SEM pictures (Chapter 7). Figure 6.8 shows two typical morphologies for this film: 65-465 nm thick islands (Ga:N:Al:O = 0.25:0.25:2:3) on a 8 nm thick continuous GaN layer. d) 180-360 nm thick islands (Ga:N:Al:O = 0.6:0.6:2:3) on sapphire.

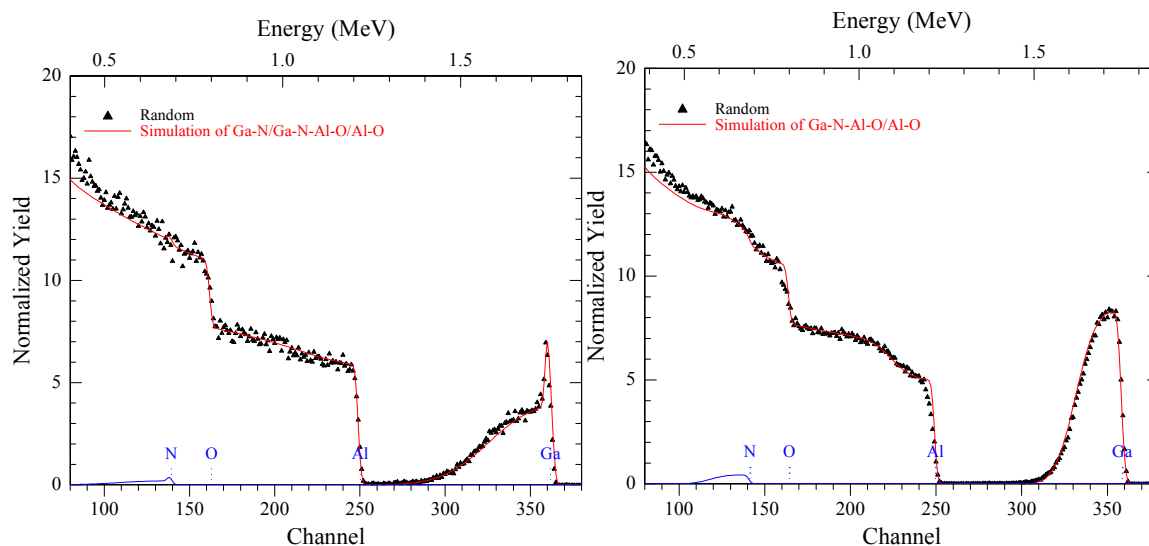


Figure 6.8: Typical RBS spectra and the RUMP simulations for films grown at 850°C

At 950°C substrate temperature the film thickness is very non-uniform from 350 nm at the thickest point down to 15 nm at the opposite corner. Figure 6.9 shows two RBS spectra and the corresponding RUMP simulations at two different points. Unlike the films grown at 850°C this time the film is continuous and SEM shows the morphology of the film to be either flat or with micron-size hexagonal islands on top of a flat film.

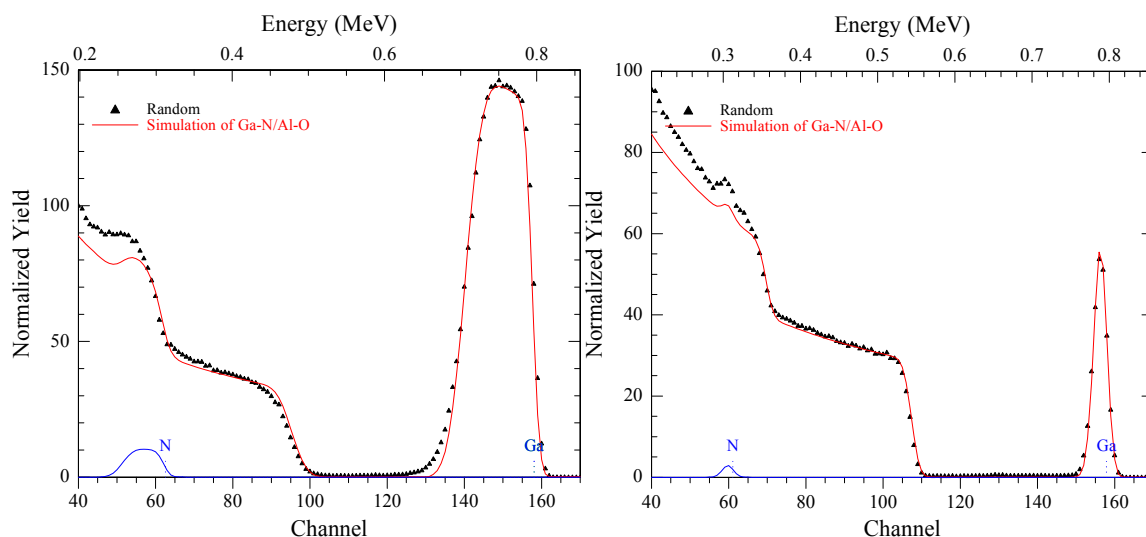


Figure 6.9: RBS and RUMP simulation for films grown at 950°C with a thickness of 185 ± 5 nm and non-uniformity of 50 nm (left) and with a thickness of 18 nm (right).

For the films grown at 1050°C we only obtain a thin layer with a maximum thickness of 14 nm and a minimum of approx. 2nm shown in Figure 6.10. The thickness uniformity across the surface is improved compared with the samples grown at 850°C and 950°C. It is not possible from RBS alone to determine if the film is continuous or it has islands.

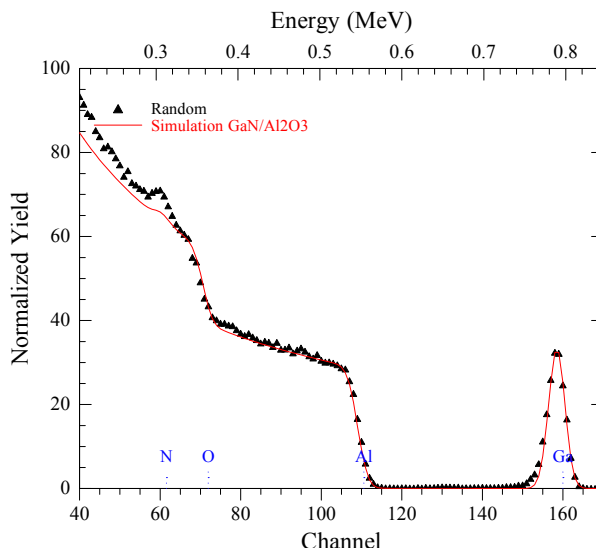


Figure 6.10: Random RBS and RUMP simulation for a GaN film grown at 1050°C with a thickness of 14 nm

6.2 Surface structure – LEED

We have investigated the surface structure and ordering of the GaN thin films using Low Energy Electron Diffraction (LEED). This experimental technique is very sensitive to surface contamination and that is why the in-situ analysis is necessary. The UHV transfer system described in the setup chapter allowed the transfer of a sample from the deposition chamber into the analysis chamber with minimal contamination. The LEED analysis shows the symmetry and structure of the surface. The two phases of GaN have either cubic or hexagonal symmetry, and this experiment it is able to identify which one of the phases is on the surface, unlike the ion-channeling method that relies on the bulk of the crystal. This two technique are used together to observe the symmetry of the film by giving complementary information. Faceting of the surface can also be determined from the diffraction patterns. One complication in the acquisition of the patterns is the

charging of the substrate due to the insulating nature of the sapphire and GaN material. This charging effect makes the observation of the patterns more difficult and it makes necessary a higher accelerating potential for the electrons in order to penetrate through the space charge that accumulates at the surface of the sample.

Typical LEED patterns for the films grown at temperatures from 610°C to 1050°C are shown in Figure 6.11-13. The common features of the LEED patterns observed for the GaN films grown is that they have hexagonal symmetry, and show no sign of faceting or reconstructions. For films grown in the range 450°C to 550°C we record no diffraction patterns. Starting with the film grown at 610°C we can see hexagonal, weak and sometimes diffuse patterns. As the substrate temperature is increased the sharpness of the patterns is improved. There is no change in the symmetry of the LEED patterns as the growth temperature is increased. The sharpest of the patterns is obtained for the film grown at 950°C. The pattern obtained for the film grown at 1050°C could be from the film or the substrate taking into account the small film thickness.

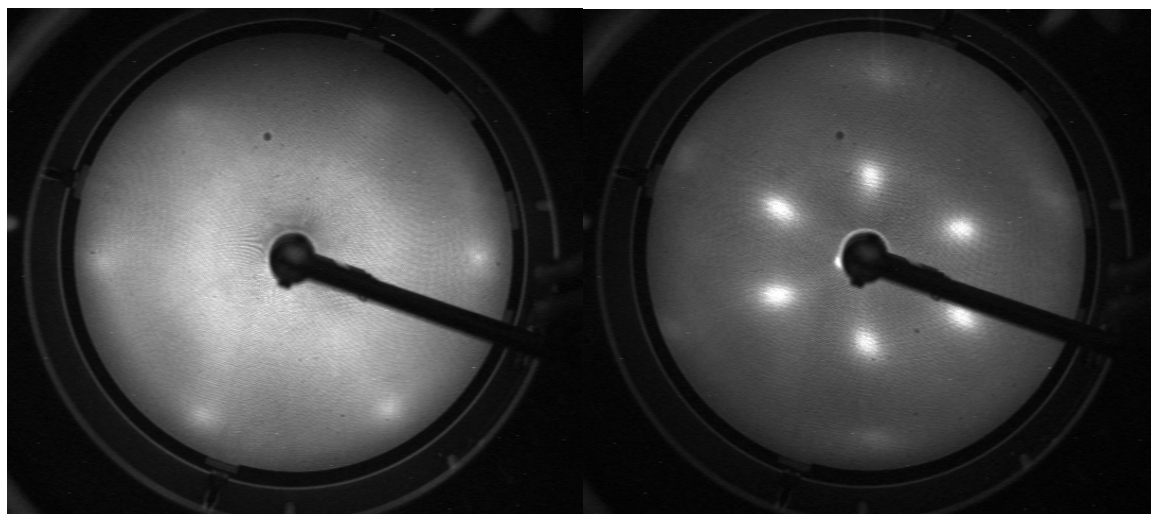


Figure 6.11: LEED Patterns for film grown at 610°C (left) and 750°C (right)

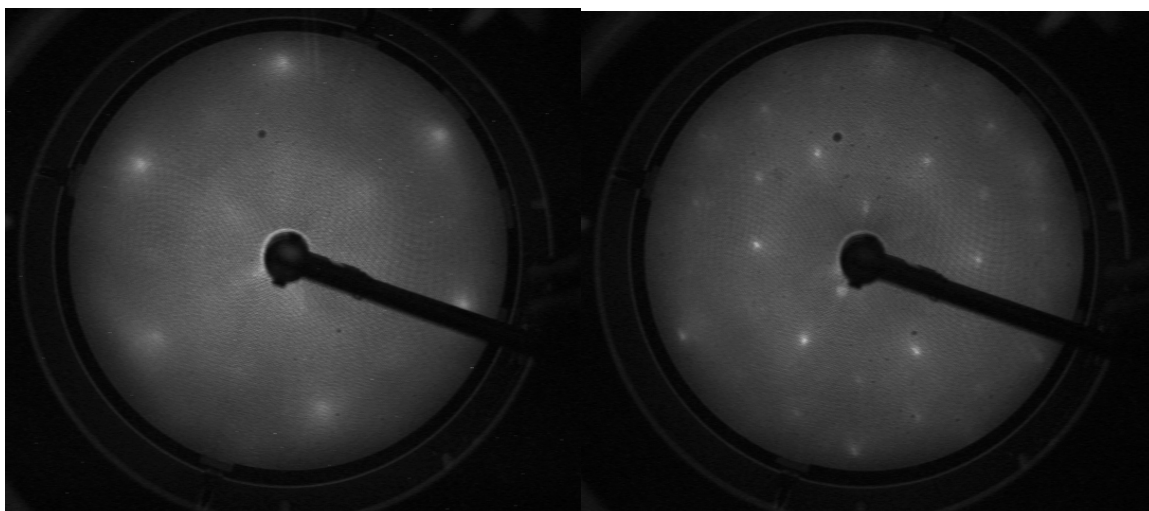


Figure 6.12: LEED Patterns for film grown at 850°C (left) and 950°C (right)

No four-fold symmetry patterns or mixed (four-fold and hexagonal) have been observed on any of the films grown, an indication that only the hexagonal (wurtzite) phase of GaN grows in our deposition conditions.

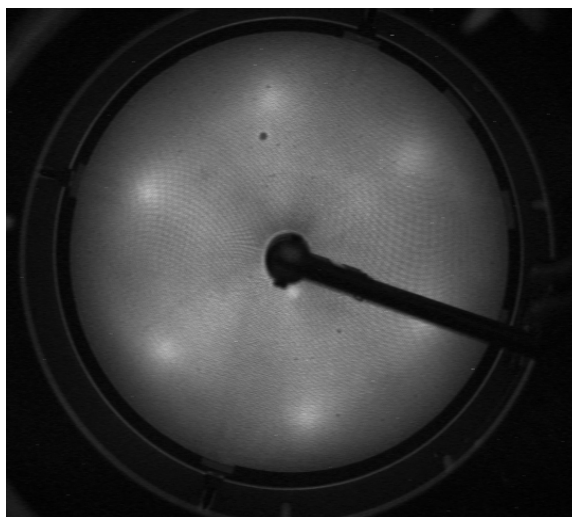


Figure 6.13: LEED Patterns for film grown at 1050°C

From this investigation we can conclude that the surface of the film is starting to be ordered at atomic level around the growth temperature of 610°C. The sharpness and intensity of the LEED patterns is improved with deposition temperature and for films

with better surface morphology as seen in SEM (Chapter 7). The hexagonal patterns observed are specific to un-reconstructed surfaces.

From the comparison of the LEED patterns with the ion channeling results we observe that the surface ordering is observed for samples showing a poor crystallinity, such as the film grown at 610°C. This is indicative that the surface ordering alone is not a good indication that the film is a single crystal and other complementary bulk-sensitive techniques are necessary (such as ion channeling) in order to establish if the film is a good crystal.

Munkholm et al. [49] have found two possible surface reconstructions for 2 μm thick GaN films, and has determined the equilibrium phase diagram (Figure 6.14) for the partial pressure of ammonia during growth in the range 1-140 Torr.

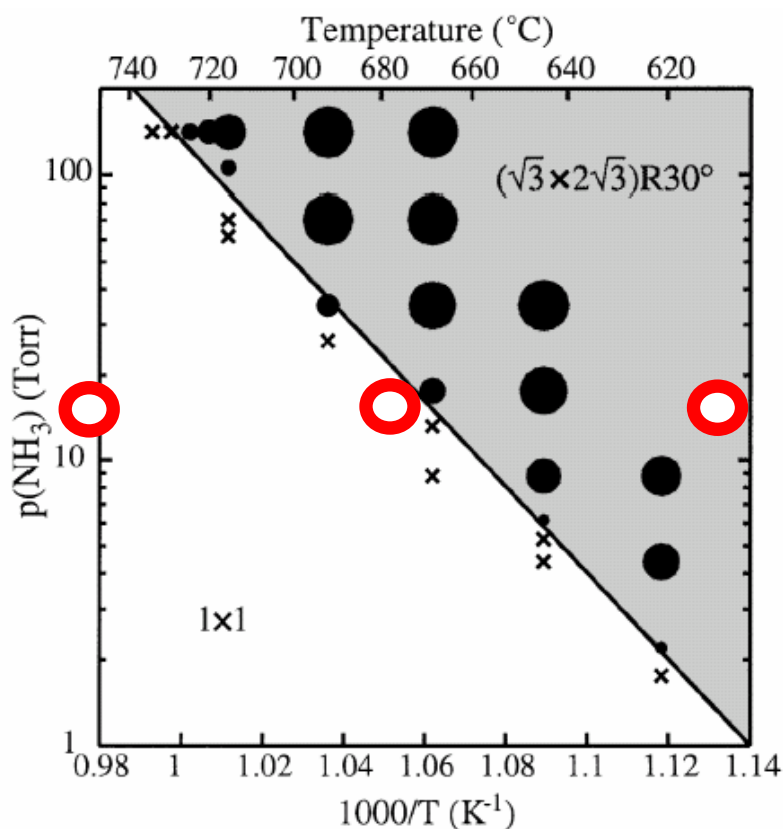


Figure 6.14: Equilibrium phase diagram of the GaN(0001) surface under MOCVD conditions, as obtained from grazing-incidence x-ray scattering [49]

Shaded area denotes conditions where the $(\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstruction is observed; crosses show conditions where the reconstruction is not present. On this phase diagram the samples grown by us are at 610°C, 680°C, and 750°C and are marked with large red empty circles. Since no such reconstruction is observed in our LEED patterns for the samples grown at 610°C we can conclude that the surface is reverting to the 1×1 configuration upon cooling down in N_2 flow. No other reports are available on the in-situ behavior of the MOCVD GaN surface upon cooling down. Samples prepared at 1050°C and exposed to air have shown bulk like 1×1 structure [111].

Unlike the 1×1 surfaces observed by Smith [69] in our case no satellites are observed and therefore no Ga-rich surface is presumed.

Janzen et al. [71] has observed the splitting of the main diffraction peaks into circular sextets for certain beam energies and has attributed this to the presence of terraces of 11 Å width and monolayer high that could be created by the spiral growth around the screw dislocations.

6.3 Surface chemistry – XPS

6.3.1 Surface composition

We have performed in-situ XPS chemical analysis of the GaN films as well as investigated the contamination by depth profiling XPS and Angular XPS. Both Al $K\alpha$ and Mg $K\alpha$ X-ray radiation has been used. The need for using two X-ray radiations for the measurements is due to the overlap of the N 1s and O 1s line with a Ga LNN Auger series when the Al $K\alpha$ x-ray is used and the overlap of the C 1s and Ga 3s XPS peaks with the Ga LNN Auger series when Mg $K\alpha$ is used. Using the two x-ray sources we can make a quantitative estimate of the surface composition. Figure 6.15 shows typical XPS spectra taken using the two sources. All the samples investigated show similar characteristics of the XPS spectra.

The region of interest is between 0 and 600 eV where most of the peaks are located as seen in Figure 6.16. Table 6.1 shows the results of the XPS analysis for samples as-deposited and exposed to air.

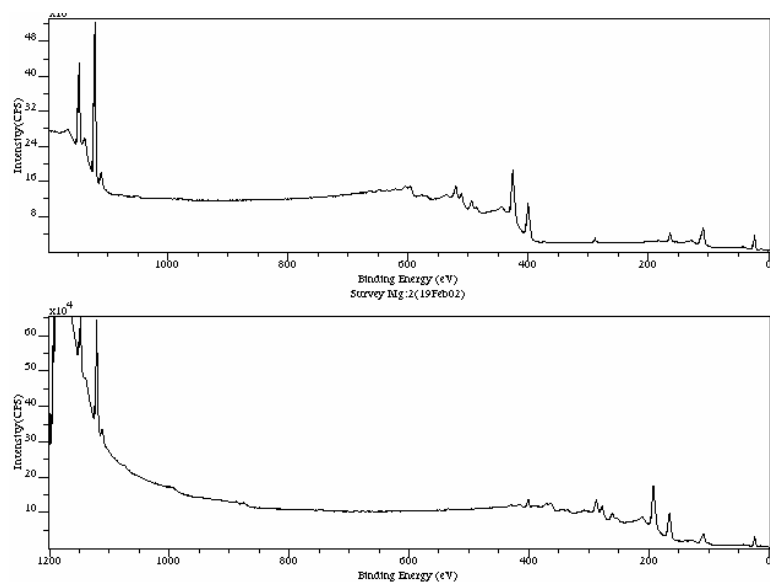


Figure 6.15: Typical XPS spectra take with the Al and Mg anode for a GaN film

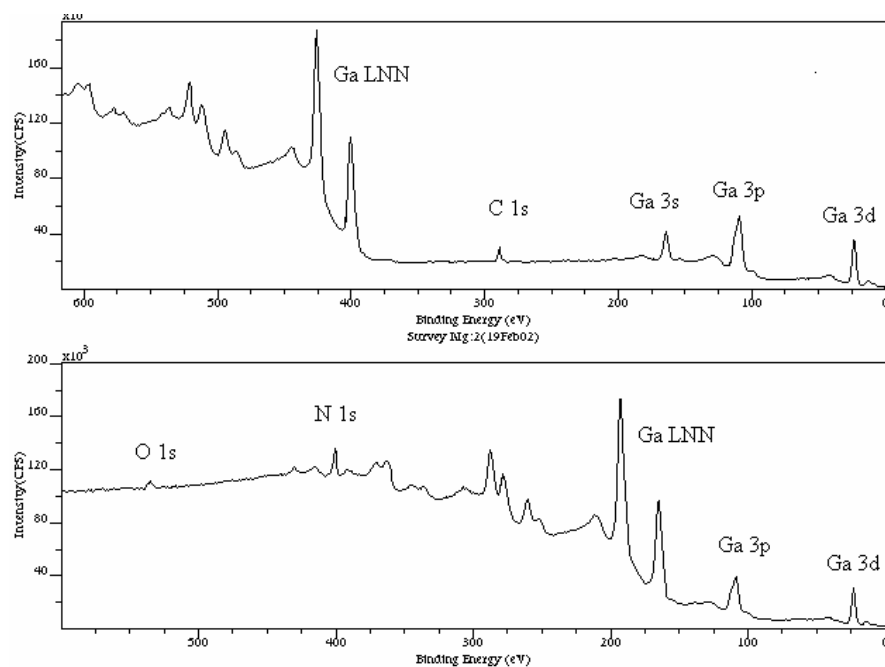


Figure 6.16: Region of interest in XPS with the main peaks

Table 6.1: XPS analysis of the GaN films

Temp (°C)	Observations	Ga 3p	N 1s	C 1s	O 1s	Al 2p
450	as-deposited	0.0666	0.096	0.135	0.401	0.301
550	as-deposited	0.453	0.327	0.176	0.044	N/A
610	as-deposited	0.369	0.269	0.267	0.093	N/A
680	as-deposited	0.4	0.35	0.176	0.072	N/A
750	as-deposited	0.387	0.40	0.136	0.076	N/A
850	as-deposited	0.368	0.343	0.1419	0.096	N/A
1050	as-deposited	0.247	0.244	0.315	0.124	0.069
550	air exposed	0.164	0.024	0.691	0.121	N/A
610	air exposed, annealed	0.395	0.261	0.18	0.163	N/A
680	air exposed	0.37	0.32	0.20	0.09	N/A
850	air exposed	0.369	0.326	0.139	0.105	N/A
950	air exposed	0.335	0.134	0.402	0.129	N/A
1050	air exposed, substrate	0.045	0.067	0.256	0.40	0.231
1050	air exposed, substrate	0.1766	0.259	0.269	0.155	0.138

The XPS has been performed in constant pass energy mode with pass energy of 80eV for surveys spectra and 20 eV for regional (peak) spectra. The step size was 1 eV for surveys and 0.1 eV for core level peaks, and the dwell time was 250 ms per step for all measurements. The range of binding energy scanned was 0-1200eV for the Mg K α source and 0-1400eV for the Al K α source. For surveys spectra the data was averaged over three spectra while for core level peaks the data was averaged over 10 spectra.

The charging effect produced a 1-5 eV shifting towards higher binding energies in some spectra, therefore all spectra is referenced to the adventitious carbon peak at 285eV.

No metallic gallium on the surface in the spectra has been observed for any of the samples nor did we observe any chemical shift or splitting of the lines.

From the Table 6.1 we estimated that the stoichiometry of the surface of the as-deposited films is close to 1:1. The average of the ratio of Ga to N atoms is 1.217 with a

standard deviation of 0.200 for the as deposited films and 2.627 with a standard deviation of 2.416 for the films exposed to the atmosphere. The higher spread for the exposed films is due to the observed tendency of the Ga to N ratio to increase with time after they are taken out of the UHV environment.

The peaks used in the quantification for the main elements present on the surface of the film (Ga, N, C, O) are shown in Figure 6.17.

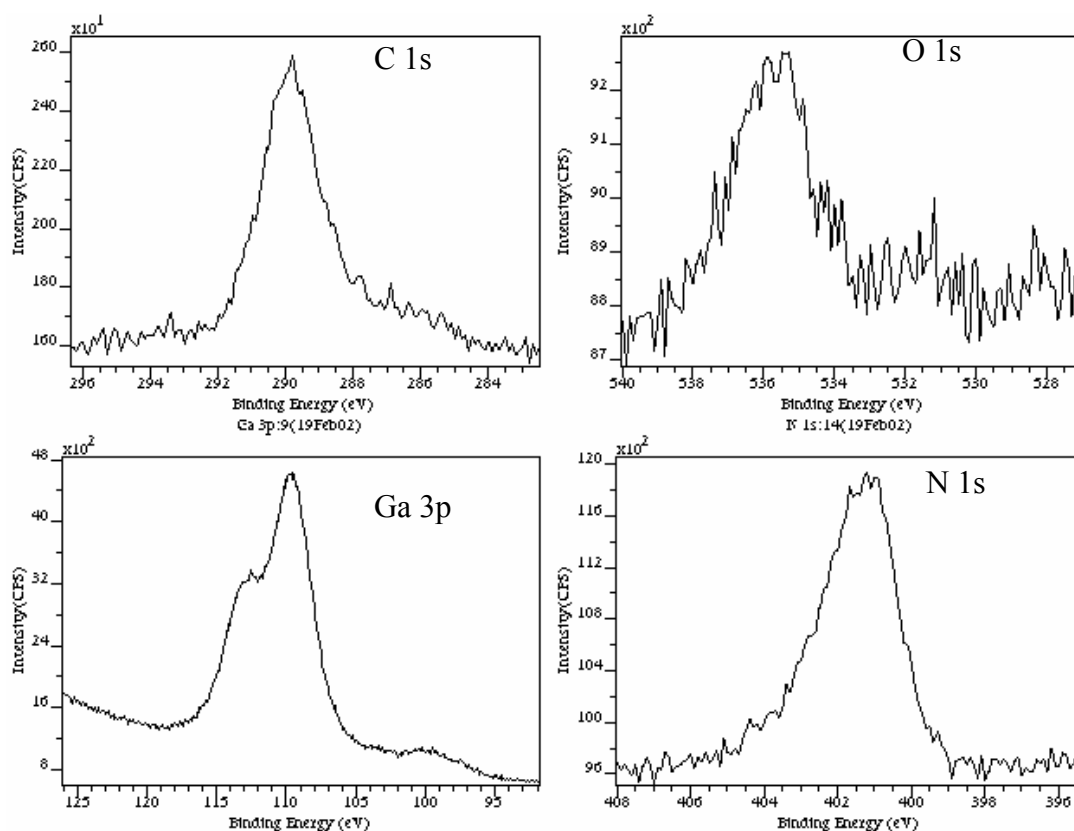


Figure 6.17 Typical peaks for C-1s, O-1s, Ga-3p and N-1s used in quantitative analysis of the GaN films

For Ga quantification there are 4 available peaks (2p, 3s, 3p, and 3d) but due to the following considerations we have used the 3p peak for quantitative analysis. The 2p peak gives inconsistent results compared to the other three peaks. The binding energy of this peak is very large compared to the other peaks used for quantitative analyze and this can give rise to miscalculations when the film thickness is of the same order of magnitude with the mean free path and mean escape depth of the electrons from the film. The 3s

peak interferes with Al peaks and cannot be used when the film is very thin or has incomplete coverage. The 3d peak has too low a binding energy compared to the other 3 elements and is very close to an O peak.

6.3.2 Surface contamination

We have investigated the contamination of the film and surface by XPS. By taking spectra from the as-deposited films and after exposure to air one can see an increase in the signal coming from oxygen and carbon and a decrease of the nitrogen and gallium peak. This is consistent with a surface contamination with CO_x and H_2O vapors. Similar results on contamination have been obtained by Ishikawa [112], but unlike this study no extra peak corresponding to a 2nm thin Ga_2O_3 has been observed. In this evaluation both XPS spectra taken with the Al and Mg anode are needed due to the overlap of the N_{1s} line with an Ga Auger line in the Al spectra and the overlap of the C_{1s} peak with an Auger line in the Mg spectra. Figure 6.18 shows the XPS spectra of the as-deposited GaN film (blue line) and the GaN exposed to the atmosphere (green line).

From the Table 6.1 one can see that after the exposure of the films to the atmosphere the surface contamination with C has increased from an average 14.8% to an average 31% and for O from an average of 7.2% to an average of 11.6%. Simultaneously with the increase in C and O the Ga to N ratio increases as shown in the previous section. The level of contamination is proportional to the length of time the sample has been kept outside of the vacuum, showing no saturation over a period of two weeks.

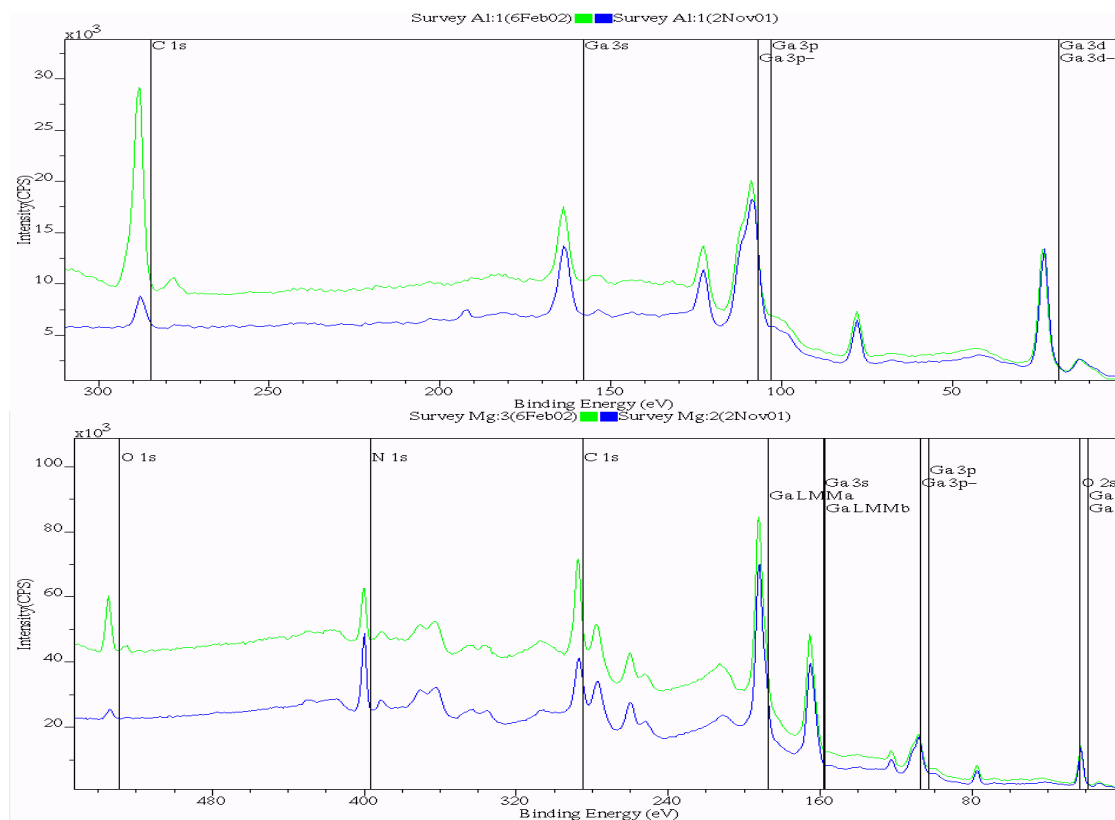


Figure 6.18: XPS for as-deposited and air-exposed sample taken with Al and Mg X-ray source

6.3.3 Angular XPS

In order to investigate the nature of the contamination with O and C we have performed an angular XPS. For this experiment we have tilted the sample with respect to the direction of the analyzing lens at an angle of 65 degrees and compared the intensity of the peaks for this tilted position with the ones given at normal incidence. Figure 6.19 shows the results for the four peaks investigated: C_{1s}, N_{1s}, O_{1s}, and Ga_{3p}. Both Al and Mg x-rays have been used due to the Auger interference with N and O peaks.

The relative composition of the film is shown in the Table 6.2 for the two take-off angles (measured with respect to the normal to the film).

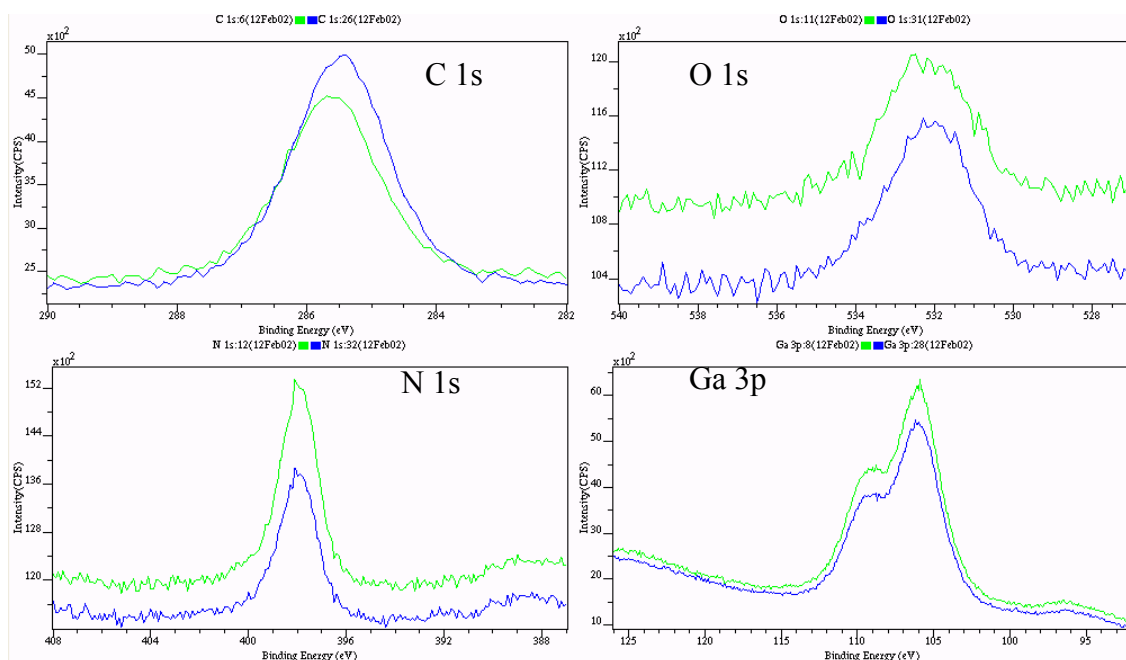


Figure 6.19 Angular XPS, green line corresponds to a 0 degree take-off angle and the blue line corresponds to a 65 degrees take-off angle with respect to the normal to the surface

Table 6.2 Composition of the film as a function of the take-off angle

Take-off angle (deg)	Ga 3p	N 1s	O 1s	C 1s
0	0.378	0.323	0.094	0.204
65	0.337	0.299	0.107	0.255

We see a decrease in the relative intensity of the Ga-3p and N-1s peaks and an increase of the O-1s and C-1s peaks. Due to the surface sensitivity of the XPS analysis this is a signature of surface contamination by C and O. The increase in C signal is relatively higher than the one in O. The position of the C-1s peak is also shifted by about 0.9eV towards the lower Binding Energy. This chemical shift is an indication of the fact that the C-1s peak is in fact of at least two peaks corresponding to different bonding of

the C atoms (C-O, C-Ga, C-N). These two or more peaks, due to the fact that are not at the same depth, have a different angular dependence and the relative variation of the intensities produces the shift in the compounded peak.

6.3.4 Etching of the GaN films by ion gun sputtering

In order to investigate the extent of bulk contamination of the film we have subjected the film to ion sputtering in order to etch out the surface layers. We have taken a as-deposited sample analyzed, taken out of the vacuum environment, re-introduced in the analysis chamber and re-analyzed. Using a beam of Ar ions with energy of 4keV scanned across the surface of the sample on an area of about 2x1 mm we have etched in steps of 10 minutes at an ion current 1μA and taken XPS spectra at the beginning and after each etch step. The last analysis step corresponds to 48 hours after the last etch and shows the rate of contamination that the sample is experiencing while in the vacuum. The pressure in the vacuum chamber where the sample has been kept was $\sim 5 \times 10^{-9}$ torr. We have used both Al and Mg X-ray radiation due to the overlap of the peaks mentioned before.

The results of the composition analysis at every step are shown in Table 6.3 and are graphed in the Figure 6.20.

Table 6.3 Surface composition as a function of etch time

Step	Description	Ga 3p	N 1s	O 1s	C 1s
0	As-deposited	0.453	0.327	0.044	0.176
1	After exposure to atmosphere	0.164	0.0244	0.121	0.69
2	Sputtering for 10 minutes at 1 μA	0.658	0.072	0.043	0.227
3	Sputtering for 10 minutes at 1 μA	0.569	0.245	0.0419	0.142
4	Sputtering for 10 minutes at 1 μA	0.590	0.263	0.041	0.109
5	After 24 hours in analysis chamber	0.581	0.099	0.104	0.216

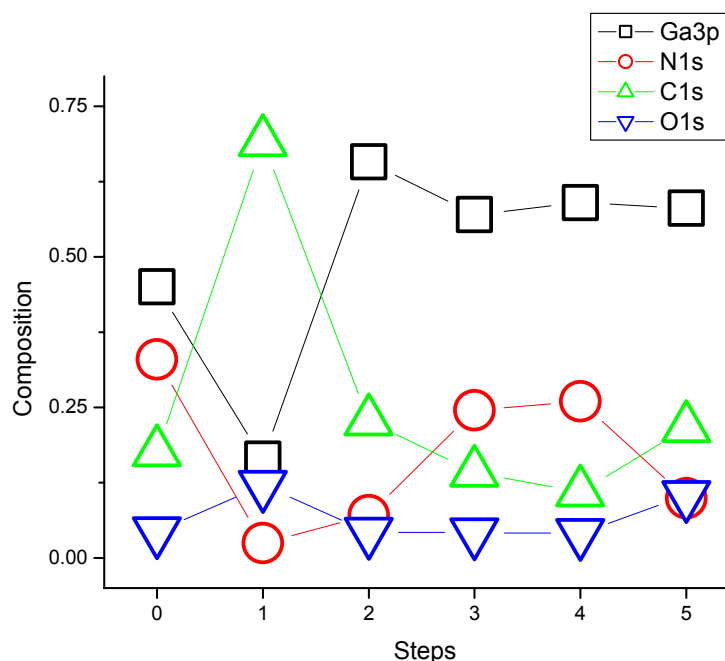


Figure 6.20: Intensity of the XPS signal coming from Ga, N, C, and O during the steps shown in Table 6.3

After the etching steps we observe a strong decrease in the oxygen and carbon peaks and increase in nitrogen and gallium. One can notice the fact that the Ar sputtering process produces a non-stoichiometric surface with traces of C and O even after long sputtering times. The intensity of Nitrogen signal does not come back to the level from in-situ analysis right after the deposition due to a higher sputtering rate of nitrogen compared to gallium atoms when the Ar ion gun is used. The ratio of the number of Ga to N atoms for the sputtered surface is of the order of 2.36 compared to an average of 1.217 for the as deposited samples. This demonstrates the danger of doing sputter cleaning in changing the stoichiometry and chemistry of the surface.

Letting the sputtered sample sit for a few days in the analysis chamber brings the level of contamination to levels close to the value before sputtering and the surface is still non-stoichiometric showing that even in UHV conditions where the partial pressure of reactive gases such as oxygen and nitrogen are less than 10^{-12} torr oxygentation of the surface occurs this effect can be amplified by a reactive and unstable surface such as the one resulted from the sputtering process.

Figure 6.21 shows a region of the survey XPS scan with the peaks used for analysis introduction in the analysis chamber and after 2 etching sessions. The procedure has the effect of increasing the intensity of the electron emission both by XPS and Auger spectra.

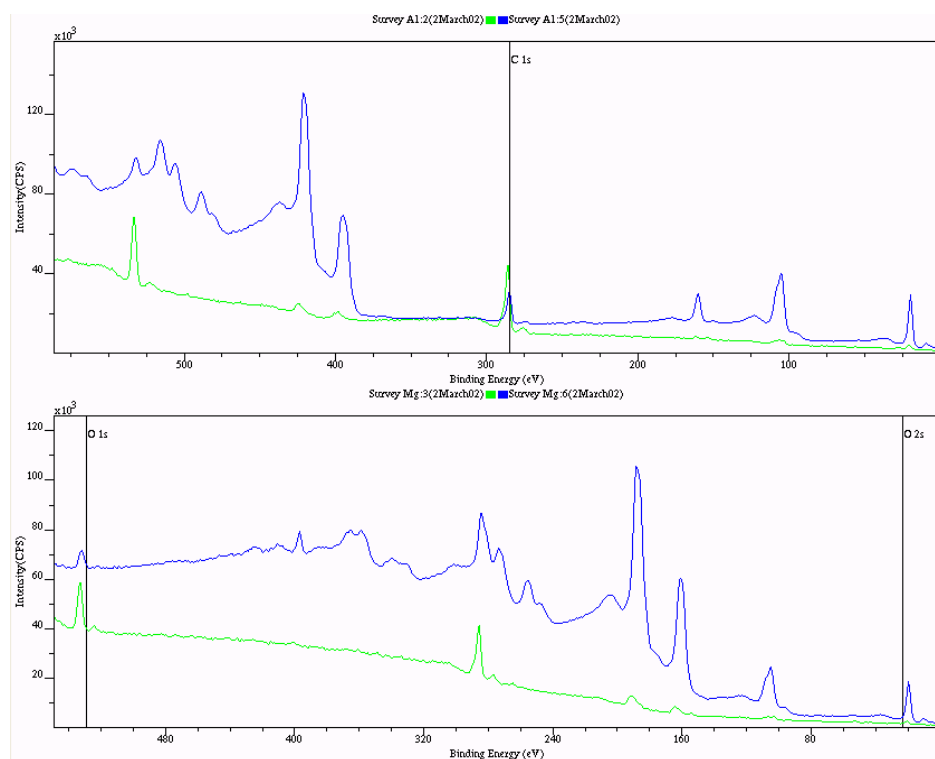


Figure 6.21: XPS survey spectra before etching (green) and after etching for 20 minutes at $1\mu\text{A}$ with Ar ions (blue) with Al and Mg x-ray

A study has found [112] a similar result that N is preferentially sputtered by the Ar beam, with a ratio of N/Ga atoms of 0.87 after 10 minutes of sputtering. The ion source used was of type Kauffman with an ion density of $20\mu\text{A}/\text{cm}^2$ and with a sample bias of -200V, these values are lower compared to the ion source that we have used. A different study of the etching of GaN has found no preferential etching for N when using Ar ions up to 500 eV [113]. Hunt [114] has found that a better surface and less N vacancies are obtained by using N ions rather than Ar, for sputtering, followed by an annealing at $\sim 600^\circ\text{C}$. Implantation with both light and heavy ions (C and Au) at energies of 40 keV to 2MeV produce amorphisation of the surface and the preferential loss of N from the surface as seen from the increase of the random RBS signal of the Ga signal [88].

The loss of nitrogen under ion bombardment is especially significant since there is the need for a method for etching of GaN and reactive ion etching will produce a non-stoichiometric surface region.

6.4 Crystalline ordering by Ion Channeling

Ion Channeling allows us to get an insight into the crystalline ordering and the symmetry of a crystal. Unlike the diffraction techniques that produce the reciprocal space image of a crystal the channeling is a direct space technique making the interpretation of the results more straightforward. Although the diffraction techniques (LEED, XRD) can determine if the surface is single crystal, with RBS/Ion Channeling one can detect the single crystals over many millimeters and determine how single crystal thin films relate to underlying single crystal substrate.

The samples grown at the lowest temperature of 450°C show no channeling at all ($\chi_{\min}=100\%$) the film can be either amorphous or polycrystalline with a random orientation. At 550°C substrate temperature there is a slight axial channeling of the order of $\chi_{\min} \approx 96\%$ in the direction perpendicular to the substrate, but we observe no channeling planes. At this temperature the film is probably amorphous or polycrystalline with some of the domains oriented along the growth direction. Figure 6.20-a shows a random (black) and aligned (red) RBS/Channeling spectra for a film grown at 550°C. While the film is very defective and/or missoriented we can still observe the channeling of the substrate below the film an indication that the ion beam is oriented along a crystallographic direction of the substrate crystal.

The sample grown at 610°C does show better channeling (Figure 6.20-b) but no crystallographic planes are visible in a complete map of the yield around the optical normal. For films with thickness from 140 nm to 270 nm the dechanneling level has values in a range $\chi_{\min} = 80 - 90\%$. From angular scans the half critical angle is 1° .

For the sample grown at 680°C one can see a higher level of crystalline ordering since both axial and planar channeling can be seen in the channeling map for Ga that is shown in Figure 6.24-a. Three points on the sample have been analyzed in detail and random and aligned RBS spectra have been taken. The minimum channeling yield is $\chi_{\min}$

=27% (Figure 6.22-c) for the sample 80 nm thick and 20% for the sample 90 nm thick. No surface peak is observed a sign that the structure is not very good. The film of 135 nm has a minimum yield of 16% and a surface peak is visible an indication that at this thickness the quality of the film is improved (Figure 6.22-d)

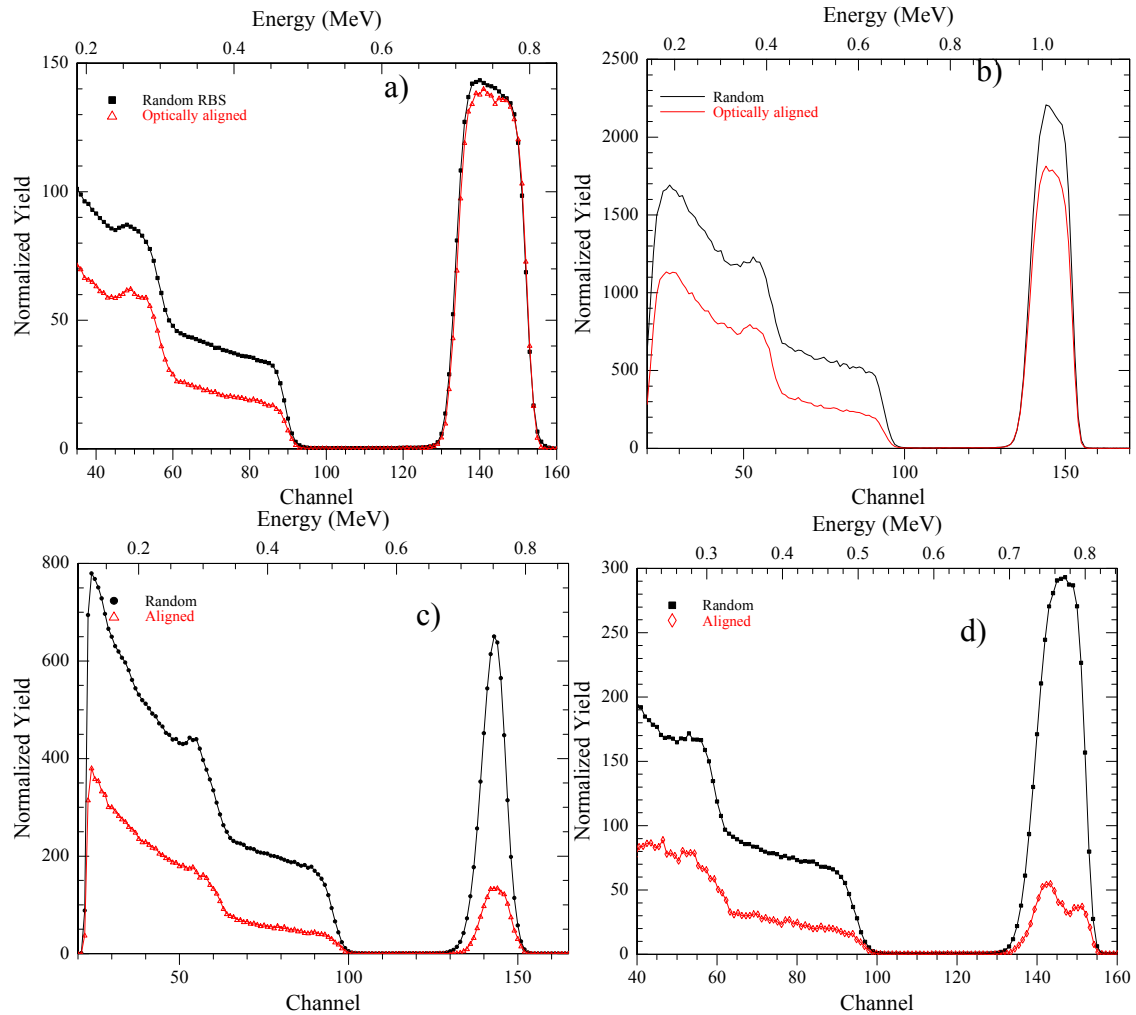


Figure 6.22: Typical RBS random and channeled spectra for samples grown at 550°C (a), 610°C (b), 680°C (c), d)

The film grown at 750°C shows better channeling, the axis as well as the planes are clearly visible in the channeling map (Figure 6.24-b). The hexagonal symmetry of the film is confirmed. The minimum yield is 8.7% for a thickness of 135 nm and non uniformity of 50 nm and the surface peak is visible (Figure 6.23-f).

The growth temperature of 850°C produces a film of two types: one with incomplete coverage and one with a thin full layer followed by an incomplete thick film (as shown previously from the RBS spectra). The channeling of this incomplete film is lower than the one exhibited by the films grown at a temperature of 750°C. Broad axial channeling of 80% is measured (Figure 6.24-c) for a film with a coverage of 35% (Ga:N:Al:O=0.85:0.85:2:3) that is formed by 155 nm tall islands (Figure 6.23-a); and 70% for a film 360nm thick with a coverage of 24% (Ga:N:Al:O=0.6:0.6:2:3). The channeling planes are not visible and the critical angle is 1.75° for both cases (Figure 6.24-c, d). The second type of film formed by islands on top of as thin film shows a better crystalline quality with a minimum yield of 53% for a 400nm thick islands film with a coverage of 34% (Ga:N:Al:O=0.85:0.85:2:3) that was growing on top of a thin 8 nm continuous layer (Figure 6.23-b).

The film grown at a substrate temperature of 950°C shows regions a very good channeling yield and consequently of good crystalline quality. The lowest channeling yield achieved is 3.02% for a thickness of 320nm (Figure 6.23-c) and also 4.5% for a thickness of 185 nm. The channeling map shows good planar and axial channeling (Figure 6.24-e) for the thick regions. The critical angle measured from the channeling map is 0.75°. In the regions of lower thickness the channeling yield is increased to 72% for film 18 nm thick (Figure 6.23-d) and the channeling map shows no planes. The high channeling yield and the absence of crystallographic planes signal a lower quality film in its initial stages of growth.

The film grown at 1050°C is very thin comparatively to the previous ones but has a better uniformity. The channeling map does show a weak maximum around the optical normal and no channeling planes (Figure 6.24-f). For a thickness of 14 nm the channeling yield is 81% (Figure 6.23-e) and the critical angle is 1.12°. This yield is lower than films with similar thickness grown at different temperatures indication that for this temperature the quality of the film in the early stages of growth is improved.

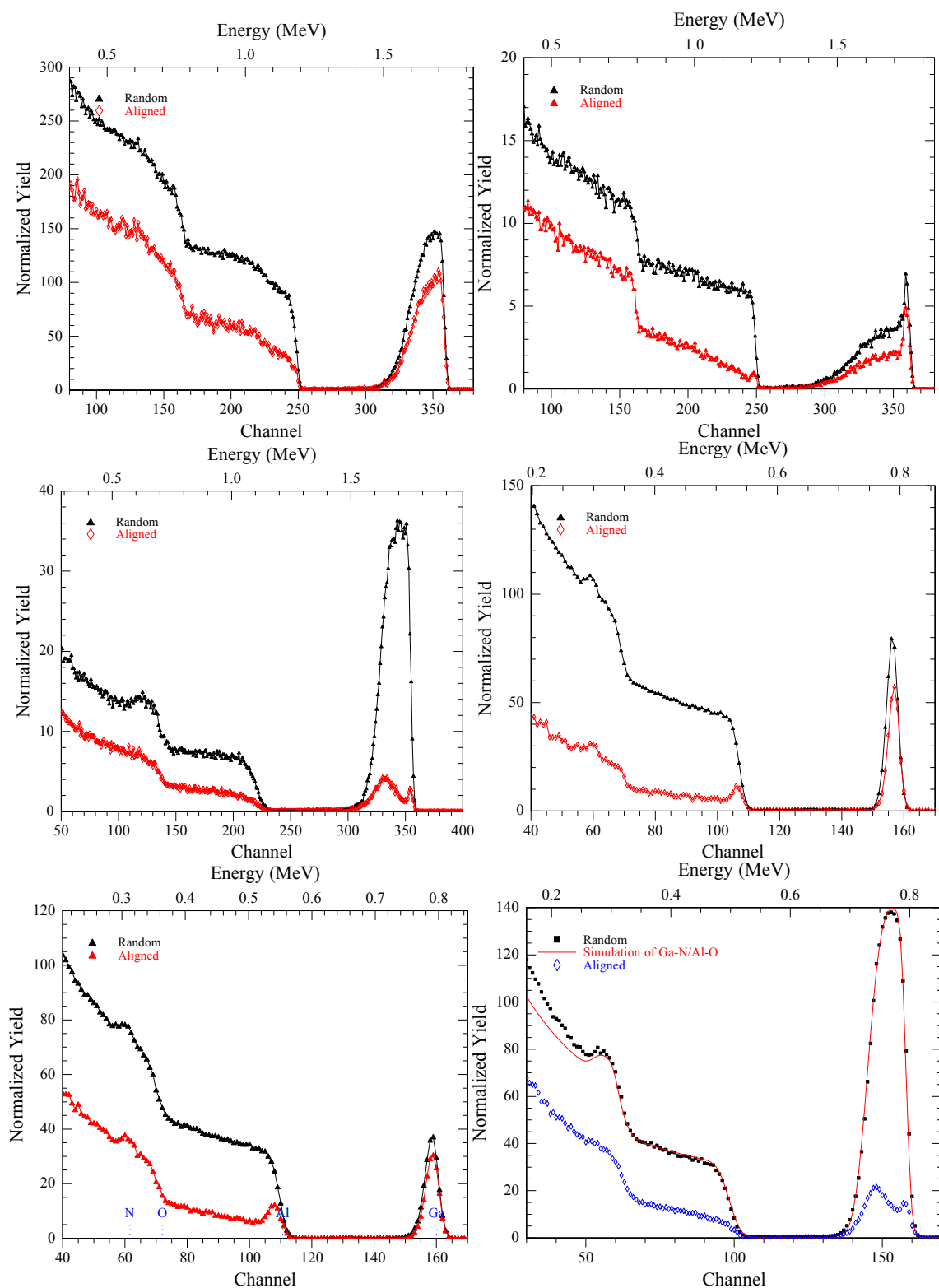


Figure 6.23: Typical RBS random and channeled spectra for samples grown at 850°C (a, b), 950°C (c, d), 1050°C (e), and 750°C (f)

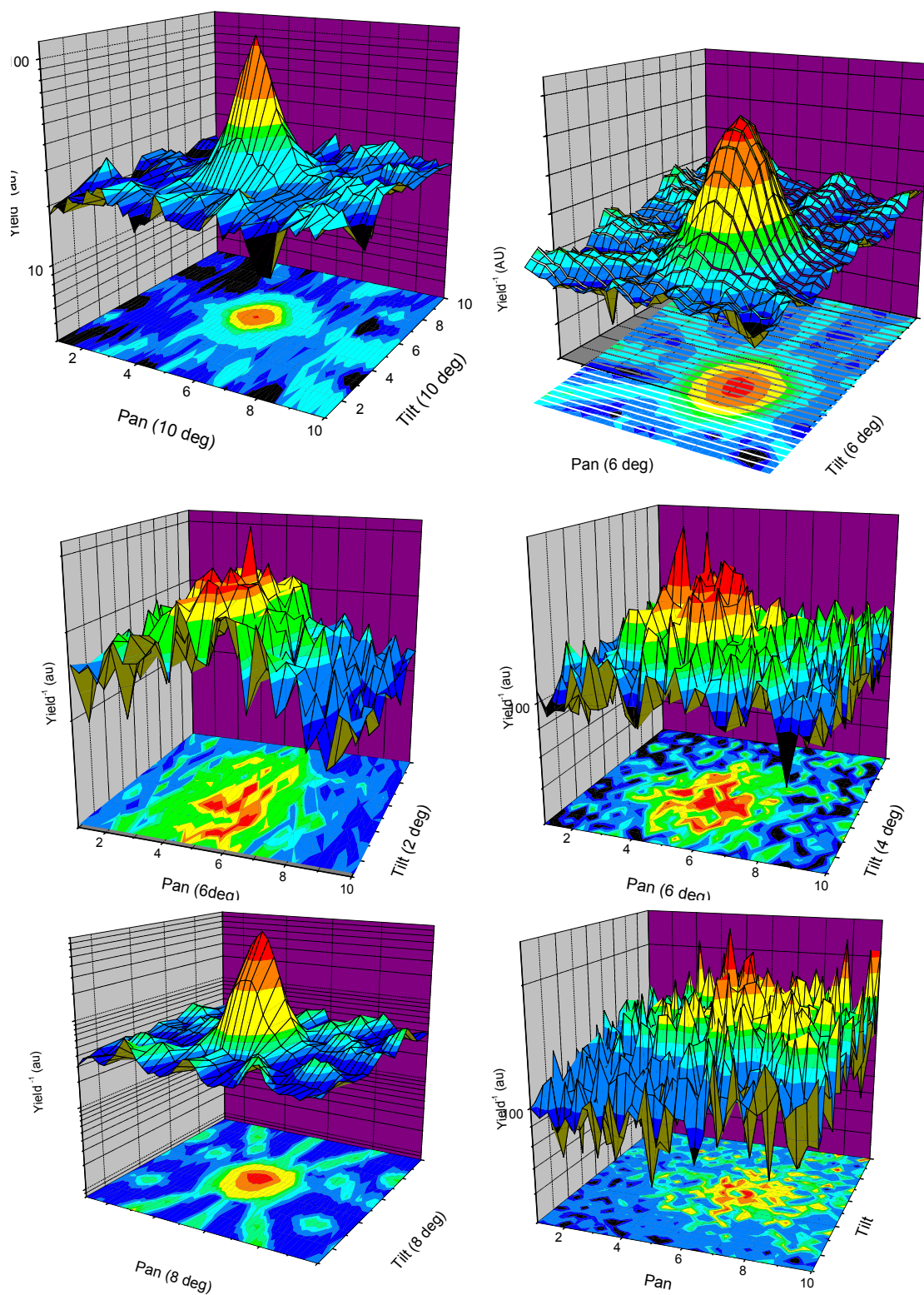


Figure 6.24: Typical minimum yield maps for GaN films grown at 680°C (a), 750°C (b), 850°C (c, d), 950°C (e), and 1050°C (f)

6.4.1 Phase identification by Ion Channeling

It is well known that GaN has two different phases, one is the cubic phase, also called Zinc-Blend (ZB), while the second is hexagonal, also known as Wurtzite (W). Due to the different nature of these two phases one can make use of ion channeling in conjunction with LEED to determine the crystallographic symmetry of the GaN films and from this information one can determine the crystalline phase. XRD on powder samples can be used to identify all the phases present in the sample. Some XRD results for these films are presented in Chapter VII.

The phase and orientation identification is based on the stereographic projection of a crystal. This projection provides an accurate representation of the angles between planes and axes of a crystal. Figure 6.25 shows the stereographic projections for the hexagonal phase (wurtzite) around in directions $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$.

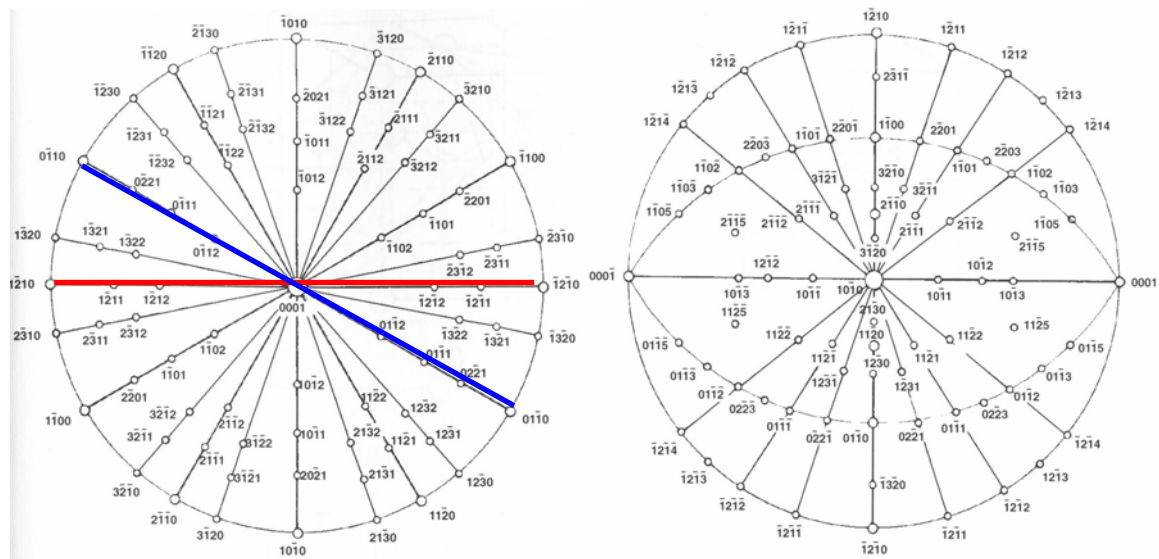


Figure 6.25: Stereographic projections for a hexagonal crystal in the $\langle 0001 \rangle$ (left) and $\langle 10\bar{1}0 \rangle$ (right) direction [115]

The $\langle 0001 \rangle$ stereographic projection is characterized by two types of low index crystallographic planes: $(11\bar{2}0)$ and $(1\bar{1}00)$ that are intersecting at 60° and separated by 30° , and marked with the two colors blue $(11\bar{2}0)$ and red $(1\bar{1}00)$ for a total of 6 planes

temperatures ($\chi_{\min}$ vs. thickness). The minimum dechanneling yield is a good measure of the crystalline quality of a crystal and the lower the yield the lower the defect density of the crystal. The presence of the crystallographic axis and planes is a good indication of single crystal nature of the films.

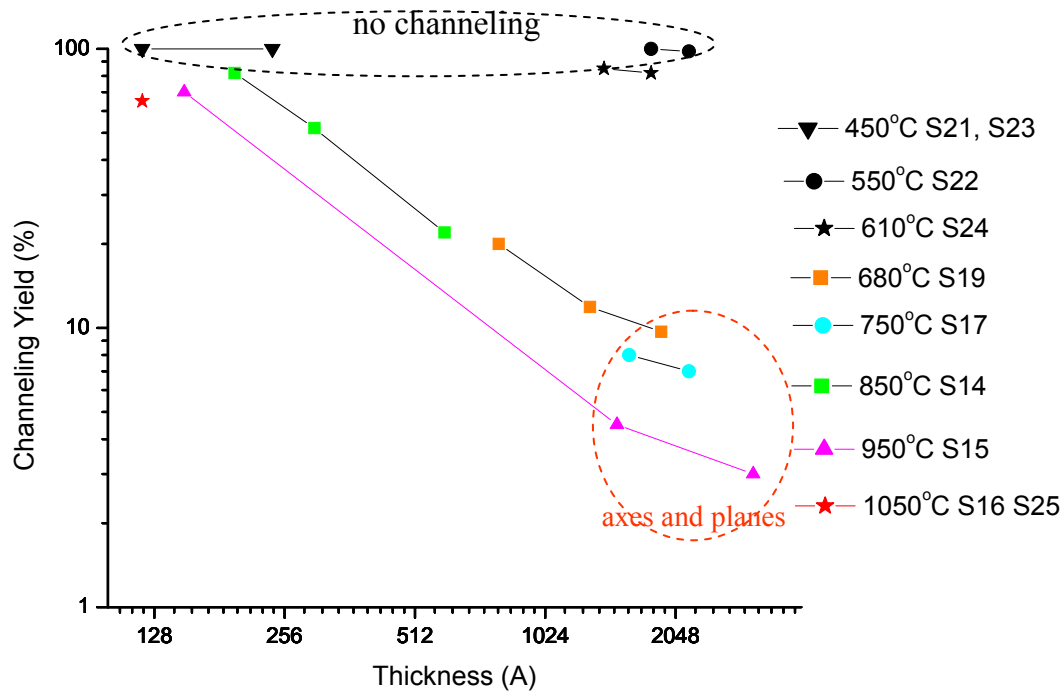


Figure 6.27: Minimum dechanneling yield as a function of film thickness and deposition temperature

No channeling is observed for films of any thickness grown in the temperature range of 450°C to 610°C since the dechanneling yield is close to 100%. An abrupt change in the nature of the channeling happens when the growth temperature is raised to 680°C and above. For the temperature of 950°C the minimum yield reaches a value of 3.01% characteristic for a good single crystal. At 1050° C the film is very thin and the channeling is not good but is relatively better than similar films grown at lower temperature. In Figure 6.27 the black dotted area represent region of amorphous or randomly oriented polycrystalline film, the red dotted area corresponds to single crystal

films and the remaining area is specific to a polycrystalline film with some degree of preferential orientation.

Using the approximation formulas for the minimum channeling yield (Formula 4.7) and the critical angle we obtain for the perfect crystal values of the minimum yield in the range 1.6-1.8 % and critical angle of 0.5° - 0.9° for beam energy 1-3 MeV.

In addition to the temperature dependence of the crystalline quality we notice strong thickness dependence. For the film thickness up to approximately 30 nm only marginal channeling is measured for films grown at any temperature. As the thickness increases the minimum yield decreases in a linear dependence that is starting to level off for thicknesses above 200 nm. This behavior is consistent with a strongly defective nucleation region with a thickness of about 30 nm followed by a region where the defect density is fast decreasing as the film grows due to defect annihilation and finally a region where the defect density decreases at a slower rate when the film is thicker than 250 nm. The growth temperature dictates if the defect annihilation takes place as the film is growing (680°C is the minimum temperature for which the film quality improves with the thickness). TEM results of various groups support this interpretation [44,46]. A similar increase in the quality of the film with the thickness has been measured for thicker films (1-2 μm) by ion channeling [87].

6.4.3 Surface peak analysis

The presence of the surface peak in the channeling spectrum is an indication that the quality of the crystal in the surface area is good. We have observed surface peaks only for the films grown at a temperature higher than 680°C and for a given temperature only for and for a thickness of the film larger than about 200 nm. The absence of the peaks for thinner films shows that the films are highly defective in the initial stages of nucleation and growth. The intensity of the surface peak can be used to determine the number of atoms that are visible on the surface when the beam is oriented with the c-axis of the crystal. This number, compared to the density of rows of atoms perpendicular to the surface gives an indication if and how much the surface is reconstructed in the direction

perpendicular to the ion beam. Figure 6.28 show the surface peak after background subtraction for sample growth temperature of 950°C

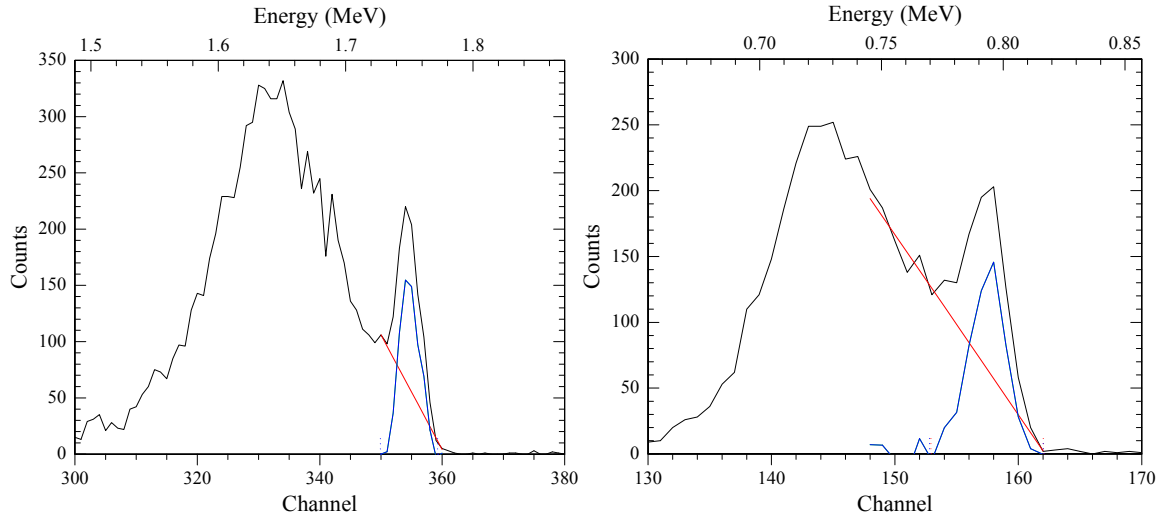


Figure 6.28: Surface peak of the Ga signal for film grown at temperature of 950°C with a thickness of 320 nm (a) and 185 nm (b)

Using the geometry of the GaN crystal and the rms vibrational amplitude of the Ga atoms at the surface of the film of $0.0735\text{\AA}$ [116] we have calculated a shadow cone radius for 2.2MeV incident ions of $0.0844\text{\AA}$. Using the “universal” curve (Figure 4.7) for these values we obtain an expected value of 2.22 atoms/row that will contribute to the surface peak. Since there are 2.27×10^{15} rows/cm² in the <0001> direction of GaN we have an expected surface density for the surface peak of 5.04×10^{15} atoms/cm².

The analysis of the surface peak is done by first removing the background followed by the integration of the total number of counts. Using the height of the random spectrum and the procedure detailed in chapter 4 we calculated a number of atoms per row that give rise to the surface peak.

For the sample grown at 950°C and for the film with a thickness of 320 nm (Figure 6.28-a) we obtain a value of 6.1×10^{15} atoms/cm² of gallium contributing to the surface. Compared to the surface density of rows of atoms which is 2.27×10^{15} atoms/cm² our value is 2.68 times higher which mean the channeling interacts with 2.68 atoms for each row of atoms parallel to the ion beam. The film with a thickness of 185 nm (Figure 6.28-

b) has a surface density of 4.93×10^{15} at/cm² corresponding to 2.17 atoms/row. Both results are close to the expected values of 2.22 atoms/row at 2.2 MeV and 1.66 atoms/row at 1 MeV for an unreconstructed surface.

The film grown at 750°C with a thickness of 135 nm (Figure 6.29-a) has a surface density of 4.56×10^{15} atoms/cm² corresponding to 2.01 atoms/row while the film grown at 680°C with a thickness of 80 nm (Figure 6.29-b) has a surface peak of 7.8×10^{15} atoms/cm² corresponding to 3.42 atoms/row.

While the films grown at 750-950°C have surface density within 20-30% of the expected surface density for unreconstructed surface, the film grown at 680°C has a higher density that agrees with up to one extra atomic layer of Ga displaced from the bulk-like positions. In fact adding of fraction of 2/3 of a layer will get the result within 24% of the expected value.

The observed numbers are systematically higher than the ones obtained from the universal curve and they seem to agree with the Feldman's results [92] that are also higher than the calculation (see Fig 4.7).

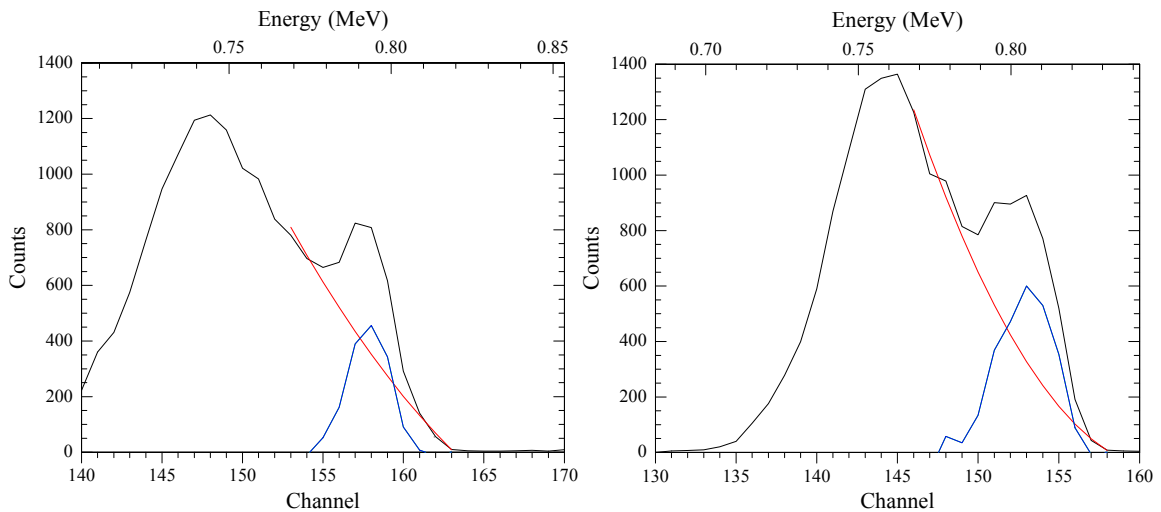


Figure 6.29: Surface peak of the Ga signal for substrate temperature 750°C and 135 nm thickness (left) and 680°C and 80 nm thickness (right)

A possible surface reconstruction (Figure 6.30) for MOCVD has been suggested [49] that can account for 2/3 of a monolayer of Ga atoms on top of the bulk structure.

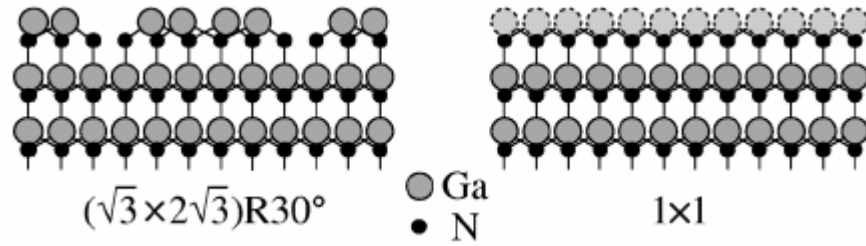


Figure 6.30 Proposed cross section for a $(\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstruction (left) and 1×1 structure (right), viewed along $[01]_{\text{surf}}$ direction [49]

The underlying theory used for estimating the numbers of atoms visible for each row in the surface peak and is based on a one element crystal. In the case of compound materials the analysis is complicated if signal from the light element interferes with the background subtraction. The fact that the atomic mass of Ga is 5 times larger than the N helps in this respect. Monte Carlo simulations have been used to fit the surface peak and the background for GaP, GaAs and InP [117] but no such work has been done for GaN. The uncertainty in the intensity of the thermal vibrations at the surface of the crystal limits the sensitivity of this technique.

6.4.4 Defects density

The defect analysis is complicated by the fact that a mixture of defect coexist in the thin films that we grow and the each defect can have different effect depending on the orientation.. This makes the result of this analysis relative rather than absolute. We have assumed that the majority of the defects introduced in the early stages of growth to accommodate the deviation from exact epitaxial relationship are of edge dislocation [59, 118] with a Burger vector of $1/3 \langle 2 \ -1 \ -1_0 \rangle$ [104,119,120,121]. The dechanneling factor calculated using the approximation of Feldman (Equation 4.13) is $44.4\text{\AA}$. A second assumption is that the increase in the channeling yield occurs by dechanneling rather than direct scattering. This assumption is justified for defects of type dislocations but will overestimate the amount of dislocations if other type of defects, for instance interstitial point defects, which produce direct scattering, will be present in the film [92].

Using the Equation 4.10 we calculate the density of dislocations for the samples that show a channeled spectra of the type shown in Figure 6.31-32. The red line in these figures is the slope of the channeled spectra that is proportional to the defect density.

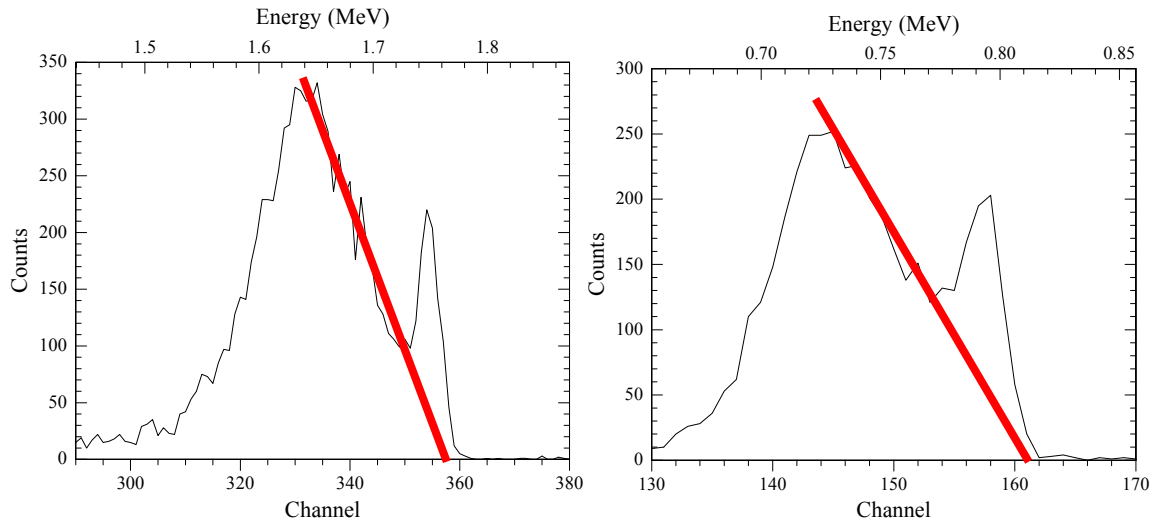


Figure 6.31: Gallium channeling peak for growth temperature of 950°C and thicknesses of 320nm (a) and 180 nm (b)

The calculated average defect densities in the surface region for the samples that exhibit a surface peak are given in Table 6.4. We observe two trends from the data: the defect density decreases with the increase in the growth temperature in the range 680-950°C and the defect density for thicker films is lower. This is similar to the results obtained from the graph of minimum channeling yield ($\chi_{\min}$) as a function of thickness for different growth temperatures (Figure 6.27).

Portman et al. [122] has used ion channeling to determine the defect density in cubic GaN and obtained values between 6×10^{10} and $2.2 \times 10^{11} \text{ cm}^{-2}$ assuming the predominant defect type is the dislocations with a average Burger vector of $3.2 \text{ \AA}$

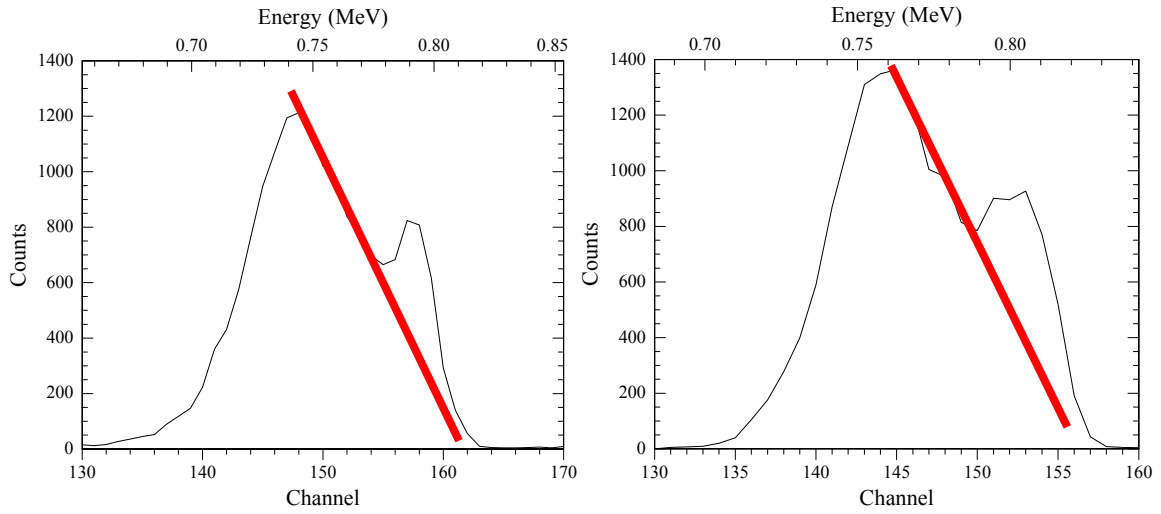


Figure 6.32: Gallium channeling peak for growth temperature of 750°C and thickness 135 nm (a) and temperature of 680°C and thickness of 140nm (b)

Table 6.4: Average dislocation density for GaN films

Temperature (°C)	Thickness (nm)	Channeling yield (%)	Depth below surface (nm)	Defect density n_D (cm ⁻²)
950	320	11.3	191	2.6×10^{10}
950	185	10	96	6.4×10^{10}
750	135	16.5	65	1.5×10^{11}
680	140	18.7	62	2.0×10^{11}

6.4.5 Epitaxial relationship of GaN film with respect to the substrate

Since the GaN films grown from 450°C to 610°C show only marginal axial channeling and no planar channeling we conclude that they are either very defective or polycrystalline and no further investigation is relevant. The films grown at 680°C are the first ones to show good axial channeling and signs of planar channeling. Figure 6.33 shows the channeling map for Ga and Al. The axis and planes of GaN and sapphire as determined from the channeling of gallium and aluminum sublattices are aligned within 0.2° which is the used step size of the goniometer.

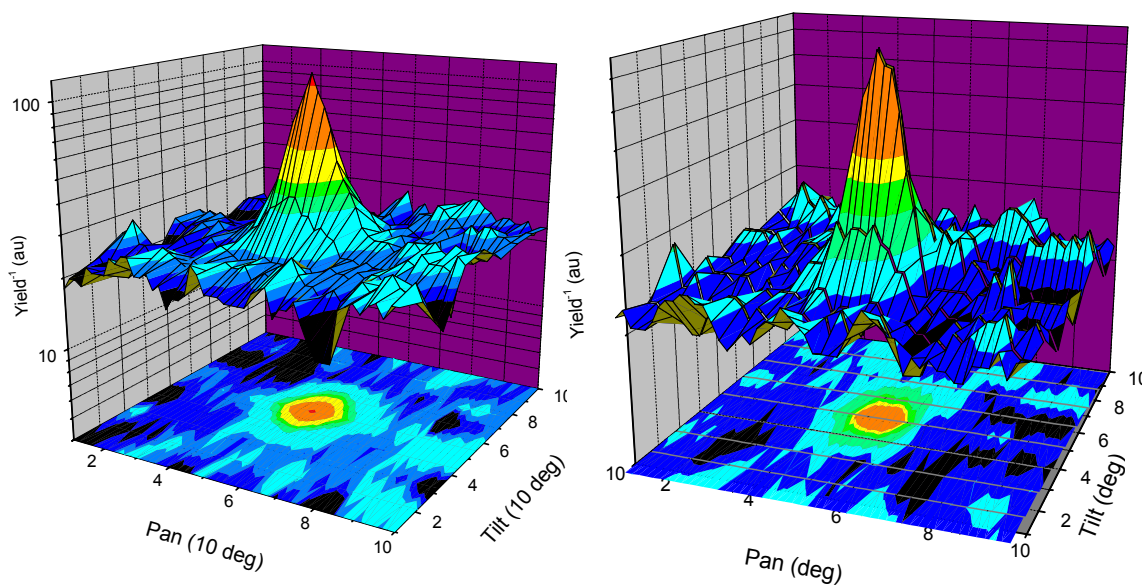


Figure 6.33 Channeling maps for Ga (left) and Al (right) for the sample grown at 680°C

Sample at 750°C shows a better structure of the GaN film as seen in the channeling map (Figure 6.34). Although the axis of sapphire and GaN are aligned within 0.2° with each other the channeling map for the substrate is not clear enough to allow for the detection of the planes. This is due to the thickness of the film that decreases the signal to noise ratio from the substrate.

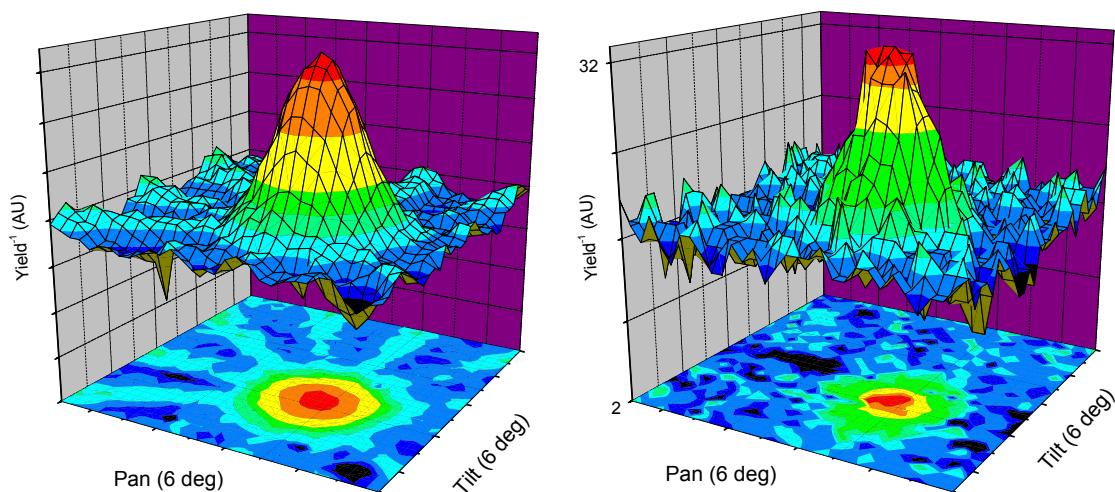


Figure 6.34: Channeling map of Ga (left) and for the Al (right) for film grown at 750°C

Channeling maps for the film grown at 950°C are shown in Figure 6.35 for the Ga and Al signal. The GaN film is 185 nm thick for the Ga map while the channeling map for Al is taken at a point 15 mm away, at a position where the GaN film is 15 nm thick and does not interfere very much with the signal from the substrate. Due to the coarse raster across the tilt direction the maps are not very clear and we have taken an additional perimeter scan around the $\langle 0001 \rangle$ direction shown in Figure 6.36 to confirm the alignment of the planes.

From the two series of channeling experiments presented we conclude that both the c -axis and the crystallographic planes of the film and substrate are perfectly aligned within the 0.2 degrees, which represent the step size of the scans.

Since the crystallographic planes of the hexagonal crystals are of two different symmetry types, this leaves us with an unknown regarding the alignment of the like planes or unlike planes for film and substrate. To further investigate the epitaxial relationship between the film and substrate we have to identify the two different symmetry planes of the film and substrate. As presented in Chapter 5 the identification of the sapphire planes is made easy by the fact that the two sub-lattices (Al and O) have different symmetry, and one of the symmetry planes in the channeling map is extinguished when both Al and O is considered. For GaN the same experiment does not

work in practice since the signal coming from the nitrogen is very small compared to the background created by the sapphire substrate. Another way to identify the planes is by measuring channeling maps along these planes and observe and identify the crystallographic axis that are oriented in this plane using the knowledge of the crystalline structure.

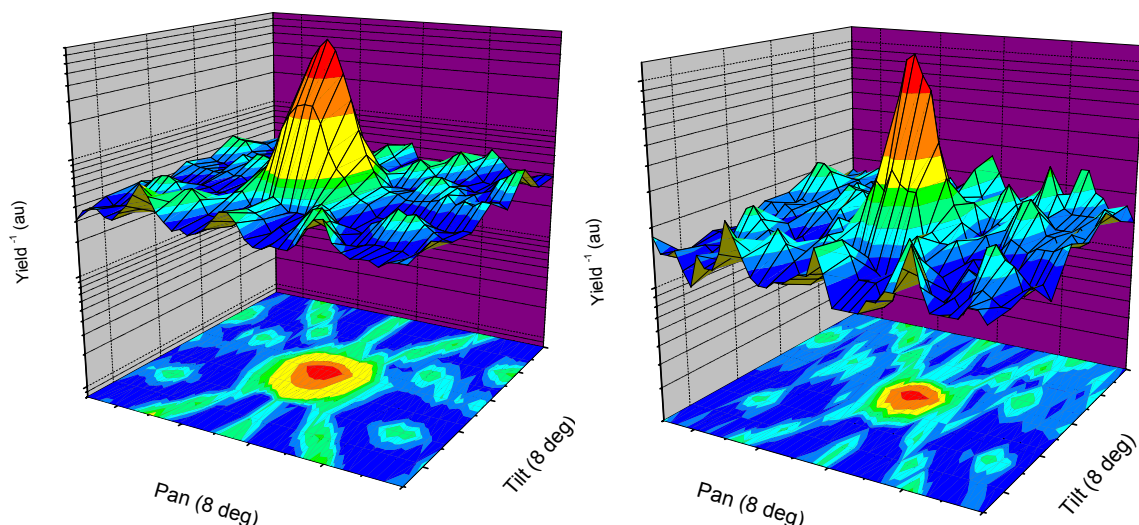


Figure 6.35: Channeling maps for Ga (left) and Al (right) for the film grown at 950°C

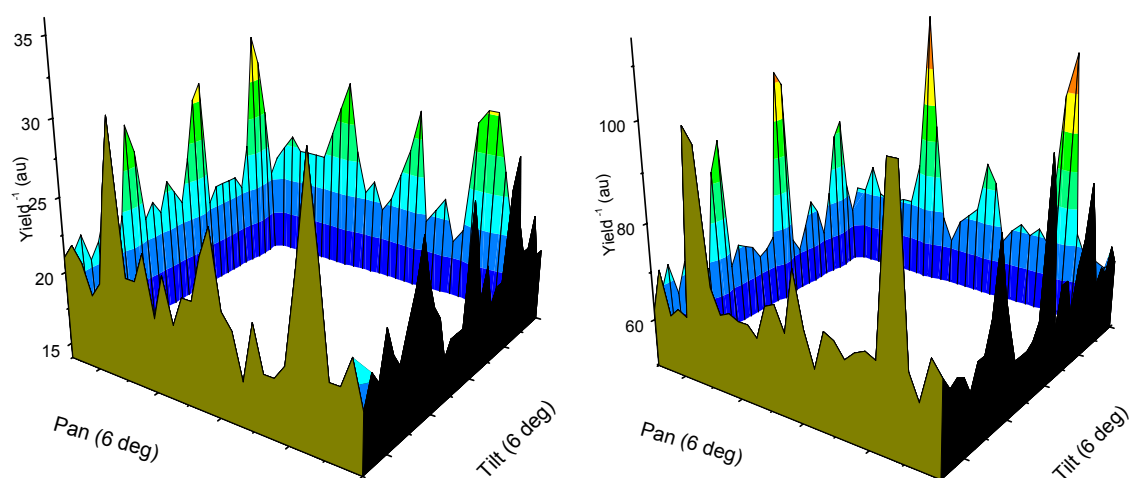


Figure 6.36 Perimeter scans for the Ga (left) and Al (right) signal for film grown at 950°C

Figure 6.37 shows the channeling maps for the Ga sub lattice (left) and the Al+O lattice (right) as well as perimeter scans around the c-axis. From the reduced symmetry of the second map the sapphire planes can be identified.

Because of the goniometer design, the plane that is to be investigated has to be aligned as well as possible with the horizontal direction (within 1–2 degrees). Misalignment of the planes will limit the maximum angle that the sample can be examined along the plane with respect to the sample normal.

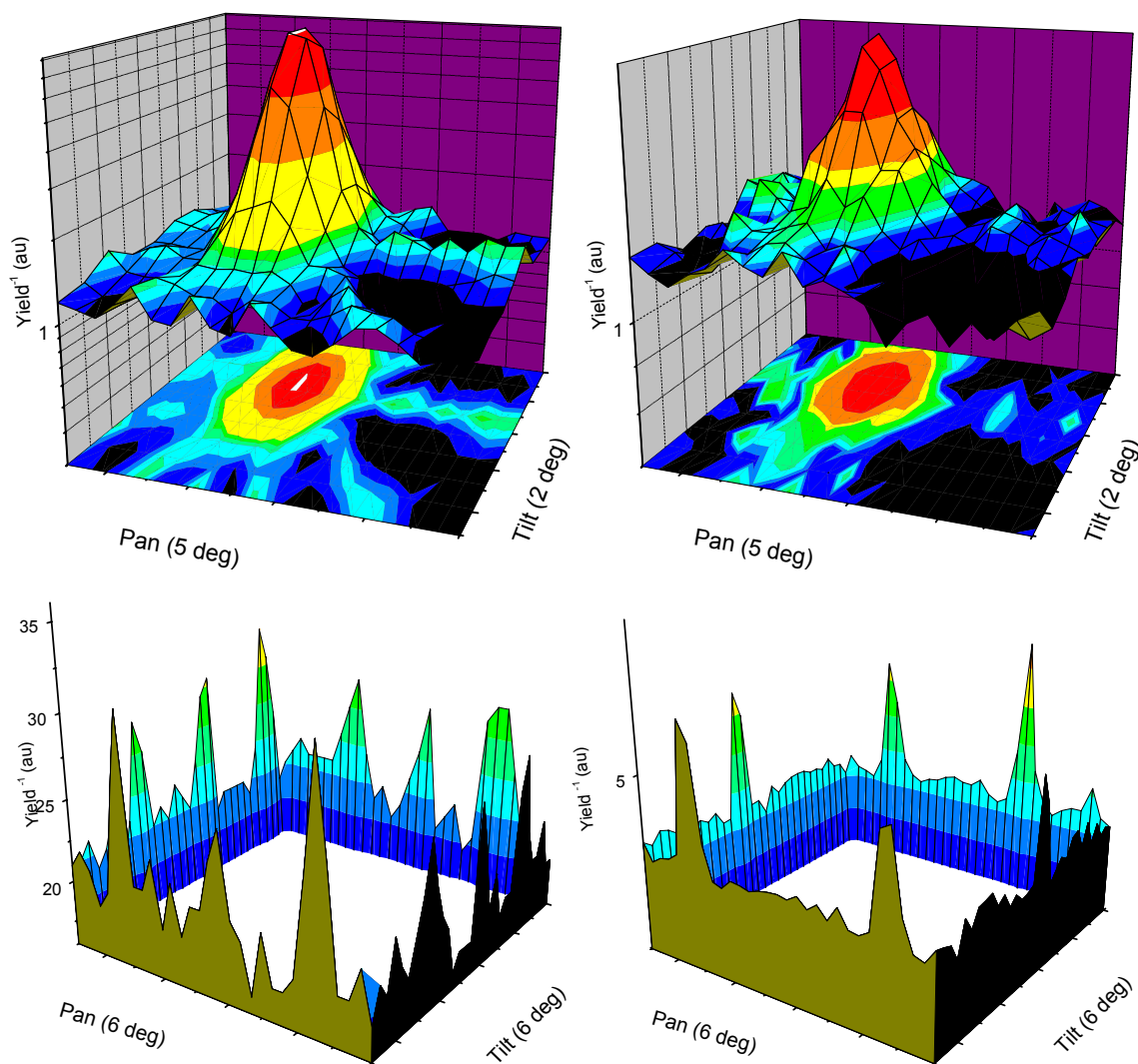


Figure 6.37 Channeling map and perimeter scan for Ga (left) and Al+O signal (right)

Figure 6.38 shows a channeling map for one of the crystallographic planes of GaN film from the c axis up to a maximum angle of 22 degrees. Three maps are taken, first one is 8 degrees wide and includes the c axis, the second is 12 degrees wide and the last one is 4 degrees wide. The total angle scanned is 22 degrees and some overlap of the maps has been allowed.

The following axis can be identified in this plane: $\langle 001 \rangle$ 0 deg, $\langle 1-19 \rangle$ 6.74 deg, $\langle 1-18 \rangle$ 7.58 deg, $\langle 1-15 \rangle$ 12.02 deg, $\langle 1-14 \rangle$ 14.91 deg, $\langle 1-13 \rangle$ 19.45 deg. Due to this identification the crystallographic plane of GaN is of type (11-20).

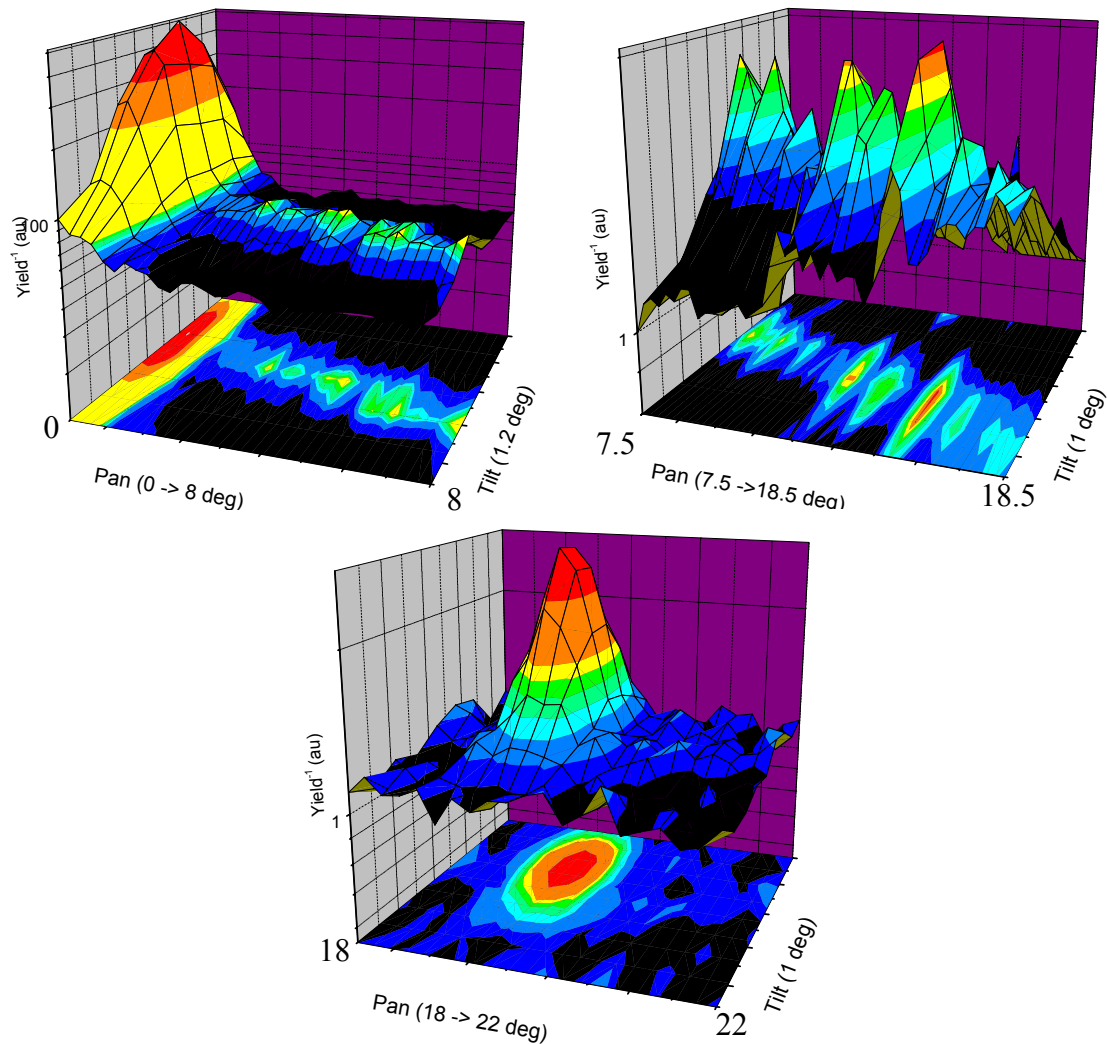


Figure 6.38: Channeling maps for the GaN channeling plan (11-20)

In chapter 5 we have identified the sapphire planes based on the experimental observation that one of the types of plane is extinguished in the channeling map when the integration window is set in such a way to probe both the Al and O sublattices. In this section we will use the method of identifying the axes that are observed in this plane and from that the plane can be identified. The 3 maps shown in Figure 6.39 start around the c-axis shown in the first graph and continue along the plane up to an angle of 22 degrees away from the normal.

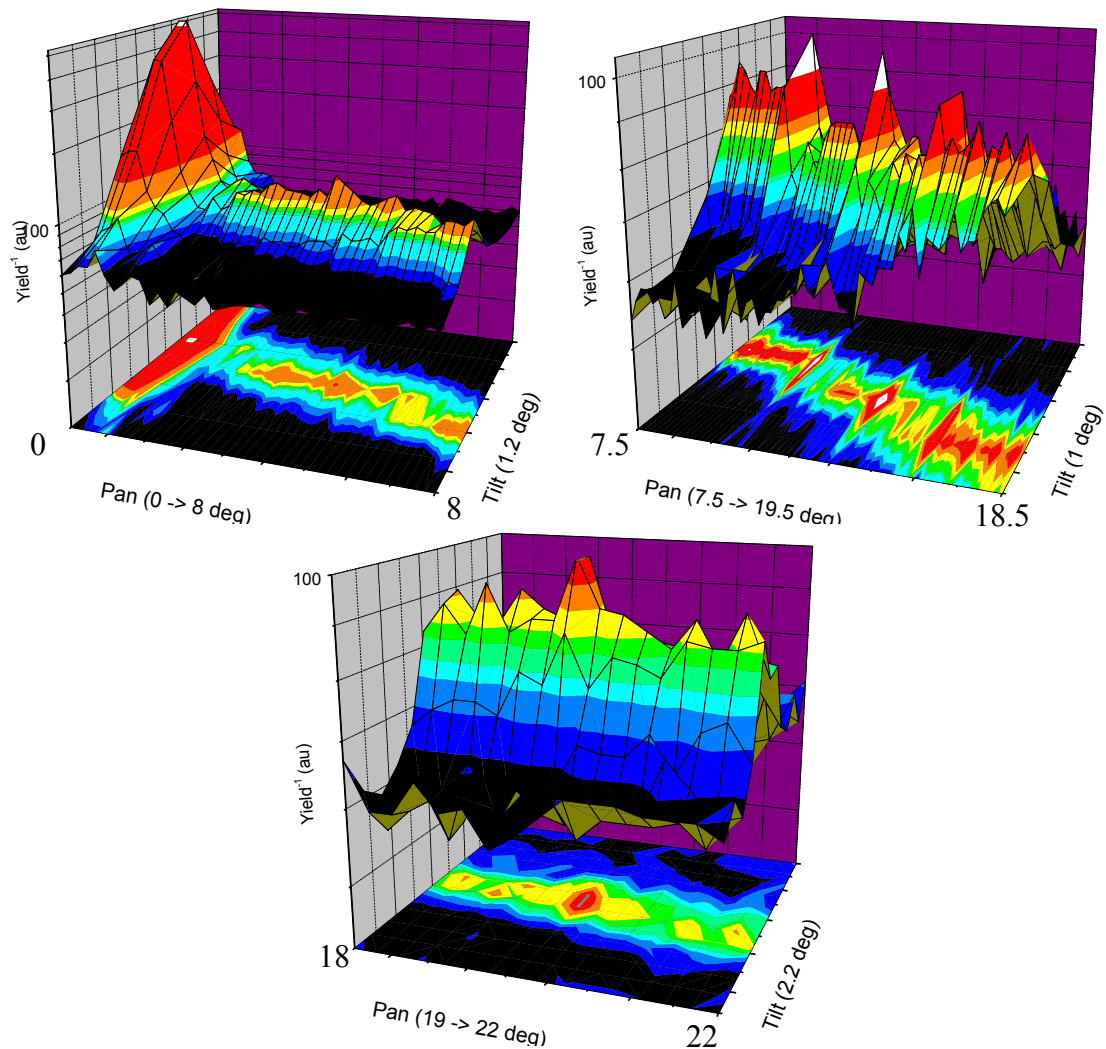


Figure 6.39: Channeling maps for the sapphire substrate in the plan (1-100)

The following axis can be identified for sapphire in this plane: $\langle 001 \rangle$ 0 deg, $\langle 105 \rangle$ 4.19 deg, $\langle 104 \rangle$ 5.23 deg, $\langle 102 \rangle$ 10.38 deg, $\langle 101 \rangle$ 20.12 deg and the plane is the (1-100). From the identification of the GaN and sapphire planes we can conclude that the film is rotated 30 degrees with respect to the substrate such that the (11-20) plane of the film is aligned with the plane (1100) from the substrate. This epitaxial relationship of the film with respect to the substrate is the one found most often in the research of other groups.

6.4.6 Ion beam damage in GaN

Radiation damage is related to the nuclear stopping power with the restriction that in the case of damage the energy transferred to the atoms has to be higher than threshold value E_d . From the behavior of nuclear stopping powers we can conclude that the rate of defect formation has to be inversely proportional to the beam energy and to vary proportional to the square of the projectile charge number [123,124] such that using $^4\text{He}^+$ with energies 1-2MeV is a good choice to keep the damage low. In our experiments we have used energies between 1 and 3.05MeV and charge number 1 and 2 (He^+ and He^{++}).

In order to minimize the damage, whenever possible we have changed the position of the beam of the sample, after alignment or extensive data gathering, in order to analyze a “fresh” spot on the film.

One way to look at the damage is the measure the minimum channeling yield before and after the sample is irradiated as well as to look at the slope of the channeled spectrum and compare it to the one as deposited. Figure 6.40 shows the channeled spectra for a film that is 200 nm thick (growth temperature 950°C) that has been bombarded with a $^4\text{He}^{+2}$ beam and a charge of 20 μC across the beam size of 2mm² that corresponds to 3.125×10^{15} He^{+2} ions/cm². We have used 2 μC of He^{+2} for taking the spectra at the beginning and after irradiation. In general 10 μC dose corresponds to a typical amount needed to take RBS spectra with good statistics. Since the two spectra are practically indistinguishable we conclude that this dose does not produce enough damage in the crystal to be distinguishable by ion channeling.

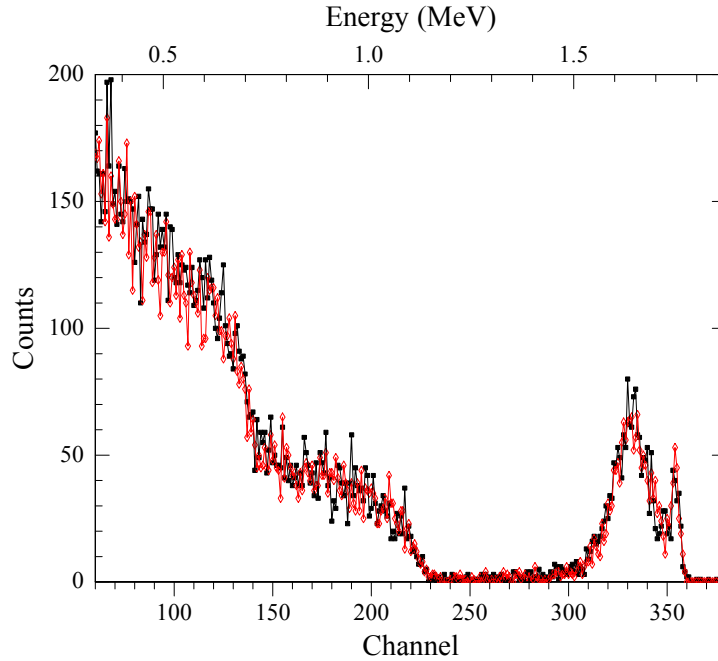


Figure 6.40: Ion channeling spectra taken before and after exposing the sample to $10\mu\text{C}$

We have tested the effect for a sample with a higher degree of initial disorder. We used $100\mu\text{C}$ of charge that corresponds to a surface density of $3.125 \times 10^{16} \text{ He}^+ \text{ ions/cm}^2$. Two channeled spectra are shown in Figure 6.41 for a film grown at a temperature of 950°C . The two spectra are very close but the integrated number of counts in the Ga peak is increased by 6.3% for the channeled spectra taken after the sample has been exposed to the ion beam. The GaN film has a thickness of $180\text{\AA}$ and shows a high degree of disorder since the minimum yield of the spectrum is $\sim 72\%$. The minimum yield exhibited by the sapphire substrate is unchanged, indicating that the substrate is not affected by the ion bombardment of this magnitude.

We have also performed often checks of the damage level by taking channeled spectra at the beginning and end of an analysis session and have found the variation in the minimum channeling yield (χ_{min}) to be less than 20%.

We conclude that the level of irradiation used in our experiments is not able to produce a high level of damage in the sample.

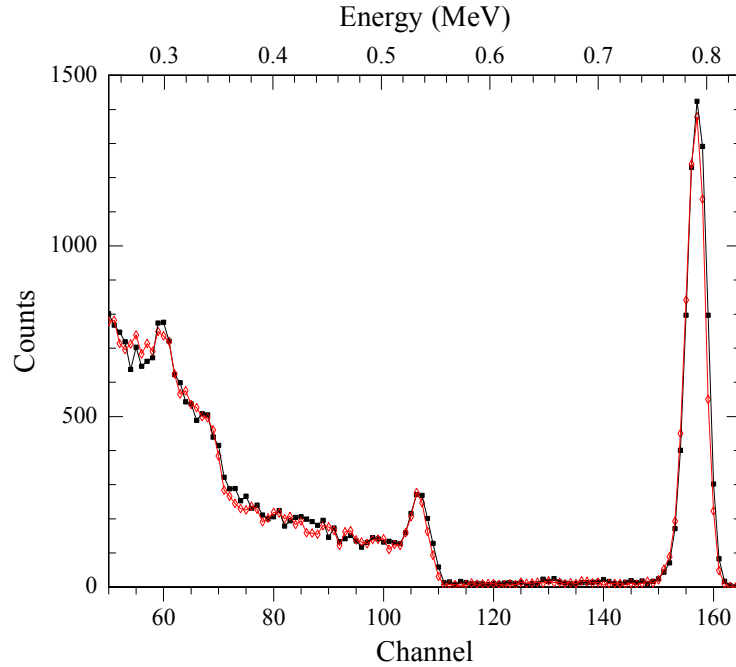


Figure 6.41: Ion channeling spectra taken before and after exposing the sample to $100\mu\text{C}$

Osipowicz has found no measurable damage has been produced during the channeled bombardment of GaN with 1 MeV He^+ ions with a fluence of 7.4×10^{16} ions/ cm^2 and an increase of about a factor of two of the minimum yield when the implantation occurred in a random direction [85]. Turos [84] has investigated the ion damage in GaN platelets due to the ion bombardment with 2 MeV $^4\text{He}^+$ and it has been found that the channeling yield increases a factor of two when the surface is bombarded with a beam fluence of 1×10^{17} ions/ cm^2 (which is about 10 times the dose that is the normal dose used for taking one spectra). Linden et al. [87] has found that a limit for starting to creating damage in the crystal of 10^{16} ions/ cm^2 for 1MeV He^+ when the irradiation occurs at random direction while for the c-axis channeled direction a dose 5 times larger is needed to create measurable damage.

6.5 In-situ annealing of the GaN film

In order to investigate the assumption that the buffer layer is recrystallized during the ramping up to the epi-layer temperature we have performed an experiment in which the buffer layer is being heated up to a higher temperature and the film is being analyzed by Ion Channeling to estimate the crystalline quality after this heating step.

The deposition of the BL has been performed at 610°C, the annealing temperature is 1000°C and the ramping up time between the two temperatures is 200 seconds. We have chosen this time as being close to the actual time needed for the ramping up the temperature in a real deposition reactor. The thickness of the annealed film is within 10% of the sample un-annealed. Other studies [81,18] speculate that the thicker films need more time in order to recrystallized than thinner films and consequently they stay polycrystalline. Another work [48] has found a differential evaporation rate during annealing phase for films with different polarity and estimate that for MOCVD both polarities can grow but with different rates.

The RBS/Channeling of the annealed films is shown in Figure 6.42. The minimum yield is $89\% \pm 5\%$ which is very close to the one for the unannealed sample.

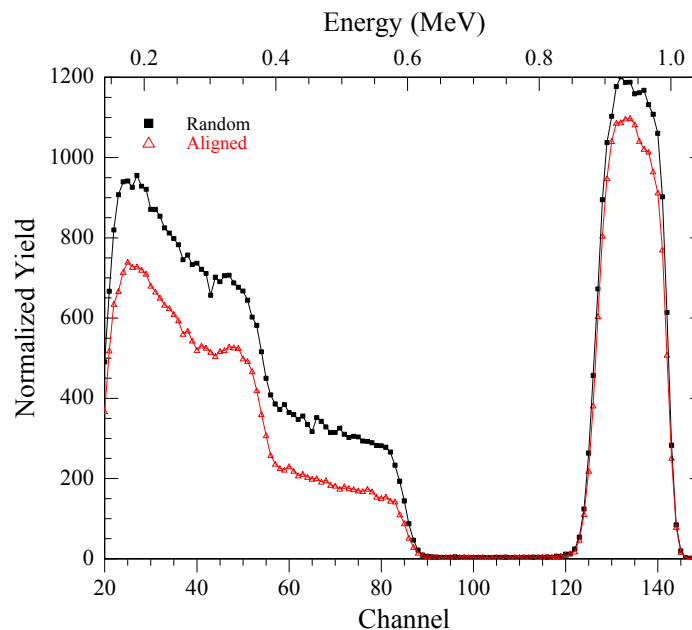


Figure 6.42: Random and aligned RBS spectrum for the sample grown at 610°C and annealed at 1000°C for 200 seconds

The minimum yield of the annealed film is not changed much compared to the film that has not been annealed. This supports the conclusion that no major crystallization of the film is happening during the time that the temperature is being ramped up for the deposition of the film on the buffer layer.

Figure 6.41 shows LEED patterns for the samples grown at 610°C with and without annealing after deposition. There is no noticeable increase in peak intensity or sharpness leading to the conclusion that the annealing does not affect the surface of the samples for this film.

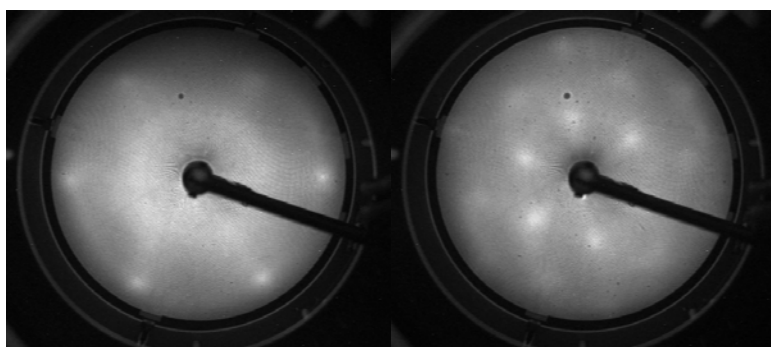


Figure 6.43 LEED patterns for the samples grown at 610°C without annealing (left) and with annealing (right)

The ex-situ XRD spectra for the two samples are shown in Figure 6.44. Both films exhibit the peaks corresponding to the hexagonal phase of GaN and to the sapphire substrate with no unidentified peaks. There is no significant change in the GaN [002] peak intensity while the higher order peaks are decreased. This could be the result of sampling a thinner GaN film in the case of the post-growth annealed sample.

In a quantitative study Munkholm et al. [49] have determined that for their deposition conditions the 20nm film grown at 525°C has a fraction of cubic to hexagonal of 0.56, and after the annealing at 1060°C the fraction changes to 0.17 [125]. Two other studies [46,104] used a buffer layer grown at 600°C and 530°C and they observed mostly cubic

GaN for the as deposited film and mixture of hexagonal and cubic after annealing at temperatures 1030-1080°C. This suggests that not only temperature but either the thickness of the film or the growth conditions (such as pressure rate, geometry) play an important role in the selection of the growth phase and that the wurtzite phase may have a higher growth rate and cover the cubic one.

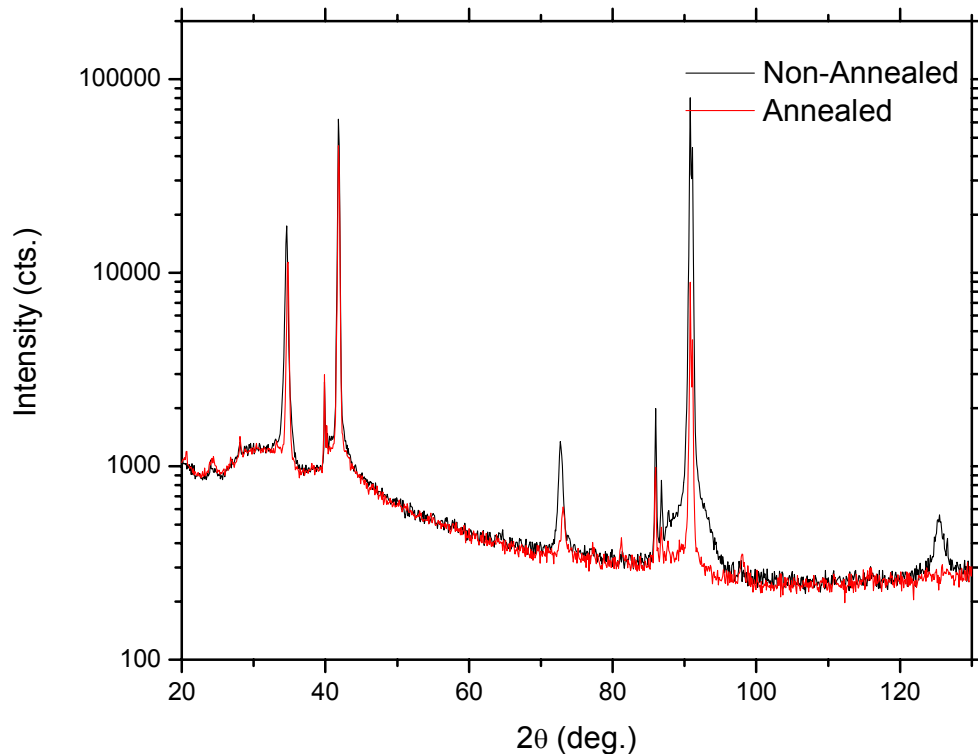


Figure 6.44: XRD θ -2 θ spectra for samples grown at 610°C with and without post-growth annealing

Kim et al. [126] has measured an improvement in the channeling level from 100% to 57% and an increase in the interface roughness between GaN and sapphire for thinner films (25nm) after annealing at 1000°C under ammonia flow. The crystalline quality improvement is more effective for thinner samples in the thickness range (20 to 550nm) but the annealing time which is a decisive parameter was not specified in the publication.

These observations together with our measurements suggest that the thickness plays an important role in the re-crystallization process of the film

6.6 Summary of results

In this chapter we have presented the experimental results of the analysis of the GaN films grown by MOCVD on sapphire substrate.

From the RBS analysis we have determined the thickness distribution across the surface of the substrate. The maximum growth rate of $\sim 20 \mu\text{m/hr}$ is attained at a temperature of 850°C , but the film is not continuous across the substrate. At the lowest temperature investigated, 450°C , and the highest, 1050°C , the film thickness is small. For the low temperature case we attribute this to the incomplete cracking of the precursor gases, while for the high temperature end, we attribute it to the high desorption rate of the GaN nuclei and the gas flow patterns in the reactor chamber created by the combination of laminar flow and convection currents. A higher flow rate of gases is needed for the growth at higher temperatures in the given geometry of our reactor chamber.

We propose a model to explain the unusual change in surface morphology and growth mode for the growth of the GaN on sapphire that explain the observations on the account of the polarity of the film. While films grown at low temperature have flatter surfaces due to the growth of the Ga polarity the films grown at higher temperatures have a rough surface with tall islands that is characteristic for N polar face.

The study of the surface structure by LEED shows that the films at temperatures 550°C and below have no surface order, while for higher temperatures the films have a hexagonal symmetry consistent with a wurtzite phase GaN. The patterns do not have sharp dots and show just a small improvement with the increase in temperature, the sharper patterns are obtained for the sample grown at 950°C . The fact that the thin sample grown at 1050°C still shows a pattern could be attributed to the fact that the film is ordered from the very early stages of growth when the substrate temperature is high, unlike the case of the lower temperature when the LEED patterns are not visible.

It is well known that it takes fractions of seconds to contaminate a surface by exposing it to the atmosphere. This effect can compromise the surface ordering and give rise to relaxation and reconstruction triggered by the adsorption of C, O and other possible contaminants. We are confident that we have observed unreconstructed surfaces with a low level of contamination.

The XPS analysis has a very important contribution to understanding the contamination of the surface, taking into account that the MOCVD growth is done at high pressures there are no in-situ methods to study the surface during the actual growth process. Our method is to transfer the sample into the analysis chamber via UHV lines and avoid the exposure to atmosphere. We have also found that after exposure to air the percentage of O and C on the surface is increasing. Using angular XPS we have confirmed that there is a surface contamination by C and O that could happen during the cool-down phase or in the high-vacuum transfer lines.

In addition to the expected contamination mentioned before, using XPS, we have identified fluorine contamination taking place as early as during the nitridation of the substrate. We have developed a method for substrate preparation and for film growth that avoids the contamination of the surface by the residual gases present in the reactor chamber.

While performing a quantitative analysis of the composition of the surface after ion sputtering the surface, we have observed the reduction of the amount of O and C. Simultaneously, the ratio of Ga to N is increased compared to the values of the as-deposited analysis. This can be an indication of preferential sputtering of the Nitrogen from the surface by the ion gun.

The Ion Channeling analysis gives us important insight into the crystalline quality of the films. MOCVD is a growth method with a high deposition rate and due to the short deposition time the films are in their initial formation stage. We have also taken channeling spectra for films with different thickness for the same temperature and determined that the crystalline quality increases as the film grows.

The first sample that shows a small amount of axial channeling is the one obtained at 610°C. Beginning with the growth temperature of 680°C the minimum yield in the axial channeling is decreased, there is a planar channeling, and we observe a surface peak for thicker films, an indication that the quality is increased. The best channeling is obtained for the sample grown at 950°C, with a minimum yield of 3.01% which is close to the value for a single crystal. The crystalline phase observed is of hexagonal type (wurtzite) as seen from the channeling maps and from the LEED patterns.

From the analysis of the surface peaks for films grown at 680°C to 950°C we estimate that the surface of the GaN film is bulk-like with the exception of the film at 680°C that has a higher amplitude peak consistent with one monolayer of Ga atoms displaced from the bulk-like positions.

The analysis of the defect density provides a relative measure of the dislocations present in the films. The dislocation density ranges from $2.6 \times 10^{10} \text{ cm}^{-2}$ for 950°C to $2.0 \times 10^{11} \text{ cm}^{-2}$ for 680°C growth temperature. The results are consistent with the trend of the minimum yield of channeling. Since the orientation of the defects relative to the ion beam has an important effect this measurements are sensitive to dislocations with Burger vectors not parallel to the ion beam direction.

The epitaxy of the film with respect to the substrate is investigated and using channeling maps around the $\langle 0001 \rangle$ direction we have found that at 750°C the very good alignment of the c axis of the film and substrate as well as the alignment of the crystallographic planes crossing the c-axis. Since the planes in the hexagonal phase are of two symmetry types the determination of actual orientation of the film with respect to the substrate requires supplemental analysis. We have identified the plans and have determined that the GaN film is rotated 30° with respect to the substrate. We have investigated the short annealing of a film during the rise in temperature between the growth temperature to 1050°C. Using the techniques to our disposal we have found that the nature of the film does not change significantly. Only marginal improvements in the channeling and LEED patterns are observed. We conclude that the film has not re-crystallized into a good crystal if the ramping-up time is of the order of 200 seconds.

Chapter 7

Ex-situ characterization of GaN films

Ex-situ characterization of the samples has been performed using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The samples grown at the extreme temperatures (450°C and 1050°C) are very thin and have been left out of this analysis since the ex-situ techniques used are not sensitive to very thin films such as these.

7.1 Analysis by Scanning Electron Microscopy

We have analyzed the film morphology using SEM. Due to the variable thickness of the films, the morphology of is different at different locations on the surface for most of the samples. We have tried to take SEM images are representative point across the surface of the sample.

This analysis is relevant in the light of the findings presented in Chapter 2 that correlate the surface morphology to the film polarity and also with the discussion presented at the beginning of Chapter 6 about the possible explanation of the film evolution in the early stages.

The sample grown at 550°C has a flatter region with occasional defects towards the region of highest thickness and has regions with high density of round pits on the rest of the surface (Figure 7.1). The regions with pits are sharply separated from the region with no pits. Due to the pattern that the pitted region occupies on the surface we can assume that the pits are due to the insufficient mass transport of the precursor gases across the surface of the sample.

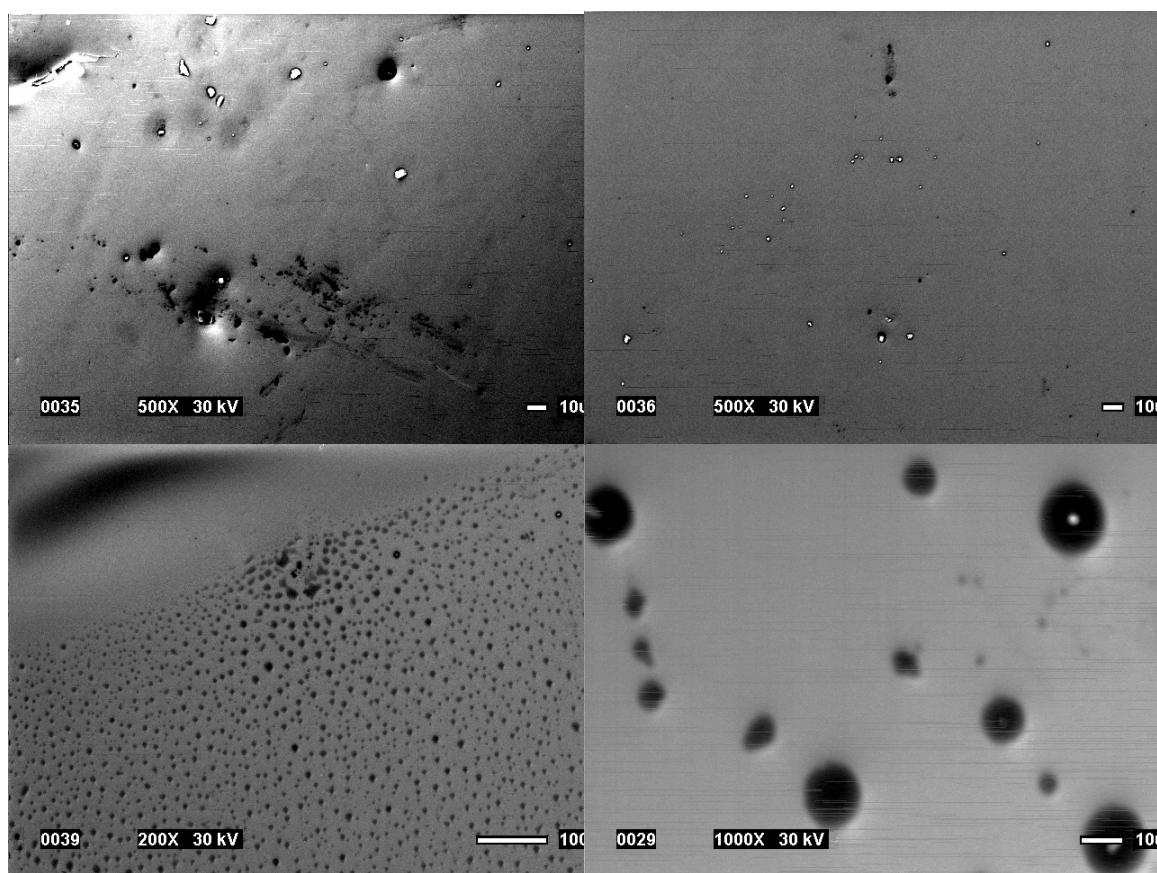


Figure 7.1 SEM micrograph of a sample grown at 550°C

The sample grown at 610°C is the one with the highest degree of uniformity as measured by RBS. The surface morphology of this surface as shown by SEM is the smoothest of the samples analyzed (Figure 7.2) Defects bunching together can be observed.

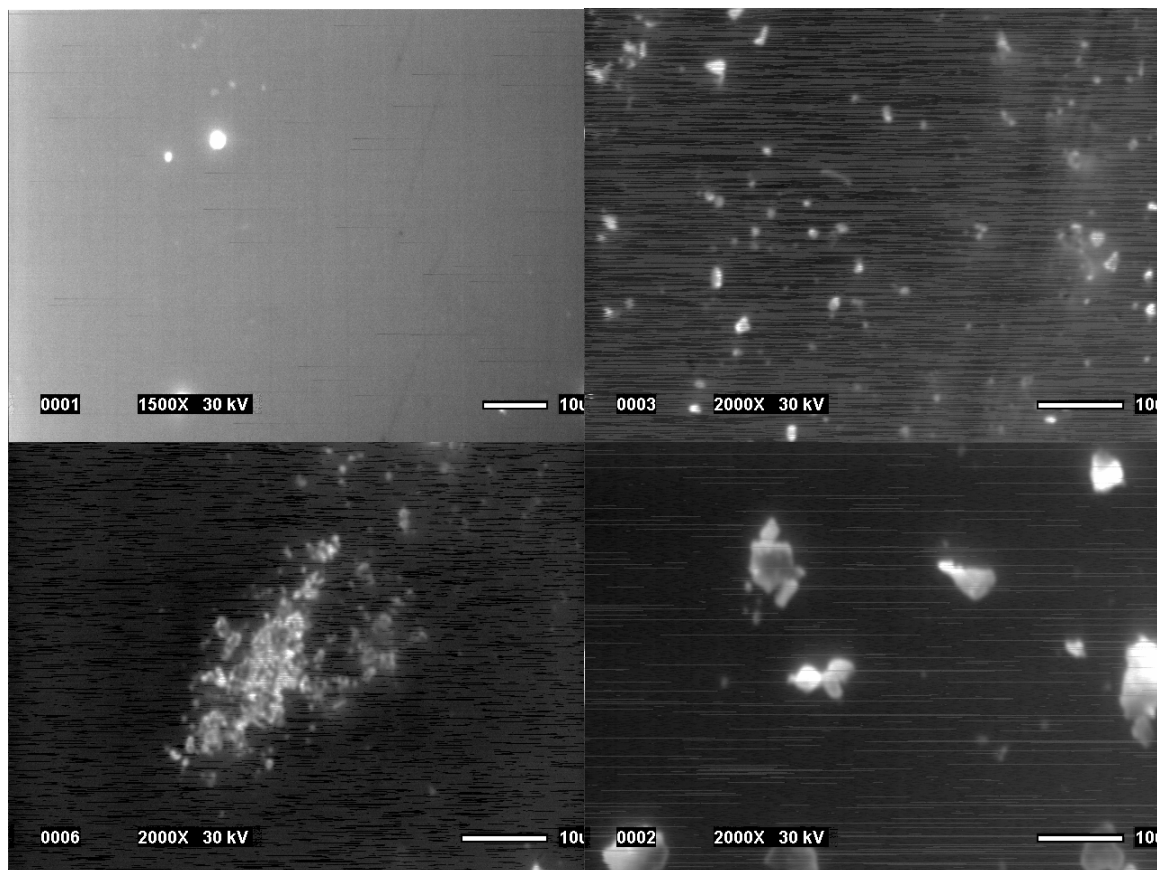


Figure 7.2 SEM micrograph of a sample grown at 610°C

The sample grown at 680°C has a surface relatively flat with occasional bumps and pits. Looking at a higher magnification the surface seems to have micron size granulation. In certain regions lines that can be cracks run parallel and in two directions intersecting at an angle of 30 degrees. (Figure 7.3)

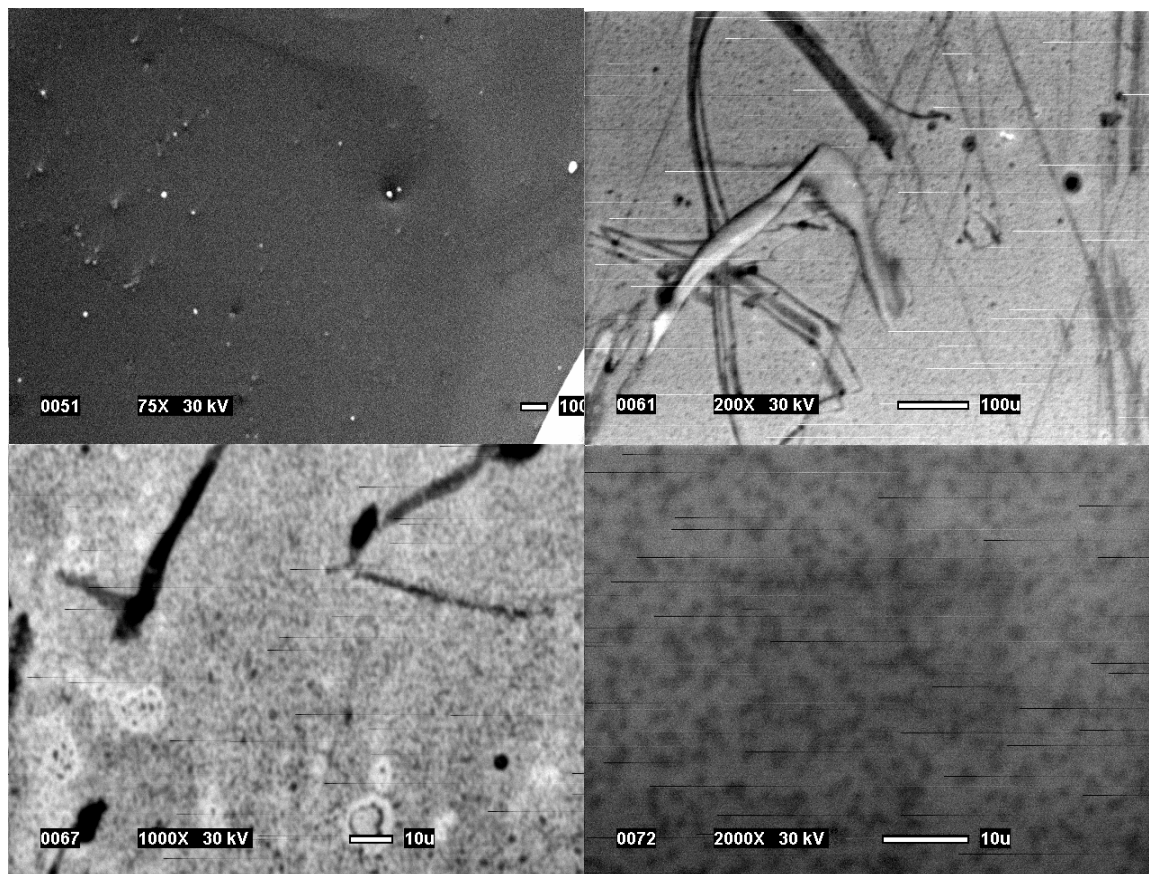


Figure 7.3 SEM micrograph of a sample grown at 680°C

At 750°C substrate temperature the film covers the substrate completely (Figure 7.4) with good uniformity in thickness and morphology across the surface; occasionally there are some pits and bumps. At smaller scale the surface has a granular structure with sub-micron size bumps.

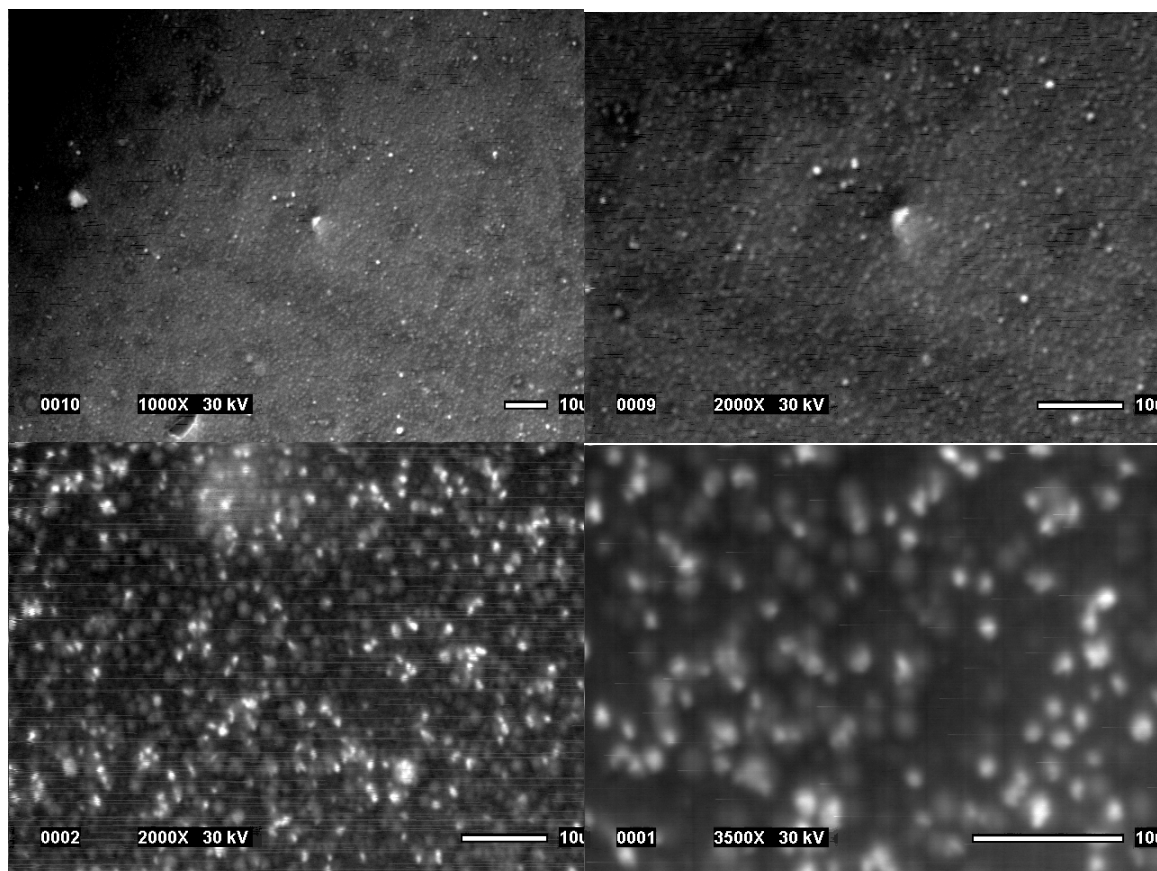


Figure 7.4 SEM micrograph of a film grown at 750°C

The sample grown at 850°C has a very high degree of non-uniformity (Figure 7.5). There are macroscopic regions with less material deposited, clearly delimited by the surrounding regions that have a larger amount of material. In the regions with incomplete coverage the SEM shows islands with irregular shapes and micron size nuclei with an average separation of 3.5 μm corresponding to a density of $8 \times 10^6 \text{ cm}^{-2}$. While this cannot be determined from these pictures RBS shows that these islands or nuclei are sitting on an 8 nm thick nucleation layer in the regions where the islands are taller (300 nm).

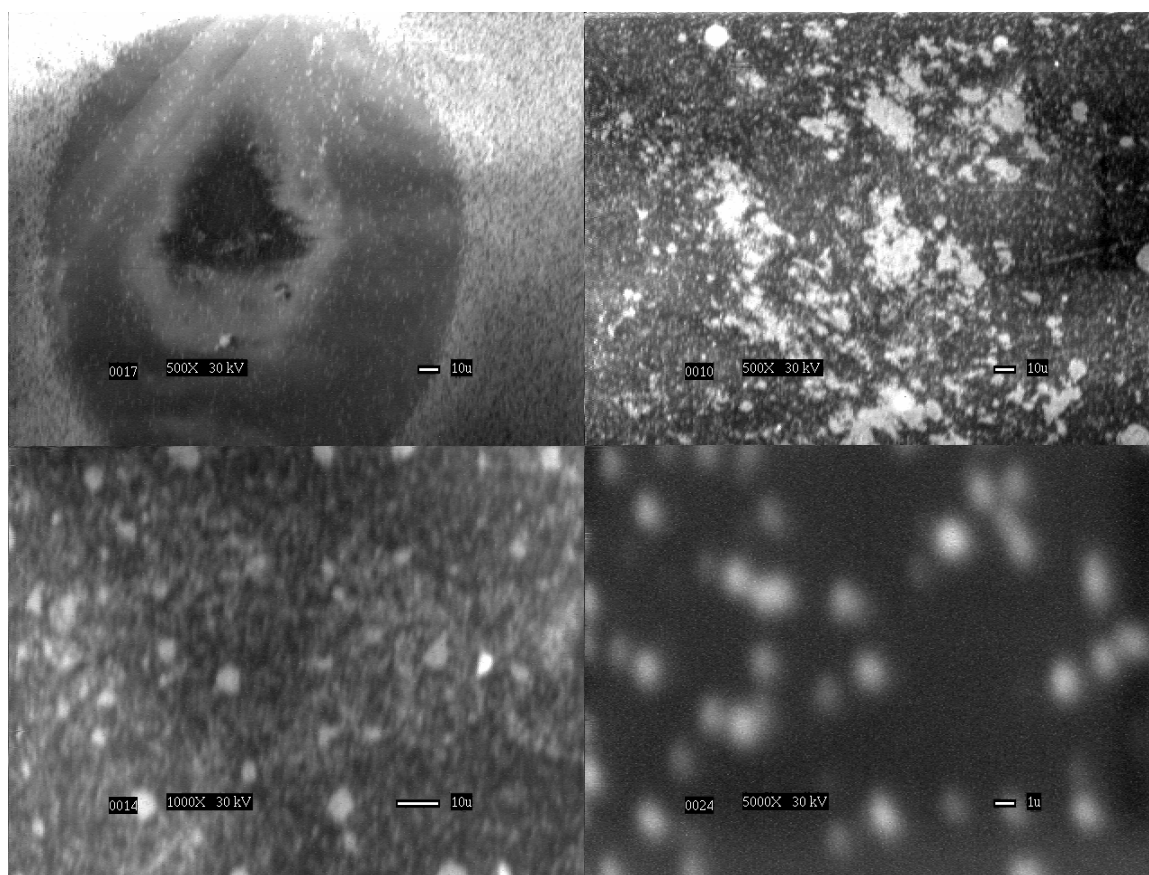


Figure 7.5 SEM micrograph of a sample grown at 850°C

The sample grown at 950°C has two different types of morphologies across the surface visible in Figure 7.6. In the region of highest growth rate the growth occurs by hexagonal shaped islands of up to 10 μm in size coalescing and forming a continuous film in other words a combination of 2D and 3D growth. The density of hexagonal islands is $\sim 5 \times 10^7 \text{cm}^{-2}$. In the surrounded regions the islands are not visible and the growth seems to be 2 dimensional with a flatter surface. In the region with hexagonal islands we can see that the hexagons are aligned with each other but we also notice a number of twinning defects.

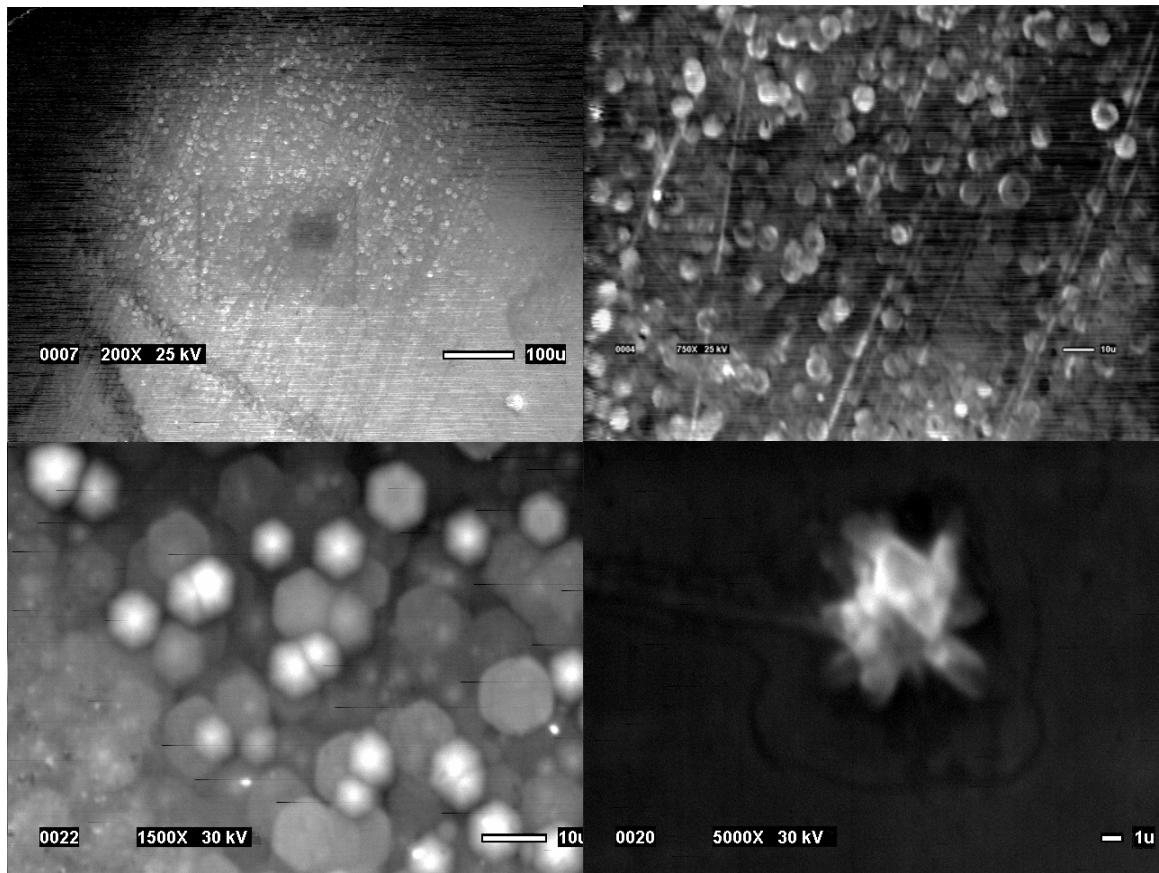


Figure 7.6 SEM micrograph of a sample grown at 950°C

Similar hexagonal island growth has been observed for slightly thicker ($0.46 \mu\text{m}$) films grown on GaN buffer layer at 1040°C [127] with a density of $2.1 \times 10^9 \text{cm}^{-2}$ and an

average size of $0.2\mu\text{m}$ while for a thick film the density was $\sim 10^5\text{ cm}^{-2}$ for a average size of $35\mu\text{m}$ [128].

The trend observed is from flat film surface from lower temperature films (550°C - 610°C) to films with a certain granularity and occasional groves (680°C - 750°C) to a film formed almost entirely of tall irregular islands (850°C) and finally at 950°C a film that exhibits tall hexagonal islands that are coalesced into a continuous film. As discussed in Chapter 6 the surface morphology has been related to the polarity of the films with flatter films being Ga-polar and more rough and with 3D features being N-polar [75].

7.2 Analysis by X-Ray Diffraction

The X-Ray Diffraction has been performed in a Rigaku Diffractometer. Both θ - 2θ scans and rocking curves of the GaN peaks have been taken. For comparison we have also taken spectra of commercial GaN in the same conditions. All the samples show similar peaks from wurtzite GaN ([0002], [0004], [0006]) and sapphire (Figure 7.7).

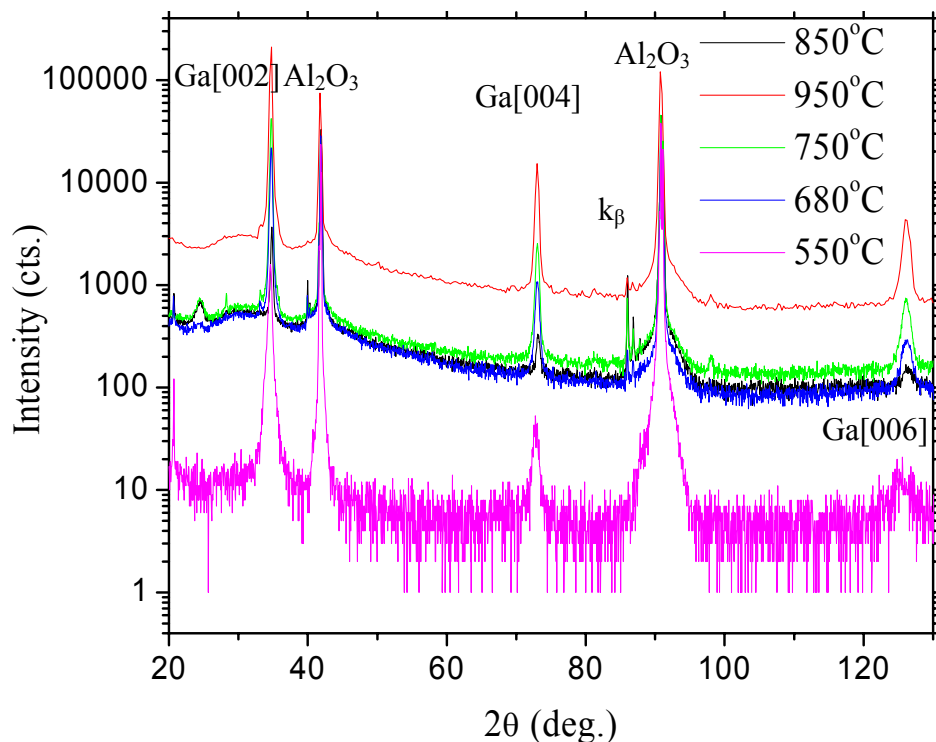


Figure 7.7: XRD spectra for GaN films on sapphire grown in the temperature range 550°C to 950°C

Figure 7.8 shows the X-Ray diffraction (left) and the rocking-curves for the main GaN diffraction peaks for the sample grown at 950°C. This is the sample with the best crystalline quality as measured both by Ion channeling and XRD (FWHM).

Using the x-ray diffraction apparatus and same slit settings and we have analyzed commercial MOCVD GaN substrates. The x-ray results are shown in Figure 7.9. In the spectrum of this sample we observe the wurtzite GaN peaks and lower intensity sapphire peaks due to the higher thickness of the film.

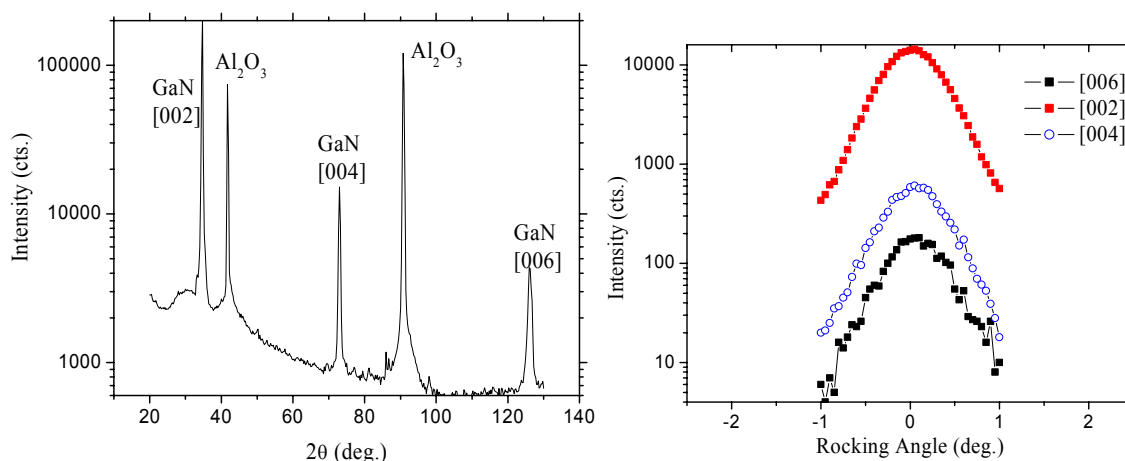


Figure 7.8: XRD scan and Rocking Curves for sample grown at 950°C

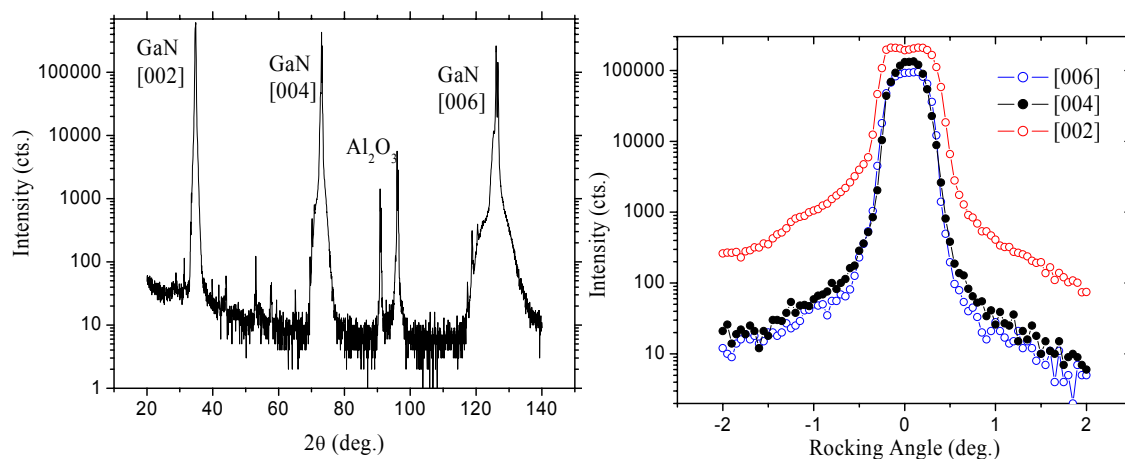


Figure 7.9: XRD scan and Rocking Curves for commercial MOCVD GaN

The dependence of the FWHM of the Rocking curves for films grown at different temperatures is shown in Figure 7.10. From this graph we observe an increase in crystalline quality of the films with the temperature with the exception of the film grown at 850°C. We attribute this behavior to the fact that the film is not contiguous across the surface of the substrate in other word the individual islands of GaN did not coalesce. This can be seen in the RBS data shown before (Figure 6.8) and the SEM pictures shown in section 7.1. This broadening is an indication that the various nuclei of GaN are slightly misaligned with respect with each other, such misalignment have been estimated up to $\pm 5^\circ$ [46]. Furthermore we also believe the sapphire substrate has sufficient damaged surface (as shown by the SEM images presented in Chapter 3) to give rise to slightly misaligned nuclei in spite of the thermal treatment that we have performed on the substrates.

The FWHM of the commercial MOCVD film is $0.39^\circ \pm 0.2^\circ$ which is not very far from the value of 0.59° obtained for the best film we have obtained.

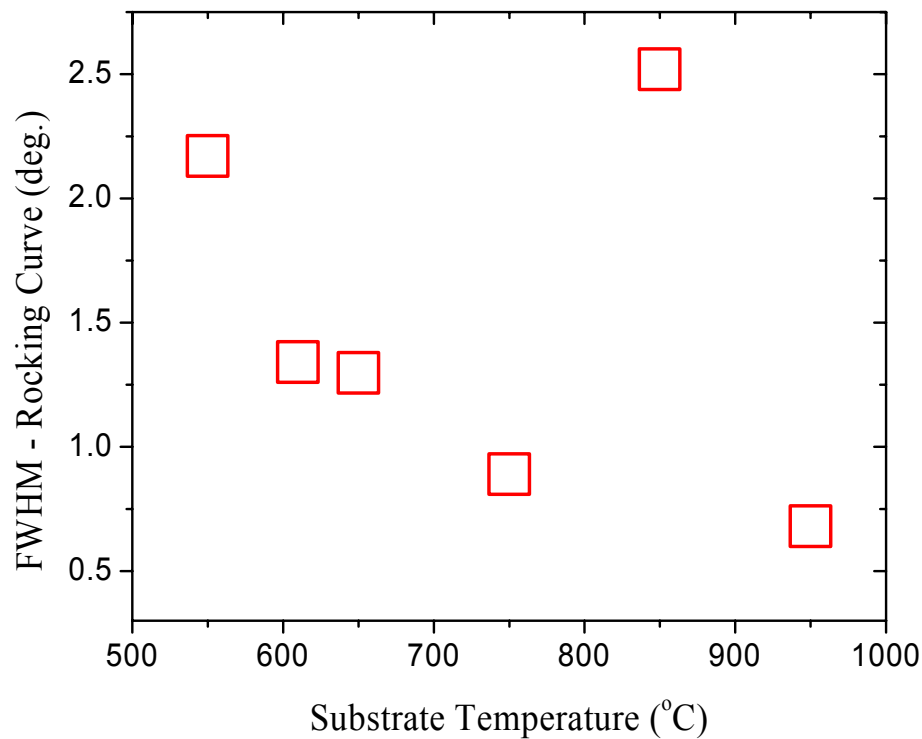


Figure 7.10: FWHM of the Rocking Curves as a function of growth temperature

The XRD technique it is not able to distinguish between polycrystalline films and single crystals and it can only analyze the films at the points where they have a high thickness. The technique confirms the result of ion channeling that no aligned cubic phase has been incorporated in the film.

We have investigated the repeatability of the growth conditions by comparing the XRD from two samples grown in similar conditions. The two samples are grown at a substrate temperature of 850°C using similar gas flows and pretreatments at approximately two-month interval. The XRD spectra shown in Figure 7.11 are similar, showing the sapphire peaks and GaN (0002), (0004) and (0006) peaks, indicating a good degree of reproducibility of the growth conditions. The slight difference in the intensity of the signal can be explained by probing a film with a different thickness.

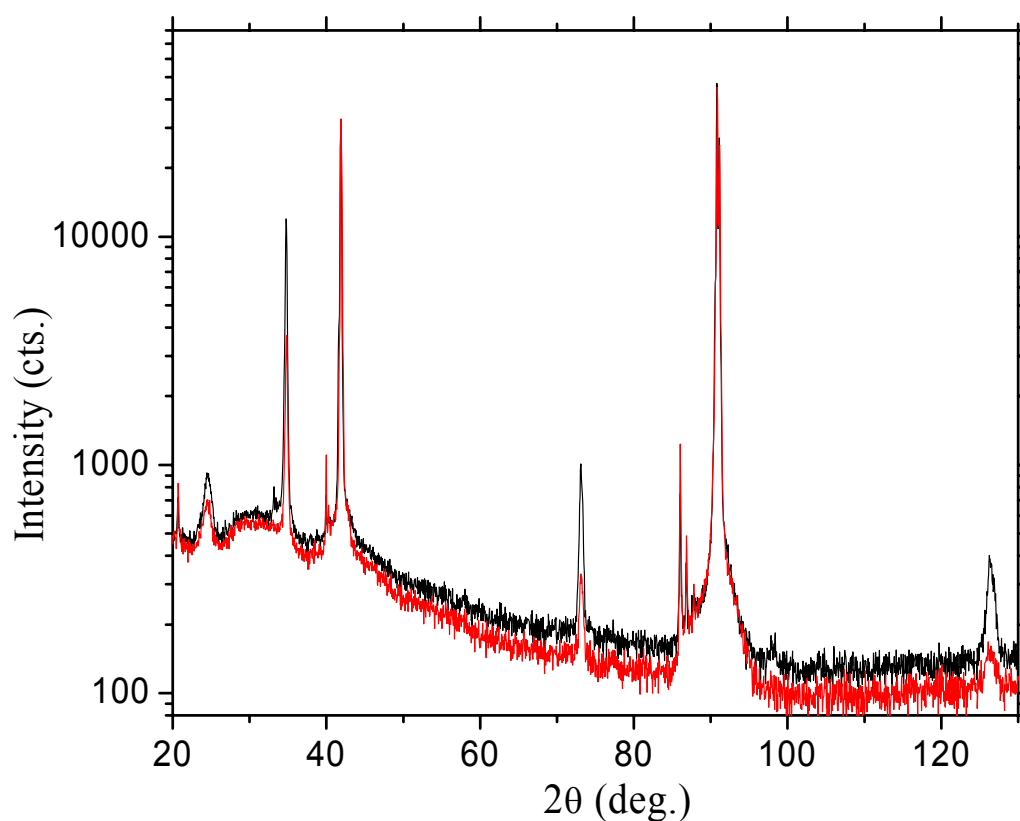


Figure 7.11: XRD spectra for two samples grown at 850°C in similar conditions

7.3 Thickness measurements

Thickness measurements have been performed using a mechanical stylus thickness profilometer, (Dektak IIA manufactured by Veeco Instruments Inc) with an accuracy of $\pm 100 \text{ \AA}$. The thickness measurements have been performed for a few of the samples in order to compare the thickness obtained with the thickness obtained by RBS using the accepted GaN density. Upon comparing the two measurements we have found an agreement of $\pm 10\%$ between the two methods.

Figure 7.12 shows such a thickness measurement performed on one of the samples. The sharp edge is due to the masking of the substrate by the Tungsten wire that is used to hold the sapphire substrate on the heating element. The measured thickness across the sharp boundary is $172 \text{ nm} \pm 2 \text{ nm}$.

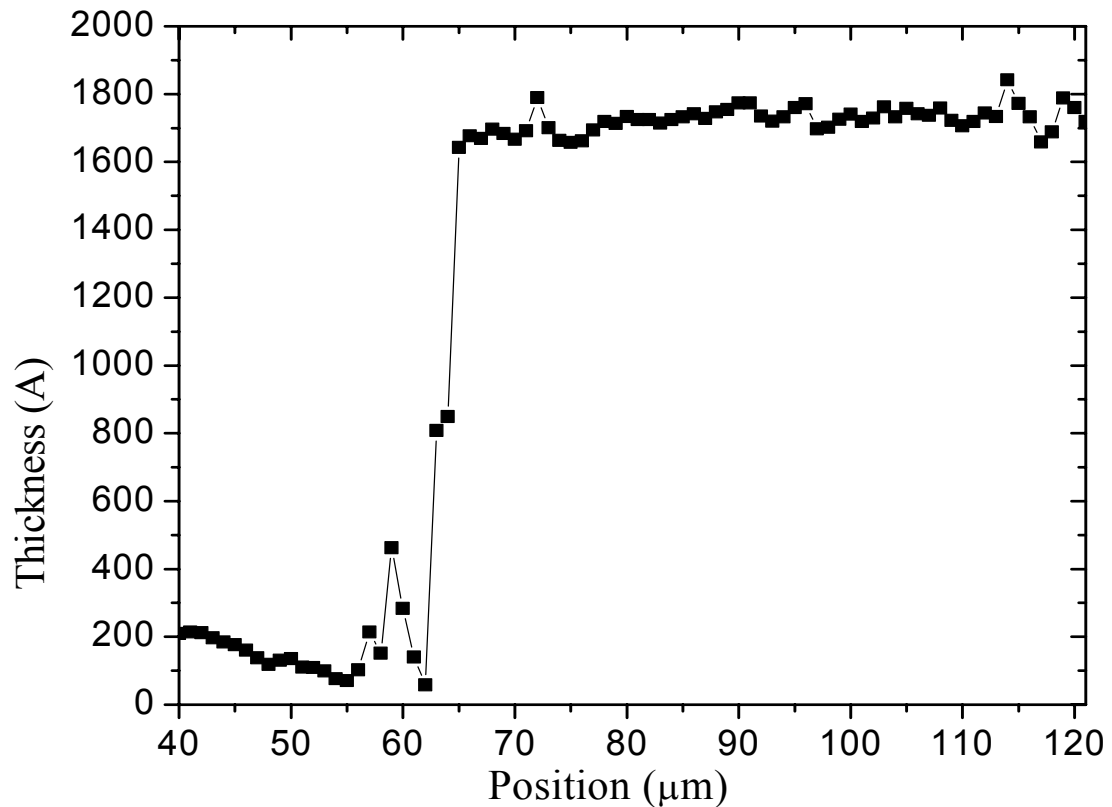


Figure 7.12 Thickness measurement of GaN on sapphire using stylus profilometer

7.4 Summary of results

The SEM investigation of the surface morphology of the films has provided use with an understanding of the growth mode and the surface roughness and structure. While the substrate temperature has the main influence on the crystalline quality of the film as measured by Ion Channeling the mass transport of the precursor gasses at the substrate surface has a strong influence on the surface morphology and even growth mode (as observed by SEM). It is apparent that both temperature and gas flow has to be optimized in order to obtain smooth films with good crystalline quality.

From the XRD analysis we conclude that all the observed peaks belong to the hexagonal GaN film of wurtzite phase and to the sapphire substrate. All the films analyzed exhibit the mentioned peaks and no unaccounted peak.

The XRD analysis of the films is consistent with the analysis provided by Ion Channeling with the provision that we are not able to determine the actual position on the sample surface where the X-rays are being diffracted and hence to determine the influence of the film thickness on FWHM of the rocking curve. The trend is that FWHM of the rocking curve is smaller for films grown at higher temperatures. The FWHM of the best crystalline film compares well with commercial MOCVD, as measured in the same conditions (same slit settings for higher resolution). The film grown at 850°C falls out of the trend mentioned before and this is because the film it is not continuous across the surface and hence the various islands may still be slightly misaligned. It is not possible to determine from XRD what is the temperature range that produces single crystal films since there is no way to connect directly the FWHM with the crystalline or polycrystalline nature of the films. Although XRD provides unambiguously the spacing between the planes of the crystal, Ion Channeling as outlined in Chapter VI provides a better way to determine the crystalline nature of the film and it is more sensitive to the crystalline quality of the film.

The repeatability in obtaining films has been investigated with XRD and good agreement has been obtained for samples grown in similar conditions.

Chapter 8

Conclusions

In order to investigate the early stages of growth of GaN on sapphire a new MOCVD reactor system has been designed and built from the ground up and integrated with into the W.M. Keck UHV thin film analysis facility. The main subsystems are: the reactor chamber; the gas admission and evacuation; the substrate heating and temperature monitor and control; the chamber pressure monitor; and the sample transfer. The sample holder that allows the transfer of the samples has been redesigned to include a ceramic heater. The gas admission and evacuation has been implemented using manual and air controlled valves. A control unit for the air valves has been built that implements safety rules for operating the valves. The reactor uses an innovative way of controlling the admission of the metallic precursor based only on mass flow controllers that proved to be very suitable for this type of gas.

Reports have shown that every step of the film growth has impact on the quality of the final crystalline film. We have analysed all the steps in the film deposition starting with the ex-situ preparation of the sample, the in-situ nitridation and the film growth.

For analysis we have used a series of complementary techniques geared towards determining the crystalline quality in bulk and surface, epitaxial relationship of the film with respect to the substrate and chemical composition and stoichiometry of the film. The

novelty of our method is the combination of techniques and the fact that the films are analyzed in-situ, right after they are grown, without exposure to the atmosphere. It is well determined that the exposure of the samples to air will perturb their surface in a matter of fractions of seconds by the physisorption and chemisorption of the various gases into the surface. We have performed in-situ analysis using RBS/Ion-Channeling, LEED and XPS/AES and the thicker samples have been analyzed ex-situ using XRD (2θ scans, and rocking curves), SEM and thickness profilometry. The goal of analyzing in-situ has been achieved by building the reactor chamber into the W.M. Keck analysis facility. The Keck facility comprise the: 1) Kratos XAS800A electron spectrometer with capabilities of performing surface studies by XPS/UPS/AES/SEM and depth profiling using the 5keV Ar ion source, 2) UHV chamber connected at the Ohio University Van de Graaf accelerator for RBS/Ion Channeling studies as well as LEED, 3) UHV transfer system with magnetic coupled manipulators and magnetic actuated sample carts for moving the samples between the various chambers without exposure to the air.

The structure of the substrate has the role of a template for the epilayer and therefore the control of the sapphire surface is critical. We have extensively characterized the sapphire substrates and have found that the surface morphology of the substrates improves after the air annealing but it is still not atomically flat and exhibits pits and grooves. From the analysis of the surface peak in the ion channeling show that the sapphire has a bulk-like termination with no lateral reconstruction. By individually probing the Al and O sub-lattices of the sapphire ion channeling provides a way to identify the crystallographic planes of the crystal. The analysis of the sapphire nitridation showed that nitrogen is absorbed into the sapphire surface region when using either nitrogen or ammonia. From XPS analysis of the surface the N_{1s} signal for the ammonia nitridated is about 3 times larger, and from the ion channeling of the two samples the N is adsorbed deeper into the surface for the ammonia nitridation, while for nitrogen no increase in the width of the surface peak is observed. LEED of the nitridated surfaces is observed only for the nitrogen nitridated sample. From these observations we conclude that the nitrogen nitridation proceeds at a slower rate and only on the upper surface of the sample while in the case of ammonia the nitrogen penetrates deeper into the sapphire and it creates crystalline disorder on the surface.

In order to grow good crystalline films we have searched to optimize the epitaxy process from the optimal growth conditions found by other research groups and published in various journals. Due to the high numbers of parameters that can impact the quality of the film we have kept constant some of the parameters while we have investigated the effect of gas flow geometry, the growth rate, and the carrier gases on the properties of the films and also the time dependence of the growth rate. For the optimization procedure we have used mainly the minimum yield of the channeling yield ($\chi_{\min}$), RUMP simulations of stoichiometric GaN, ratio of Ga to N peaks in XPS, film coverage and, visual aspect of the films. After this procedure of finding the right growth parameters specific to our reactor chamber we have been able to grow GaN films in a wide temperature range. The growth time was chosen such that the film goes over the initial phase, of discrete nuclei scattered across the surface, and is contiguous across the surface.

Using identical growth conditions with the exception of the substrate temperature that was varied in the temperature range 450-1050°C we have obtained a series of GaN films. The analysis of this samples allows us to to investigate the role of the substrate temperature on the early stages of growth and epitaxy of GaN on sapphire. We have found that films grown in our reactor chamber have variable thickness due to a combination of factors such as the asymmetric flow pattern of the gases with respect to the substrate and a non-uniform boundary layer with variable thickness created by the convection currents above the heated substrate. We have used this feature of the films and have taken measurements at points across the surface. The film at different positions across the surface have similar preparation and growth conditions with the exception of a smaller growth rate due to the lower mass transport of the reactants to the substrate. This allows us to investigate the role of the film thickness on the epitaxy of GaN on sapphire.

We have observed that there are two types of films as a function of the growth temperature: at lower temperatures the films are flatter and more uniform in thickness while at higher temperatures they become rougher, exhibit islands and the film may not cover the entire substrate or is not contiguous. We have correlated the surface morphology of the film with findings in the literature on the polarity of the GaN films and proposed a model that can account for the experimental observations.

From the analysis of the growth rate as a function of the substrate temperature in the kinematic controlled regime we have extracted the activation energy of 169 kJ/mol which is slightly higher than other experimental results [82,110]. This signifies that in our reactor chamber the Ga and N precursor fragments need more energy in order to react and the chemical reaction depends on and takes place on the hot sapphire substrate.

From the RBS analysis and the corresponding RUMP simulations we have determined that the GaN films have the correct stoichiometry and they have thickness that span between 7Å to 5500Å depending on the substrate temperature and the position on the substrate. The LEED surface analysis provided us with a measure of the ordering at the surface of the film. In the temperature range 610°C-1050°C we observed both diffuse and sharp patterns with the best diffraction patterns for the films grown at 950°C. All the patterns are hexagonal with no reconstruction and no faceting such that we conclude that only observe wurtzite phase growths in our experimental conditions. Our analysis has been performed after the samples have been cooling down to room temperature and they differ from the results of Munkholm [49] that has performed the analysis while the film is at high temperature. This can point towards a change in the surface symmetry during the cooling down phase.

The surface analysis by XPS provided us with a method to investigate the extent of surface contamination for sample exposed to air. We have only found contamination with carbon and oxygen that is usual for the air exposure. A continuous increase of the contamination levels can last up to a few weeks from the time the sample has been exposed to air. Using a 5keV Ar ion gun we have sputtered the surface of the GaN films and have found that while we do get rid of the contaminants, to the level prior to the exposure to air, the stoichiometry of the surface is perturbed due to the preferential sputtering of the nitrogen atoms. Our results are obtained for thin films are similar with the findings by other groups for films of higher thickness. The sputtered GaN surface is very unstable and reactive and it will contaminate even when it is kept under UHV conditions

We have performed analysis of the crystalline ordering of the films by measuring the minimum yield ($\chi_{\min}$) for sample grown at different temperature and with different

thickness. We have determined two trends: the thicker films tend to have a better crystalline quality and the higher substrate growth temperature is also producing better films. An additional measure of the crystallinity has been obtained from the channeling maps around the c-axis of the GaN lattice. From the channeling maps and the stereographic projections for hexagonal and cubic crystals we have determined that the wurtzite phase of GaN has been grown and we have determined that the film's crystallographic axis and planes are aligned with the substrate within 0.2° , in other words we have achieved epitaxy. An axial alignment is first observed for films grown at 610°C while the full alignment of the planes is observed for films at 680°C . These points to a polycrystalline film below 610°C and a epitaxial single-crystal film for films grown at 680°C and higher. The substrate temperature of 950°C give rise to a film with the best quality and a minimum yield of $\chi_{\min}=3\%$, which is close to the predicted value and to commercial GaN substrates and indicates that the rate of defect annihilation is higher towards the interface and decreases after the film is thicker than about 300nm. The surface peak analysis in ion channeling for films $750\text{-}950^\circ\text{C}$ reveals that the GaN film has bulk-like termination and the film grown at 680°C has one more atom/row visible to the ion beam. This can be caused by a lateral reconstruction such as the $(\sqrt{3}\times 2\sqrt{3})R30^\circ$ observed by Munkholm [49] for MOCVD grown GaN. We have calculated average defect density in the surface region from the Ga signal of the channeling spectrum for films grown at temperature $680\text{-}950^\circ\text{C}$ and thickness 140-320 nm and have obtained values $6.4\times 10^{10}\text{-}2\times 10^{11}\text{cm}^{-2}$. The trend is similar to the one observed from the minimum yield dependence on temperature and thickness. In general the values reported for best commercial GaN are 10^8cm^{-2} but for much thicker films ($>10\mu\text{m}$).

By comparing the channeling and LEED results for samples grown at different temperatures we observed that samples for which we observe LEED diffraction patterns (610°C) can in fact be very poor crystals as measured by ion channeling yield. This is indicative of the fact that surface ordering can be achieved for polycrystalline films and that surface diffraction alone cannot be used as an indication of crystallinity and has to be complemented by a bulk-sensitive technique.

In ion channeling we have determined the epitaxial relationship between the film and substrate. The method used to identify the sapphire planes did not work for GaN since the signal from nitrogen is too small compared to the background signal from the substrate. In order to identify the GaN planes we scanned along a GaN plane and find the axis in that plane and by identifying the axis we have identified the plane. Using this method we have determined that the epitaxy of GaN is achieved by a rotation of the epilayer with respect to the substrate by 30° . We have found that the damage created by the ion beam is negligible if the analysis dose is kept below $20\ \mu\text{C}$. The damage is only visible in the value of the minimum channeling level and would not affect the shape of the channeling maps. The measurement procedure includes the change of the measurement spot on the sample before taking the channeled spectrum.

The ex-situ analysis included X-ray diffraction and rocking curves, SEM and thickness profilometry. The surface morphology of the films differs widely with the growth temperature. Smoother surfaces are obtained for low temperature while at high temperature 3D islands are visible. The XRD measurements have confirmed the wurtzite phase is grown but the measurement cannot differentiate between single crystal and polycrystalline phase.

Bibliography

1. Ed. S. J. Pearton GaN and Related Materials (1997).
2. S. Yoshida, S. Misawa, and S. Gonda, *Applied Physics Letters*. **42**, 427 (1983).
3. V.W. L. Chin, T. L. Tansley, and T. Osotchan, *J. Appl. Phys.* **75**, 7365 (1994).
4. H. P. Maruska and J. J. Tietjen, *Applied Physics Letters* **15**, 327 (1969).
5. B. Monemar, *Physical Review* **B10**, 676 (1974).
6. E. K. Sichel and J. I. Pankove, *Journal of Physical Chemistry of Solids* **38**, 330 (1977).
7. E. Ejder, *Physica Status Solidi*, **A6**, 445 (1971).
8. A. S. Barker and M. Ilegems, *Physical Review* **B7**, 743 (1973).
9. M. S. Shur and M. A. Khan, *Material Research Bulletin* **22**, 44 (1997).
10. S. Yoshida, S. Misawa, and S. Gonda, *Journal of Vacuum Science and Technology* **B1**, 250 (1983).
11. S. Sivaram, Chemical vapor deposition (1995).
12. Amano H. Sawaki N., Akasaki I., Toyoda N., *Applied Physics Letters* **48** 353-355 (1986).
13. S.T. Sheppard, K. Doverspike, W.L. Pribble, S.T. Allen, and J.W. Palmour, *56 th Annual Device Research Conference*, (1998).
14. R. Gaska, J.W. Yang, A. Osinsky, Q. Chen, M. Asif Khan, A.O. Orlov, G.L. Snider, M.S. Shur, *Applied Physics Letters* **72**, 707-709 (1998).
15. T.S. Zheleva, H. Nam, M.D. Bremser, and R.F. Davis, *Applied Physics Letters* **71**, 2472-2474 (1997).

16. D. Kapolnek, S. Keller, R. Ventury, R.D. Underwood, P. Kozodoy, S.P. Den Baars, and U.K. Mishra, *Applied Physics Letters* **71**, 1204-1206 (1997).
17. S. Nakamura, *Japanese Journal of Applied Physics* **30**, L1705-7 (1991).
18. S. Nakamura, M. Senoh, S.I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H.Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano and K. Chocho, *Applied Physics Letters* **72**, 211-213 (1998).
19. P. Kozodoy, J.P. Ibbetson, H. Marchand, P.T. Fini, S.Keller, J.S. Speck, S.P. DenBaars, and U.K.Mishra, *Applied Physics Letters* **73**, 975-977 (1998).
20. Nakamura S., Mukai T., Senoh M., *Applied Physics Letters* **64**, 1687 (1994).
21. Melton W.A., Pankove J.I., *Journal of Crystal Growth* **178**, 168-173 (1997).
22. Strite S., Morkoc H., *Journal of Vacuum Science and Technology B* **10**, 1237 (1992); Strite B., Lin M.E., Morkoc H., *Thin Solid Films* **23**, 197 (1993).
23. Detchprohm T., Hiramatsu K., Itoh K., Akasaki I., *Japanese Journal of Applied Physics* **31**, L1454 (1992).
24. C. Kim. I. K. Robinson, J. Myoung, K. Shim, M.-C. Yoo, K. Kim, *Applied Physics Letters*. **69**, 2358 (1996).
25. J. Cui, A. Sun, M. Reshichkov, F. Yun, A. Baski, H. Morkoç, *MRS Internet Journal of Nitride Semiconductor Research* **5**, 7 (2000).
26. M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, O. Ishiyama, M. Shinohara, M. Kubo, R. Miura, A. Miyamoto, *Applied Physics Letters* **75**, 2615 (1995).
27. Heinlein C., Grepstad J., Riechart H., Averbek R., *Materials Science and Engineering* **B43**, 253-257 (1997).
28. F. Widmann, B. Daudin, G. Feuillet, Y. Samson, M. Arlery, J.L. *MRS Internet Journal of Nitride Semiconductor Research* **2**, 20(1997).
29. S. Fuke, H. Teshigawara, K. Kuwahara, Y. Takano, T. Ito, M.Yanagihara, K. Ohtsuka, *Journal of Applied Physics* **83**, 764-767 (1998).
30. H.C. Lin, J.Ou, W.K. Chen, W.H. Chen, M.C. Lee, *Japanese Journal of Applied Physics* **36**, L598-600 (1997).
31. Uchida K., Watanabe A., Yano F., Kouguchi M., Tanaka T., Minagawa S., *Journal of Applied Physics* **79**, 3487-3491 (1996).
32. A.R. Woll, R.L. Headrick, S. Kycia, J.D. Brockl, *Physical Review Letters* **83**, (1999).
33. Briot O., Alexis J.P., Tchounkeu M., Aulombard R.L., *Materials Science and Engineering* **B43**, 147-153 (1997).
34. Hwang C.Y., Schurman M.J., Mayo W.E., Li Y, Lu Y., Liu H., Salagaj T., Stall R.A., *Journal of Vacuum Science and Technology* **A13**, 672-675 (1995).

35. Hwang C.Y., Mayo W.E., Lu Y., Liu H., Proceedings of the Material Research Society Symposium **326**, 347 (1994).
36. Grandjean N., Massies J., Martinez Y., Venegues P., Leroux M., Laugt M., *Journal of Crystal Growth* **178**, 220-228 (1997).
37. Paek J-S., Kim K-K., Lee J-M., Kim D-J., Yi M-S., Noh D.Y., Kim H.G., Park S-J., *Journal of Crystal Growth* **200**, 55-62 (1999).
38. Suetsugu T., Yamazaki T., Tomabechi S., Woda K., Tsubouchi K., *Applied Surface Science* **117/118**, 540 (1997).
39. Balakrishnan K., Okumura H., Yoshida S., *Journal of Crystal Growth* **189/190**, 244 (1998).
40. Grandjean N., Massies J., Leroux M., *Applied Physics Letters* **69**, 2071 (1996).
41. Yamaguchi T., Araki T., Saito Y., Kano K., Kanazawa H., Nanish Y., Teraguchi N., Suzuki A., *Journal of Crystal Growth* **237-239**, 993-997 (2002).
42. Kim K-S., Kim K-B., Kim S-H., *Journal of Crystal Growth* **233**, 167-176 (2001)
43. Akasaki I., Amano H., Koide Y., Hiramatsu K., Sawaki N., *Journal of Crystal Growth* **98**, 209 (1989).
44. Lorenz K., Gonsalves M., Wook Kim, Narayanan V., Mahajan S., *Applied Physics Letters* **77**, 3391-3393 (2000).
45. Kobayashi Y., Akasaka T., Kobayashi N., *Japanese Journal of Applied Physics* **37**, L 1208-L 1210 (1998).
46. V. Narayanan, K. Lorenz, W. Kim, S. Mahajan, *Philosophical Magazine A* **82**, 885 (2002).
47. B. Daudin, J.L. Rouviere, M. Arlery, *Applied Physics Letters* **69**, 2480-2482 (1996).
48. M. Sumiya, T. Ohnishi, M. Tanaka, A. Ohtomo, M. Kawasaki, M. Yoshimoto, H. Koinuma, K. Ohtsuka, S. Fuke, *MRS Internet Journal of Nitride Semiconductor Research* **G6.23**, (1999).
49. A. Munkholm, I. G.B. Stephenson, J.A. Eastman, C. Thompson, P. Fini, J.S. Speck, O. Auciello, P.H. Fuoss, and S.P. DenBaars, *Physical Review Letters* **83**, 741-744 (1999).
50. Sitar Z., Smith L.L., Davis R.F. *Journal of Crystal Growth* **141**, 11-2 (1994).
51. Kim K.S., Oh C.S., Lee K.J., Yang G.M., Hong C-H., Lim K.Y., Lee H.J., Yoshikawa A., *Journal of Applied Physics* **85**, 8441-8444 (1999).
52. Degave F., Ruterana P., Nouet G., Je J.H., Kim C.C., *Diamond and Related Materials* **11** 901-904 (2002).
53. Ebel R., Fehrer M., Figge S., Einfeldt S., Selke H., Hommel D., *Journal of Crystal Growth* **201-202**, 433-436 (2002).

54. Chih-Hao Lee, G. C. Chi and C. F. Lin, M. S. Feng, J. D. Guo, *Applied Physics Letters* **68**, 3440 (1996).
55. Rouviere J.L., Arlery M., Daudin B., Feuillet G., Briot O., *Materials Science and Engineering* **B50**, 61-71 (1997).
56. K. Hiramatsu, S. Itoh, H. Amano, I. Akasaki, N. Kuwano, T. Shiraishi, K. Oki, *Journal of Crystal Growth* **115**, 628-633 (1991).
57. Wickenden D.K., Faulkner K.R., Brander R.W. Isherwood B.J. *Journal of Crystal Growth* **9**, 158 (1971).
58. Sato M., Aoki M., *Japanese Journal of Applied Physics* **15** 1943 (1976).
59. Ning X.J., Chien R.F., Pirouz P., Yang J.W., Asif Khan M., *Journal of Materials Research* **11**, 3 580-592 (1996).
60. Asif Khan M., Kuznia J.N., Van Hove J.M., Olson D.T., Krishnankutty S., Kolbas R.M., *Applied Physics Letters* **58**, 526 (1991).
61. B. Sundaravel, E. Z. Luo, J. B. Xu, and I. H. Wilson, W. K. Fong, L. S. Wang, C. Surya, *Journal of Applied Physics* **87**, 955-957 (2000).
62. Paul D. Brown, *Journal of Crystal Growth* **210**, 143-150 (2000).
63. S.J. Rosner, E.C. Carr, M.J. Ludowise, G. Girolami, H.I. Erikson, *Applied Physics Letters* **70**, 420 (1997).
64. T. Sugahara, H. Sato, M. Hao, Y. Naoi, S. Kurai, S. Tattori, K. Yamashita, K. Nishino, L.T. Romano, S. Sakai, *Japanese Journal of Applied Physics* **37**, L398 (1998).
65. Z.L. Liao, R.L. Aggarwal, P.A. Maki, R.J. Molnar, J.N. Walpole, R.C. Williamson, I. Melngailis, *Applied Physics Letters* **69**, (1996).
66. B. Heying, X.H. Wu, S. Keller, Y. Li, D. Kapolnek, B.P. Keller, S.P. DenBaars, and J.S. Speck, *Applied Physics Letters* **68**, 643 (1996).
67. L. Cheng, Z. Zhang, G. Zhang, D. Yu, *Applied Physics Letters* **71**, 25, (1997).
68. Vennegues P., Beaumont B. Vaille M., Gibart P., *Journal of Crystal Growth* **173**, 249-259 (1997).
69. A.R. Smith, R.M. Feenstra, D.W. Greve, M. -S. Shin, M. Skowronski, J. Neugebauer, and J.E. Northrup, *Journal of Vacuum Science and Technology B* **16**, 2242-2249 (1998).
70. A.R. Smith, R.M. Feenstra, D.W. Greve, M.-S. Shin, M. Skowronski, J. Neugebauer, and J.E. Northrup, *Applied Physics Letters* **72**, 2114-2116 (1998).
71. O. Janzen, Ch. Hahn, T.U. Kampenb, and W. Mönch, *European Physics Journal B* **7**, 14 (1999).
72. R.M. Feenstra, J.E. Northrup, J. Neugebauer *MRS Internet Journal of Nitride Semiconductor Research* **7**, 3(2002).

73. E.S. Hellman, MRS Internet Journal of Nitride Semiconductor Research **3**, 11(1998).
74. T. Hoshimoto, Y. Terakoshi, M. Ishida, M.Yuri, O. Imafuji, T. Sugino, A.Yoshikawa, K. Itoh, *Journal of Crystal Growth* **189/190**, 254-258 (1998).
75. M. Seelman-Eggebert, J.L. Weyher, H. Obloh, H. Zimmermann, A. Rar, S. Porowsky, *Applied Physics Letters* **71**, 2635 (1997).
76. H. Yamane, M. Shimada, T. Endo, F. J. DiSalvo; *Japanese Journal of Applied Physics* **37**, 3436 (1998).
77. J.E. Northrup, J. Neugebauer, L. T. Romano, *Physical Review Letters* **103**, (1996).
78. L. T. Romano, J. E. Northrup, M. A. O'Keefe, *Applied Physics Letters* **69**, 2394-2396 (1996).
79. M. Sumiya, N. Ogusu, Y. Yotsuda, M. Itoh, and S. Fuke, T. Nakamura, S. Mochizuki, T. Sano, S. Kamiyama, H. Amano, and I. Akasaki, *Journal of Applied Physics* **93**, 1311 (2003).
80. T. Yang, K. Uchida, J. Kasai, J. Goth, *Physica Status Solidi a* **180**, 45 (2000).
81. F. Widmann et al. MRS Internet Journal of Nitride Semiconductor Research **2**, 201 (1997).
82. R. A. Fischer, A. Wohlfart, A. Devi, and W. Rogge, *MRS Internet Journal of Nitride Semiconductor Research* **5**, W3.18 (2000).
83. B. Hollander, S. Mantl, M. Mayer, C. Kirchner, A. Pelzman, M. Kamp, S. Christiansen, M. Albrecht, H.P. Strunk, *Nuclear Instruments and Methods in Physical Research B* **136-138**, 1248-1252 (1998).
84. A. Turos, L. Nowicki, A. Stonert, M. Leszczynski, I. Grzegory S. Porowski, *Materials Science Forum* **248-249**, 419-423 (1997).
85. T. Osipowicz, S.Y. Chiam, F. Watt, G. Li, S.J. Chua, *Nuclear Instruments and Methods in Physical Research B* **158**, 653-657 (1999).
86. B. Daudin, J.L. Rouviere, M. Arley, *Materials Science and Engineering*, **B43**, 157 (1997).
87. M. Linden, E. Ejder, R. Helborg, *Physica Status Solidu a* **45**, K167 (1978).
88. S. O. Kucheyev J. S. Williams, C. Jagadish, G. Li, S.J. Pearton *Applied Physics Letters*, **76**, 3899 (2000).
89. Chemical Properties, EPICHEM (2002).
90. T. Yuasa, Y. Ueta, Y. Tsudo, A. Ogawa, *Jpn. J. Appl. Physics*, **38**, L703-L705 (1999).
91. J.W. Niemantsverdriet, *Spectroscopy in Catalysis* (1993).
92. L.C. Feldman, J.W. Mayer, S.T. Picraux, *Materials Analysis by Ion Channeling – Submicron Crystallography* Academic Press (1982).

93. W.K. Chu, J.W. Mayer, M.-A. Nicolet, *Backscattering Spectrometry*, Academic Press (1978).
94. Barrett J.H., *Physical Reviews B* **3**, 325 (1971).
95. E. Alves, F.M. DaSilva, J.C. Soares, J. Bartels, R. Vianden, C.R. Abernathy, S.J. Pearton, *MRS Internet Journal of Nitride Semiconductor Research* **4S1**, 11.2(1999).
96. D. E. Carter, G.Randers-Pehrson, *Nuclear Instruments and Methods* **199**, 497-503 (1982).
97. C.R Brundle, CA Evans, S Wilson, *Encyclopedia of Material Characterization* (1992).
98. *AXIS HIS, 165, ULTRA operators Manual*, Kratos Analytical Ltd., (1995-1998).
99. E. A. Soares, M. A. Van Hove, C. F. Walters and K. F. McCarty, *Physical Review B*, **65**, 195405 (2001).
100. T.M. French, G.A. Somorjai, *Journal of Physical Chemistry* **74**, 2489 (1970).
101. C. Heinlein et al., *Journal of Applied Physics* **83**, 6023 (1998).
102. N. Grandjean, J. Massies, and M. Leroux, *Applied Physics Letters*. **69**, 2071 (1996).
103. RUMP simulation software, www.genplot.com.
104. X. H. Wu, D. Kapolnek, E. J. Tarsa, and B. Heying, S. Keller, B. P. Keller, and U. K. Mishra, S. P. DenBaars, J. S. Speck, *Applied Physics Letters* **68**, (1996).
105. M. Sumiya, M. Tanaka, K. Ohtsuka, S. Fuke, T. Ohnishi, I. Ohkubo, M.Yoshimoto, H. Koinuma, and M. Kawasaki, *Applied Physics Letters* **75**, 674(1999).
106. M. Sumiya, K. Yoshimura, N. Ogusu, S. Fuke, K. Mizuno, M. Yoshimoto, and L. T. Romano, *Journal of Vacuum Science and Technology* **20**, 456 (2002).
107. M. Stutzmann, O. Ambacher, M. Eickhoff, U. Karrer, A. Lima Pimenta, R. Neuberger, J. Schalwig, R. Dimitrov, P.J.Schuck, R.D. Grober, *Physica Status Solidi (b)* **228**, 505 (2001).
108. D. Huang, P. Visconti, K.M. Jones, M.A. Reshchikov, F. Yun, A.A. Baski, T. King, H. Morkoc, *Applied Physics Letters* **78**, 4145 (2001).
109. A. Kazimirov, G. Scherb, J. Zegenhagen, T.-L. Lee, M.J. Bedzyk, M.K. Kelly, H. Angerer, O. Ambacher, *Journal of Applied Physics* **84**, 1703 (1998).
110. Fujieda S, Matsumoto Y, *Japanese Journal of Applied Physics* **30**, (1991).
111. F.S. Tautz, S Sloboshanin, U. Starke and J.A. Schaefer, *Journal of Physics – Condensed Matter* **11**, 8035–8048 (1999).
112. H. Ishikawa, S. Kobayashi, Y. Koidea, S. Yamasaki, S. Nagai, J. Umezaki, M. Koike, M. Murakami, *Journal of Applied Physics*. **81**, (1997).

113. S.J. Pearton, C.R. Abernathy, F. Ren, J.R. Lothian, *Journal of Applied Physics* **76**, (1994).
114. R.W. Hunt, L. Vanzetti, T. Castro, K.M. Chen, L. Sorba, P.I. Cohen, W. Gladfelter, J.M. Van Hove, J.N. Kuznia, M.A. Khan, A. Franciosi, *Physica B* **185** (1993).
115. Ed: J.R. Termer, M. Nastasi, Handbook of Modern Ion Beam Materials Analysis (1995)
116. A. Yoshiasa, K. Koto, H. Maeda and T. Ishii, *Japanese Journal of Applied Physics* **36**, 781 (1997).
117. A. Dygo, A. Turos, *Physical Review B* **40**, 7704 (1989).
118. X.H. Wu, L.M. Brown, D. Kapolnek, S. Keller, B. Keller, S.P. DenBaars, J.S. Speck, *Journal of Applied Physics* **80**, (1996).
119. G.P. Dimitrakopoulos, P. Komninou, R.C. Pond, *Physica Status Solidi*. **227**, (2001).
120. K. Dovidenko, S. Oktyabrsky, J. Narayan, M. Razeghi, *MRS Internet Journal of Nitride Semiconductor Research* **4S1**, (1999).
121. T. Wang, T. Shirahama, H. B. Sun, H. X. Wang, J. Bai, S. Sakai, H. Misawa, *Applied Physics Letters* **76**, 2220-2222 (2000).
122. J. Portmann, C. Haug, R. Brenn, T. Frey, B. Schottker, D.J. As, *Nuclear Instruments and Methods in Physical Research B* **155**, 489-497 (1999).
123. H.E. Schiøtt, P.V. Thomsen, *Radiation Effects* **14**, 39 (1972).
124. H. Ellmer, R. Aichinger, S. Maser, D. Semrad, *Nuclear Instruments and Methods in Physical Research B* **155**, 479-488 (1999).
125. Munkholm A., Thomson C., Foster C.M., Eastman J.A., Aciello O., Stephenson G.B., Fini P., DenBaars S.P., Speck J.S., *Applied Physics Letters* **72**, (23) 2972 (1998).
126. B.-Y Kim, Y.-H. Choi, C.-H. Hong, S.-H. Kim, T.-K. Yoo, *Inst. Phys. Conf. Ser.* **145**, 291 (1996).
127. F.K. de Theije, A.R.A. Zauner, P.R. Hageman, W.J.P. van Enckevort, P.K. Larsen, *Journal of Crystal Growth* **197**, 37-47 (1999).
128. J.L. Weyher, P.D. Brown, A.R.A. Zauner, S. Müller, C.B. Boothroyd, D.T. Foord, P.R. Hageman, C.J. Humphreys, P.K. Larsen, I. Grzegory, S. Porowski *Journal of Crystal Growth* **204**, 419-428 (1999).

9 Appendix

9.1 Calculation of the depth scale in the RBS spectra

The following calculation is performed in order to establish the depth scale at the surface of the sapphire crystal assuming the following: incidence angle $\theta_1 = 0^\circ$, backscattered angle $\theta_2 = 168^\circ$, incident particles: $^4\text{He}^{+2}$ with an energy of $E = 2.2 \text{ MeV}$.

First we need to calculate the kinematic factors (K) for He ions incident on Al and O atoms using the formula:

$$K(M_1, M_2) = \left[\frac{\sqrt{M_2^2 - M_1^2 (\sin(\theta_1 + \theta_2))^2} + M_1 (\cos(\theta_1 + \theta_2))}{M_1 + M_2} \right]^2 \quad (9.1)$$

and $K(\text{He}, \text{Al}) = 0.5536$, $K(\text{He}, \text{O}) = 0.36369$. This allows us to calculate the energy of the backscattered particles in the surface area: $E_{\text{Al}} = E \times K(\text{He}, \text{Al}) = 1.21792 \text{ MeV}$ and $E_{\text{O}} = E \times K(\text{He}, \text{O}) = 0.80013 \text{ MeV}$.

The elemental stopping cross sections are dependent on the energy of the ion and for the incident He ions at 2.2 MeV on Al and O have been experimentally measured and are good within 10% [115]. Using interpolation with the data measured and tabulated [115] we can estimate the stopping cross sections at the energies of the particles incident and backscattered (at E , E_{Al} , and E_{O}) and they are shown in Table 9.1. The backscattered

stopping cross sections (ε) are only calculated for backscattering on Al atoms since this calculation is intended to estimate the depth scale in the Al RBS peak.

Table 9.1 Stopping cross sections for Al and O

	$\varepsilon_{Al} (\times 10^{-14} \text{ eV cm}^2)$	$\varepsilon_O (\times 10^{-14} \text{ eV cm}^2)$
Incident ion (E)	4.2382	3.0804
Backscattered ion (E_{Al} , E_O)	5.12197	4.37118

The stopping cross section for the incident ion beam is given by the formula 10.2 using the values from Table 9.1.

$$\varepsilon_{in}^{Al_2O_3} = 2 \varepsilon_{Al} + 3 \varepsilon_O \quad (9.2)$$

this corresponds to a value of $1.77176 \times 10^{-13} \text{ eV cm}^2$ for the incident ions and $2.33575 \times 10^{-13} \text{ eV cm}^2$ for the backscattered ions.

The stopping cross section factor for Al is given by formula:

$$[\varepsilon_o]_{Al}^{Al_2O_3} = K_{Al} \varepsilon_{in}^{Al_2O_3} \frac{1}{\cos(\theta_1)} + \varepsilon_{out,Al}^{Al_2O_3} \frac{1}{\cos(180^\circ - \theta_2)} = 3.36878 \times 10^{-13} \text{ eV cm}^2 \quad (9.3)$$

Using the molecular density of sapphire we can calculate the energies of the ions scattered from Al relative to the ions scattered at the surface ΔE_{Al} :

$$\Delta E_{Al} = [\varepsilon_o]_{Al}^{Al_2O_3} N^{Al_2O_3} x = 791.66337 \frac{\text{eV}}{\text{nm}} \times x \quad (9.4)$$

with $N^{Al_2O_3} = 2.35 \times 10^{22} \text{ cm}^{-3}$ and x is the depth in the target where the backscattering has been taking place.

A similar calculation for GaN gives:

$$\Delta E_{Ga} = [\varepsilon_o]_{Ga}^{GaN} N^{GaN} x = 833.25636 \frac{\text{eV}}{\text{nm}} \times x \quad (9.5)$$

9.2 Calculation of the surface peak for sapphire

From the random RBS spectrum we extract the height of the random spectrum in the Al surface region $H = 3377$ counts and from the channeled spectrum (Figure 9.1) we measure the area of the surface peak after the subtraction of the background $A = 667$ counts and the ratio of the two is $\frac{A}{H} = 0.1975$.

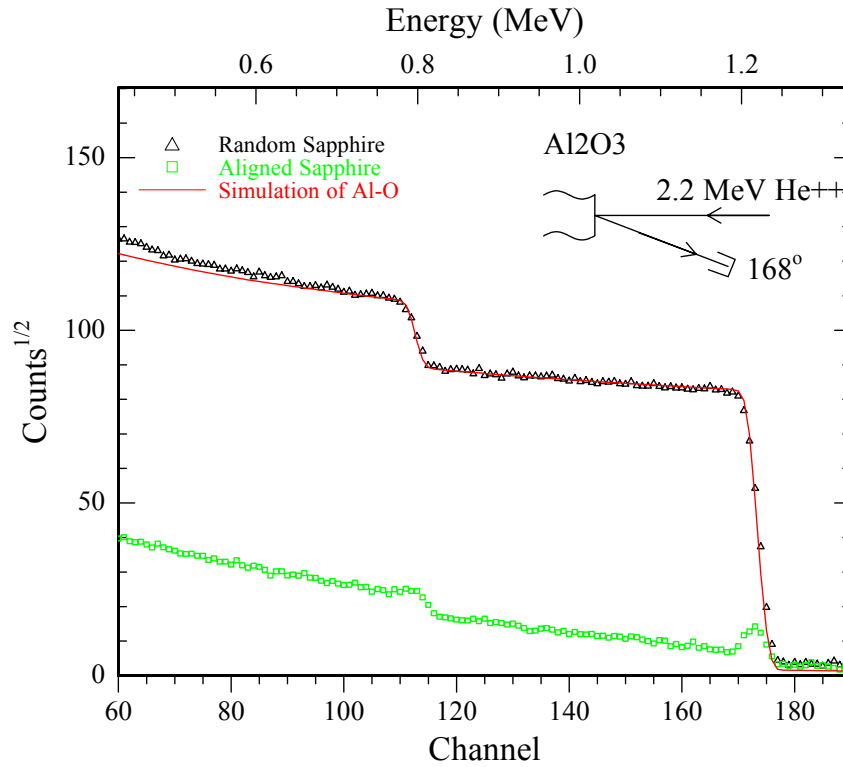


Figure 9.1: Random RBS and RUMP simulation and aligned channeling spectrum for sapphire substrate

The energy per channel in the RBS spectra can be estimated from the Al surface energy $\varepsilon = \frac{1.22 \text{ MeV}}{177 \text{ channel}} = 6.893 \text{ keV/channel}$. The stopping cross section factor for Al in sapphire has been calculated in Appendix 9.1 to be: $[\varepsilon_o]_{Al}^{\text{Al}_2\text{O}_3} = 3.36878 \times 10^{-13} \text{ eV cm}^2$.

Using the formula of the height of the random peak for a compound materials and the area density of a surface peak [115] we obtain the following for the number of Al atoms per unit area that contribute to the surface peak in the channeled spectrum:

$$N \cdot t = \frac{2\varepsilon}{[\varepsilon_0]_{Al}^{Al_2O_3}} \frac{A}{H} \cos(\theta) = 8.1 \times 10^{15} \text{ at} / \text{cm}^2$$

where the angle $\theta = 12^\circ$ is the backscattering angle from the geometry of the experiment.

From the atomic density of Al atoms in sapphire the surface density is $S_{Al} \cong 1.3 \times 10^{15} \text{ cm}^{-2}$. The ratio of the areal density obtained from the surface peak to the areal density of Al atoms in sapphire gives the number of atoms visible for each row:

$$\frac{Nt}{S_{Al}} = 6.221 \text{ atoms/row}$$

This result is comparable to the one obtained from the rms of the vibrational amplitude of the Al atoms at the surface and the “universal curve” that gives an estimate of 6.71 atoms/row.