Deep Level Defects in Advanced III-Nitride Semiconductors: 
Presence, Properties and Impact of Proton Irradiation

Dissertation

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Abstract

The development of the next generation GaN-based electronic and optoelectronic devices primarily depends on the capability of growing high quality novel materials and improving device reliability to support new functionalities. Essential to both is a comprehensive understanding of the electrically active crystalline defects, as these defects may introduce deep states in the bandgap, thus substantially impacting material properties and device performance. To date, in spite of large amounts of research on defects in III-nitrides, there is still an extraordinary gap of knowledge. Thus, the goal of this dissertation has been to explore the presence and properties of defect states in a wide range of state-of-the-art III-nitride materials, and investigate their role in device level degradation, particularly, under high energy proton irradiation as intended for space communication applications.

To enable these objectives, a set of capacitance-based measurements, including deep level transient/optical spectroscopy (DLTS/DLOS) that facilitate the quantitative characterization of deep states throughout the 3.4 eV GaN bandgap, have been performed on a variety of materials, such as non-polar m-plane GaN, NH$_3$MBE grown p-type GaN, proton irradiated n-type and p-type GaN. Systematically varied growth, irradiation and annealing conditions allowed for methodical investigation of defect behaviors and properties, thus shedding light on the defect physical sources and atomic configurations.
Specifically, by comparing simultaneously grown c-/m-plane GaN, substantial impacts of the growth surface on the defect formation were revealed, as both external and native defects formed with much higher concentrations in m-plane GaN. M-plane growth also created traps at $E_C - 0.14$ eV, $E_C - 0.20$ eV and $E_C - 0.66$ eV that were absent in c-plane GaN, among which the $E_C - 0.14$ eV and $E_C - 0.66$ eV states closely correlated with V/III ratio (and/or oxygen content). In proton irradiation study, monotonic but differential concentration increases were observed for almost all pre-existing traps, along with the generation of “new” states at $E_C - 0.13$ eV and $E_C - 0.16$ eV. Systematically controlled thermal annealing led to differential responses for individual irradiation induced traps, suggestive of different introduction/reduction mechanisms linked to their physical origins. In addition, a specially devised p$^+/p^/n^+$ diode structure enabled the quantitative characterization of defects in p-GaN. Significant impacts of growth method (NH$_3$MBE vs. MOCVD) and proton irradiation were observed, and possible origins for major p-GaN traps were discussed.

Moreover, how these defects affect materials electrical and optical properties, and ultimately the device performance, were carefully examined where possible. Particularly, the proton irradiation induced defect states at the materials level have been correlated with the primary degradation mode at device level (i.e., threshold voltage instability). Not only the sub-linear evolution of $V_T$ as a function of proton fluence can be well modeled using experimentally measured GaN buffer trap energy and introduction rate, but also changing buffer designs substantially altered the $V_T$ evolution, clearly demonstrating the role of GaN buffer traps in causing $V_T$ shift. An analytic model was developed and suggested particular material and structural optimization path to mitigate such degradation, among which,
scaling down the barrier thickness has been demonstrated as one of the most effective approaches for improving the radiation hardness of AlGaN/GaN HEMT.
Dedication

This document is dedicated to my family
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# Table of Contents

Abstract .................................................................................................................................................. ii  
Dedication ........................................................................................................................................ v   
Acknowledgements ........................................................................................................................... vi  
Vita ................................................................................................................................................... vii  
Table of Contents ............................................................................................................................ viii  
List of Tables ...................................................................................................................................... x  
List of Figures ..................................................................................................................................... xv  

Chapter 1  
Introduction ................................................................................................................................--------- 1  
1.1 Motivation ..................................................................................................................................... 1  
1.2 Dissertation Objectives ............................................................................................................... 5  
1.3 Dissertation Organization ........................................................................................................... 6  
1.4 References ................................................................................................................................... 8  

Chapter 2  
Background ........................................................................................................................................... 9  
2.1 Introduction .................................................................................................................................... 9  
2.2 Crystal Defects and Deep Level States ....................................................................................... 9  
2.3 Novel Materials Grown Along Unconventional Crystal Orientations for Polarization Engineering .................................................................................................................. 17  
2.4 Defect Formation in Materials Grown by Emerging NH₃-MBE Technology ........................... 26  
2.5 High Energy Particle Radiation Effects in GaN Materials and Devices ................................. 30  
2.6 References ................................................................................................................................... 38
Chapter 3
Characterization Techniques ................................................................. 43
3.1 Overview .................................................................................. 43
3.2 Physics of Bandgap States ............................................................. 44
   3.2.1 Emission and Capture Processes ............................................ 44
   3.2.2 Thermal Emission ................................................................. 45
   3.2.3 Optical Emission ................................................................. 48
3.3 Capacitance-based Measurement for Quantitative Characterization ...... 52
3.4 Capacitance-frequency (C-f) and Capacitance-temperature (C-T) Methods .... 55
3.5 DLTS ..................................................................................... 59
3.6 DLOS .................................................................................... 64
3.7 Correspondence of DLTS, DLOS and Photoluminescence (PL) in Terms of a Configuration-Coordination Model ......................................................... 69
3.8 Summary .................................................................................. 74
3.9 Reference .................................................................................. 76

Chapter 4
Impact of Crystal Orientation on Deep Level States in NH$_3$MBE grown GaN ........ 77
4.1 Introduction ................................................................................ 77
4.2 Experimental Details .................................................................... 78
4.3 Correlating Impurity Incorporation and Background Doping ....................... 80
4.4 Deep Level Characterization ......................................................... 82
4.5 Photoluminescence ..................................................................... 86
4.6 A Detailed Investigation of $E_C - 2.50$ eV Trap ...................................... 87
4.7 Summary .................................................................................. 91
4.8 References ................................................................................ 92

Chapter 5
Impact of V/III ratio on Deep Level States in NH$_3$MBE Grown m-plane GaN .......... 94
5.1 Introduction ................................................................................ 94
5.2 Experimental details .................................................................... 95
5.3 Correlation between Impurity and Background Doping ............................ 96
5.4 Deep Level State Characterization .................................................. 98
Chapter 6
Comparison of Deep Level States in p-GaN grown by NH₃MBE and MOCVD ........................................ 108
6.1 Introduction ................................................................................................................................. 108
6.2 Sample Structure and Experimental Details ................................................................. 109
6.3 Basic Capacitance Characteristics ....................................................................................... 113
6.4 Characterizing Deep Acceptor States .................................................................................... 115
6.5 Deep level state characterization ............................................................................................ 118
6.6 Summary ................................................................................................................................. 122
6.7 Reference ................................................................................................................................. 124

Chapter 7
Impact of Proton Irradiation on Deep Level States in n-GaN ..................................................... 126
7.1 Introduction ................................................................................................................................. 126
7.2 Experimental Details ............................................................................................................... 128
7.3 Basic I-V C-V Characteristics ............................................................................................... 130
7.4 Deep Level State Characterization ........................................................................................ 133
7.5 Correlating Carrier Removal and Radiation Induced Traps ................................................ 140
7.6 Summary ................................................................................................................................. 142
7.7 Reference ................................................................................................................................. 143

Chapter 8
Thermal Stability of Proton Irradiation Induced Deep Traps in n-GaN ........................................ 146
8.1 Introduction ................................................................................................................................. 146
8.2 Experimental details ............................................................................................................... 147
8.3 Deep Level Characterization ................................................................................................. 150
8.4 Annealing Kinetics of Proton Irradiation-induced Defect States ........................................ 165
8.5 Annealing of Irradiation-induced Traps and Carrier Recovery ........................................... 167
8.6 Summary ................................................................................................................................. 170
8.7 Reference ................................................................................................................................. 171
Chapter 9
Impact of Proton Irradiation on Deep Level States in p-GaN .......................................................... 173
  9.1 Introduction ................................................................................................................................. 173
  9.2 Experimental Details ................................................................................................................ 175
  9.3 Basic C-V characteristics .......................................................................................................... 176
  9.4 Deep Level State Characterization ......................................................................................... 178
  9.5 Discussion ............................................................................................................................... 184
  9.6 Summary ................................................................................................................................. 186
  9.7 Reference ............................................................................................................................... 188

Chapter 10
Proton Irradiation Induced Threshold Voltage Shift in AlGaN/GaN HEMT devices and Heterostructures .......................................................................................................................... 191
  10.1 Introduction ............................................................................................................................ 191
  10.2 Proton Irradiation Induced Degradations in HEMT Device ................................................ 193
  10.3 Proton Irradiation Induced Threshold Voltage Shift in AlGaN/GaN Heterostructures ... 195
  10.4 Factors That May Impact Threshold Voltage in AlGaN/GaN Heterostructure ............ 198
  10.5 Impact of Proton Irradiation Induced Defects on Threshold Voltage ......................... 201
  10.6 Modeling the Buffer Trap Impact on Threshold Voltage .................................................... 208
  10.7 Possible Approaches to Mitigate Irradiation Induced Threshold Voltage Instability ..... 212
    10.7.1 Irradiation Induced Defect Density ................................................................................. 212
    10.7.2 Buffer Design ................................................................................................................. 217
    10.7.3 Barrier Thickness ............................................................................................................ 219
  10.8 Summary ............................................................................................................................... 221
  10.9 Reference ............................................................................................................................... 222

Chapter 11
Conclusions and Future Directions ............................................................................................... 225
  11.1 Conclusions .......................................................................................................................... 225
    11.1.1 The Presence and Properties of Defect States in III-Nitride materials .................... 226
    11.1.2 The Impact of Proton Irradiation Induced Defects on AlGaN/GaN HEMT Device Performance ............................................................................................................................. 228
  11.2 Future Directions .................................................................................................................... 229
11.3 Reference ........................................................................................................................................233

Bibliography ............................................................................................................................................234
List of Tables

Table 1.1 Comparison of key electronic properties of Si, GaAs and GaN. .........................3
Table 2.1 Fundamental differences between MOCVD and MBE. .................................27
Table 4.1 Concentrations for deep level states in c-plane and m-plane GaN detected by DLTS and DLOS. .........................................................................................................................83
Table 5.1 Summary of SIMS result and deep level concentrations in m-plane GaN films grown by NH$_3$-MBE with different V/III ratios. .................................................................99
Table 7.1 Summary of deep level states and their concentrations in proton irradiated NH$_3$-MBE grown n-GaN. ....................................................................................................................134
Table 7.2 Apparent introduction rates for 1.8 MeV proton irradiation induced states. ....139
Table 8.1 Concentrations of deep levels in n-GaN samples before irradiation, after irradiation, and after post-irradiation annealing at different temperatures. .................157
Table 9.1 Summary of deep level states and corresponding concentrations in NH$_3$-MBE grown p-GaN exposed to different proton fluences. .........................................................178
List of Figures

Figure 1.1 Applications of GaN-based materials and devices........................................2
Figure 1.2 Comparison of bandgaps for major semiconductor material systems............3
Figure 2.1 Major degradation mechanisms in GaN HEMT.............................................11
Figure 2.2 Traps induced by high off-state bias in the access region that substantially
degrade GaN HEMT dynamic on-resistance.............................................................12
Figure 2.3 (a) High voltage off-state biasing of GaN HEMT induces $R_{ON}$ degradation
through creating $E_C - 2.0$ eV trap; (b) RF-stressing of GaN HEMT introduces $R_{ON}$
degradation through generating or modulating another trap at $E_C - 0.57$ eV. .............13
Figure 2.4 Illustration of several popular crystal orientations of wurtzite GaN.............17
Figure 2.5 (a) Unit cell of wurtzite GaN; (b) Illustrations of spontaneous polarization due
to non-ideal $c_0/a_0$ ratio..........................................................................................18
Figure 2.6 (a) Atomic configuration of Ga-face GaN. (b-c) Polarization fields in Ga-polar
AlGaN/GaN and InGaN/GaN heterostructures. (d) Calculated bounded interface charges
of pseudomorphic Ga-polar alloys on relaxed GaN.......................................................19
Figure 2.7 (a) Band structure of Ga-polar Al$_{0.3}$Ga$_{0.7}$N/GaN heterostructure; (b) InGaN/GaN
quantum well................................................................................................................20
Figure 2.8 (a) Atomic configuration of N-polar GaN; (b-c) Polarization fields in N-polar
AlGaN/GaN and GaN/AlGaN/GaN heterostructures; (d) Calculated bounded interface of
N-polar material on relaxed GaN....................................................................................22
Figure 2.9 Comparison of the band diagrams and 2DEG distribution of Ga- polar and N-
polar HEMT..................................................................................................................22
Figure 2.10 (a) Atomic configuration of non-polar a-plane GaN. (b) Illustration of
polarization fields in a-plane InGaN/GaN quantum well structure..............................23
Figure 2.11 Top and side view of the atomic structures at the Ga-polar, N-polar and non-polar m-plane surfaces, plotted using VESTA 3D crystal visualization program. .................................................24

Figure 2.12 Comparison of deep level states in n-type GaN grown by different techniques. ........................................................................................................................................................................28

Figure 2.13 Van Allen Belt trapping of high energy protons, electrons and neutrons around earth................................................................................................................................................................................................................................................................................................31

Figure 2.14 Schematic of ionizing radiation effect in an n-channel MOS capacitor................31

Figure 2.15 Comparison of displacement threshold energy for GaN, Si and GaAs. ..........32

Figure 2.16 Comparison of radiation induced damage in (a) LED and (b) HEMT devices employing GaN and other compound semiconductor technologies. ..............................................33

Figure 2.17 Evolutions of major device parameters in AlGaN/GaN HEMTs as a function of proton irradiation fluence. ................................................................................................................................................................................34

Figure 3.1 The processes possible for a bandgap state involving transitions to or from a band: (a) electron capture from conduction band; (b) electron emission to conduction band; (c) hole capture from valence band; (d) hole emission to valence band...........................44

Figure 3.2 Thermal emission rates and time constants for bandgap states as a function of temperature. A carrier capture cross section of $1 \times 10^{-16}$ cm$^2$ is assumed for all states. .....47

Figure 3.3 Schematic illustration of the recombination of a localized hole with a free electron..................................................................................................................................................................................................................49

Figure 3.4 Configuration coordination diagram accounting for both electronic energy and lattice potential energy..................................................................................................................................................................................................................50

Figure 3.5 Typical Schottky diode and p-n diode structures for study n-type GaN through capacitance-based measurements...............................................................................................................................................................................................................50

Figure 3.6 Illustration of deep state response to capacitance sampling frequency. ...........53

Figure 3.7 (a) C-f curves measured at different temperatures at 0 V bias in p-type GaN. (b) C-V characteristics obtained at 110 K with sampling frequencies of 1 kHz and 1 MHz, respectively. ..........................................................................................................................................................................................57

Figure 3.8 (a) G/ω vs. f plot for a p-GaN sample; (b) Arrhenius analysis for obtaining the dopant activation energy and capture cross section.............................................................58
Figure 3.9 (a-c) Schematic diagrams of trap modulation in n-type Schottky diode; (d) Timing diagram of applied voltage and capacitance signals. .................................................................60
Figure 3.10 (a) DLTS double boxcar method; (b) DLTS spectra and Arrhenius analysis........................................................................................................................................62
Figure 3.11 Band diagrams for Schottky diode at $V = 0$ V and -0.5 V. ........................................63
Figure 3.12 (a) Schematic diagram of optical modulation in n-type Schottky diode. (d) Timing diagram of applied voltage, shutter opening and capacitance signals. ...........65
Figure 3.13 Illustration of possible competition between electron emission and hole emission processes during DLOS measurements. .................................................................67
Figure 3.14 SSPC spectrum and optical cross section analysis for investigating the deep states in m-plane n-type GaN. The solid line is a fit to the Lucovsky model while the dashed line is a fit to the Passler model. .................................................................68
Figure 3.15 Optical excitation of a defect in CC diagram.................................................................69
Figure 3.16 Photon emission process of defect states in CC diagram.................................72
Figure 3.17 Illustration of how different characterization techniques should be used for probing deep states at different region of the bandgap.........................................................74
Figure 4.1 Structure of c-plane and m-plane n-type Schottky diodes.................................78
Figure 4.2 SIMS concentration profiles of silicon, oxygen and carbon in both m-plane and c-plane GaN. The square markers indicate the measured effective doping concentration from $C-V$ analysis. ........................................................................................................80
Figure 4.3 (a) DLTS spectra of m-plane and c-plane GaN for the $80 \, s^{-1}$ rate window revealing much higher trap concentration for the m-plane GaN material. (b) Arrhenius plots for the different deep levels corresponding to the peaks from each rate windows...........82
Figure 4.4 Steady state photo-capacitance spectra of m-plane and c-plane GaN. Inset shows the optical cross section spectra for m-plane and c-plane GaN. Solid lines are fits to the Lucovsky model, whereas dashed line is a fit to the Passler model. ..................84
Figure 4.5 (a) Room temperature PL spectra for unprocessed m-plane and c-plane GaN samples, plotted in logarithmic scale. (b) PL spectra of unprocessed m-plane GaN, plotted in linear scale. ..................................................................................................................86
Figure 4.6 Structure for m-plane GaN pn-junction diode.........................................................88
Figure 4.7 (a) DLTS spectra of m-plane GaN pn-diode performed with a filling bias of 1.5 V. (b) Arrhenius plot for the major minority carrier trap observed in DLTS. ...........................89

Figure 4.8 CC diagram of $E_C - 2.50$ eV trap in GaN and the correspondences of the results obtained by different characterization techniques. .................................................................90

Figure 5.1 M-plane n-type Schottky diodes grown with different V-III ratios. ..................95

Figure 5.2 Impurity concentrations detected by SIMS in m-plane GaN samples grown under different V/III ratios plotted along with the net n-type doping concentration measured by $C$-$V$ analysis (square symbols). .................................................................96

Figure 5.3 DLTS spectra of the 80 s$^{-1}$ rate window for m-plane GaN samples grown with V/III ratios of 400, 1000 and 2500. The DLTS peak around 120 K in the highest V/III ratio sample is fit by two electron traps. .................................................................98

Figure 5.4 Arrhenius analysis for the deep levels observed in all three m-plane GaN samples.........................................................................................................................99

Figure 5.5 Concentrations of the traps present at $E_C - 0.14$ eV, $E_C - 0.21$ eV and $E_C - 0.67$ eV as a function of oxygen impurity concentration measured by SIMS. .........................100

Figure 5.6 Room temperature steady state photocapacitance spectra of m-plane GaN grown with different V/III ratios. .................................................................................102

Figure 5.7 DLOS detected trap concentrations for $E_C - 2.50$ eV and $E_C - 3.28$ eV state and SIMS measured carbon density as a function of V-III ratio..................................102

Figure 5.8 Room temperature PL spectra for unprocessed m-plane and c-plane GaN samples.........................................................................................................................104

Figure 5.9 DLOS detected trap concentration for $E_C - 3.28$ eV state and SIMS measured carbon density as a function of V-III ratio.................................................................104

Figure 6.1 Test structures for performing capacitance-based characterizations of p-type GaN (a) conventional p-/p+ Schottky diode; (b) Schottky diode formed on p+ layer; (c) p+/p- /n+ diode; (d) a comparison of C-f dispersion measured in structure (a) and (c) ...109

Figure 6.2 (a-b) Schematic diagrams of NH$_3$MBE and MOCVD grown sample structures. Both samples contain p+/p-/n+ junctions to enable capacitance based p-GaN characterizations. .................................................................................................111
Figure 6.3 (a) Room temperature capacitance-based characterizations ($C-V$, $C-f$) of NH3MBE and MOCVD grown p-GaN; (b) Net p-type doping profiles for both samples extracted from 1 MHz $C-V$ measurements.

Figure 6.4 (a-b) $C-f$ characteristics for the two samples at low temperatures. (c-d) Corresponding $G/w$ plots for investigating the emission processes of major acceptors in both samples.

Figure 6.5 Arrhenius analyses for p-type dopant state detected in both samples.

Figure 6.6 (a) Optical cross section spectra for NH3MBE and MOCVD grown p-GaN; (b) SSPC spectra obtained at the same depletion depth in the two samples.

Figure 6.7 DLTS spectra at 10 s$^{-1}$ for the two samples. Inset shows the Arrhenius analysis.

Figure 6.8 Summary of deep level states in NH3MBE and MOCVD grown p-GaN.

Figure 7.1 Structure for n-type Schottky diodes used in this study.

Figure 7.2 Room temperature $I-V$ characteristics of GaN samples exposed to different proton fluences.

Figure 7.3 Room temperature 1 MHz $C-V$ curves of GaN samples exposed to different proton fluences. The inset shows the evolution of extracted n-type doping concentration at a reverse bias of -0.5 V for each proton fluence.

Figure 7.4 (a) DLTS spectra of rate window 80 s$^{-1}$ for GaN samples exposed to different proton fluences. (b) Arrhenius analyses for deep levels in n-type GaN before and after proton irradiation. The dashed lines represent the fitting results.

Figure 7.5 DLOS Steady State Photocapacitance (SSPC) spectra of GaN samples exposed to different proton irradiation fluences.

Figure 7.6 (a) DLTS detected 1.8 MeV proton irradiation-induced trap concentration as a function of proton fluence. (b) DLOS detected 1.8 MeV proton irradiation induced trap concentration as a function of proton fluence.

Figure 7.7 Extracted net doping concentrations at - 0.5 V from lighted $C-V$ measurements. Different illumination conditions, i.e. no light, 1.24 eV, 2.48 eV, 3.24 eV and 3.38 eV are presented from left to right, while the unirradiated control sample and the two samples experienced large proton fluence.
Figure 8.1 Room temperature 1 MHz C-V characteristics for n-GaN samples before irradiation, after irradiation and after annealing at different temperatures.

Figure 8.2 DLTS spectra (80 s\(^{-1}\) rate window) for n-GaN samples before irradiation, after irradiation and after annealing at different temperatures.

Figure 8.3 Multi-peak fitting of DLTS spectra for samples at all conditions. The dashed lines are the total fitting results.

Figure 8.4 Arrhenius plots for DLTS-detected traps (a) in pre-rad and post-rad samples without annealing, and (b) post-rad samples annealed at different conditions. The dashed lines are fitting results.

Figure 8.5 DLTS spectra (80 s\(^{-1}\) rate window) for the unirradiated control sample before and after 400 ºC annealing.

Figure 8.6: (a) The remaining concentrations for irradiation-induced traps at \(E_C - 0.13\) eV, \(E_C - 0.16\) eV, \(E_C - 0.20\) eV and \(E_C - 0.25\) eV, as a function of annealing temperature. The solid lines are fitting results for traps at \(E_C - 0.13\) eV and \(E_C - 0.16\) eV.

Figure 8.7 Room temperature DLOS SSPC spectra for n-GaN samples before irradiation, after irradiation and subsequently annealed at different temperatures.

Figure 8.8 DLOS optical cross section spectra analysis for n-GaN samples (a) before and after irradiation, and (b) post-irradiation and subsequently annealed at different temperatures.

Figure 8.9 DLOS SSPC spectra for the unirradiated control sample before and after 400 ºC annealing.

Figure 8.10 The remaining concentrations for irradiation-induced traps at \(E_C - 1.25\) eV, \(E_C - 2.50\) eV and \(E_C - 3.25\) eV as a function of annealing temperature.

Figure 8.11 (a) Effective n-type doping density \((N_D^+ - N_A^-)\) of irradiated samples before and after annealing, extracted from room temperature 1 MHz C-V measurements. (b) A comparison of the carrier removal effect and the evolution of irradiation-induced EC.

Figure 9.1 Schematic diagram of the p+/p-/n+ diode structure used in the measurements.

Figure 9.2 Room temperature 1 MHz C-V characteristics for diodes exposed to different proton fluences.
Figure 9.3 Comparison of the DLTS spectra at 10 s\(^{-1}\) rate window for samples exposed to different proton fluences. The inset shows the Arrhenius plot of the dominant irradiation induced trap. An effective hole mass of 0.9 \(m_o\) was used in the calculations.................178

Figure 9.4 (a) Room temperature DLOS steady state photocapacitance spectra for samples exposed to different proton fluences. (b) Optical cross sections obtained from the photocapacitance transient data. The fits to the data (solid line) were generated using Lucovsky model..................................................181

Figure 9.5 Summary of proton irradiation induced traps in p-GaN.................................184

Figure 9.6 Theoretically calculated formation energies as a function of Fermi level for native point defects in GaN..........................................................184

Figure 10.1 (a) Output \(I-V\) characteristics for AlGaN/GaN HEMT before and after 1.8 MeV proton irradiation at a fluence of \(1 \times 10^{14}\) cm\(^{-2}\). A significant drop in saturation current (\(I_{DS, max}\)) in irradiated device is clearly revealed. (b) Triode region of the \(I-V\) curve..............193

Figure 10.2 (a) Transfer \(I-V\) curves for AlGaN/GaN HEMT before and after proton irradiation. Proton irradiation clearly induced a positive threshold voltage (\(V_T\)) shift. (b) Transconductance (\(g_m\)) vs. voltage for AlGaN/GaN HEMT before and after proton irradiation.................................................................194

Figure 10.3 Schematic diagram of the AlGaN/GaN test sample structure.........................195

Figure 10.4 Room temperature 1 MHz \(C-V\) results for AlGaN/GaN Schottky diodes before and after irradiation. The inset reveals the shift of measured \(V_T\) as a function of proton fluence.................................................................197

Figure 10.5 Schematic band diagram of Ni/AlGaN/GaN Schottky diode.........................198

Figure 10.6 Internal Photoemission (IPE) measurement results for AlGaN/GaN Schottky diodes before and after \(5 \times 10^{13}\) cm\(^{-2}\) and \(1 \times 10^{14}\) cm\(^{-2}\) 1.8 MeV proton irradiation. The solid lines are linear fittings for obtaining the onset energies (Ni/AlGaN Schottky barrier). ..200

Figure 10.7 Carrier removal effect as a function of 1.8 MeV proton fluence in a separate n-type GaN sample. The dashed line is for fitting the carrier removal rate. Inset shows the n-type doping profiles extracted from \(C-V\) measurements..................................................202

Figure 10.8 TCAD simulation of \(\Delta V_T\) as a function of proton fluence. The compensating trap at \(E_C\) - 3.25 eV is assumed to be present only in the GaN buffer. Simulation results
using introduction rates of 400, 500 and 600 cm\(^{-1}\) are shown, as well as experimentally obtained values.

Figure 10.9 The band diagrams at equilibrium conditions for AlGaN/GaN Schottky diodes before and after \(4 \times 10^{13}\) cm\(^{-2}\) and \(1 \times 10^{14}\) cm\(^{-2}\) proton irradiation, assuming irradiation induced traps at \(E_C - 3.25\) eV were only present in GaN layers, with an introduction rate of 400 cm\(^{-1}\).

Figure 10.10 The growth structures for AlGaN/GaN heterostuctures with unintentionally doped (UID) buffer and Si-doped buffer.

Figure 10.11 Comparing threshold voltage shifts (\(\Delta V_T\)) as a function of proton fluence for two AlGaN/GaN Schottky diodes with unintentionally doped (UID) buffer and Si-doped buffer, respectively.

Figure 10.12 Schematic diagrams of back-gating effect in n-channel Si MOSFET. By applying a negative back-gate voltage \(V_{SB}\), threshold voltage shifts toward more positive values.

Figure 10.13 Comparison of the irradiation induced threshold voltage shifts that are obtained from experiment, TCAD simulation and analytic modeling (Equation (10.2)). Also listed are the parameters used in analytic modeling.

Figure 10.14 TCAD simulations of buffer trap introduction rate influencing threshold voltage shift. The plots assume a 25 nm AlGaN barrier, pre-existing background n-type doping \(2 \times 10^{15}\) cm\(^{-3}\), no pre-existing acceptors and major compensating center at \(E_C - 3.25\) eV.

Figure 10.15 Structures for n-type GaN samples grown by NH\(_3\)MBE and PAMBE.

Figure 10.16 (a-b) \(C-V\) results and n-type doping profiles in both samples before and after proton irradiation.

Figure 10.17 Summary of proton irradiation induced traps in GaN samples grown by two different techniques.

Figure 10.18 Transconductance characteristics of AlGaN/GaN HEMT device before, after proton irradiation and after post-rad annealing.

Figure 10.19 TCAD simulations of pre-existing acceptor-like states in GaN buffer affecting proton irradiation induced threshold voltage shift.
Figure 10.20 Schematic diagram of AlGaN/GaN heterostructures with different barrier thickness.

Figure 10.21 (a-d) Room temperature 1 MHz C-V measurement results for AlGaN/GaN Schottky diodes with different barrier thicknesses before and after proton irradiation.

Figure 10.22 TCAD simulation and experimentally obtained threshold voltage shifts ($\Delta V_T$) as a function of AlGaN barrier thickness at proton irradiation fluences of $4 \times 10^{13}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$. The dashed lines are linear fits to the simulation results.

Figure 11.1 Summary of as-grown deep states in c-plane and m-plane n-type GaN, and proton irradiation induced deep states in n-type GaN.
Chapter 1

Introduction

1.1 Motivation

III-nitride materials and devices are of expansive interest for applications that include high frequency and high power electronics, solid state lighting, data storage, ultraviolet detectors and sensors, as summarized in Fig.1.1. [1, 2] The interest in III-nitrides arises from their unique combination of excellent materials properties. As seen in Table 1.1, [3] compared with traditional Si and GaAs-based semiconductors, GaN-based materials are of much larger bandgaps, higher electron mobility and saturation velocity as well as excellent thermal conductivity. This combination of features enables GaN-based devices to be operated at high voltage, high current density and high switching frequency conditions, thus are desirable for power and RF electronic applications. [4, 5] Moreover, as shown in Fig. 1.2, GaN-based materials all have direct bandgaps, which cover the spectra from 0.7 eV to 6.2 eV, an interval ranging from infrared to ultraviolet, and are tunable for meeting distinct requirements for a variety of optoelectronic applications. [6, 7] In addition, GaN-based materials have also shown superior chemical inertness and radiation tolerance, thus are ideal candidates for advanced devices used in harsh
environments. [8, 9] Over the last two decades, remarkable technological breakthroughs have led to rapid commercialization of many GaN devices, and making them a driving force in system integration. For example, GaN-based high efficiency blue light emitting diodes (LEDs), which emit white light when coupled with yellow phosphorus, have revolutionized the solid state lighting industry. This is also the case for AlGaN/GaN high electron mobility transistors (HEMTs), which deliver unprecedented performance and have become the choice for electronic applications such as RF power amplifiers, power switches. These initial successes, combined with the continuous evolution of device design and integration, foreshadow an even broader range of applications for III-nitride semiconductors in the future.

Figure 1.1 Applications of GaN-based materials and devices. [1]
Table 1.1 Comparison of key electronic properties of Si, GaAs and GaN. [3]

<table>
<thead>
<tr>
<th></th>
<th>Eg (eV)</th>
<th>Vs (10^7 cm/s)</th>
<th>Breakdown field (MV/cm)</th>
<th>Thermal conduct. (W/K/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.1</td>
<td>1.0</td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.4</td>
<td>1.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>SiC</td>
<td>3.2</td>
<td>2.0</td>
<td>3.0</td>
<td>4.9</td>
</tr>
<tr>
<td>GaN</td>
<td>3.4</td>
<td>2.7</td>
<td>3.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure 1.2 Comparison of bandgaps for major semiconductor material systems. [6]

However, like all prior semiconductor technologies, these successes were achieved only when high quality materials with low crystal defect density became available. The presence of crystal defects is known to be detrimental for semiconductors because they may not only hamper the growth of a uniform film and smooth structure, but also degrade materials properties and device performance, thus keeping them from attaining the full potential. In fact, many of the major obstacles during early GaN technology development – high density of dislocations and stacking faults due to large lattice-mismatch, [10]
pervasive unintentional n-type conductivity, [11, 12] and low efficiency p-type dopants [13, 14] – were all directly related to crystal imperfections and impurities. To some extent, many of the technological breakthroughs seen over the years are directly attributable to the crystal defect reduction.

Currently, further developments of the next generation GaN technology depend on advances in areas such as novel materials and structures, growth and integration optimization, high-quality low-cost substrates, device reliability, and new device functionalities, etc. However, almost all of these different research areas rely on the ability of suppressing the crystal defects, and mitigating their effects in devices. For example, one of the most active research fields in III-Nitrides in recent years is polarization engineering, where novel materials and structures grown along unconventional crystal orientations (with respect to the conventional c-plane) are used for engineering the electrical polarization to improve device performance or meet specific application requirements. [15] However, due to the novelty of the materials and the difficulties encountered in characterizing defects in general, important information regarding the presence, origin and behavior of defects in these materials has been sparsely reported and less understood. Similarly, the emergence of advanced growth techniques has also necessitated the use of quantitative methods in characterizing defects for establishing optimization guidelines, as existing knowledge of defect reduction under conventional growth techniques may not be directly transferrable.

Not only is the defect information important for developing new materials and growth technologies, it is also required for understanding and improving the reliability of more traditional GaN devices in order to explore new application opportunities. During the last decade, the degradation of GaN-based devices has been intensively investigated. [16-
These studies have clearly shown that deep traps can indeed be created and/or modulated under operational conditions, leading to performance instability or even catastrophic failure. This can be a more significant issue when incorporating GaN transistors into space communication satellites, as deep traps within the device structure will surely be created as a result of high energy particle radiation. [9] However, a fundamental understanding of the properties and behavior of GaN and defects under such harsh conditions does not yet exist. How the device will accommodate increased radiation-induced defects while minimizing performance degradation becomes critically important in the context of these applications.

Overall, a comprehensive understanding of the presence and properties of crystal defects and their impacts in devices is essential for further development of GaN technology. Despite intensive research on electronic defects and traps in nitride semiconductors, there is still an extraordinary knowledge gap, particularly for novel materials, advanced growth techniques and the reliability of GaN devices in new applications. Thus, the purpose of this study is to apply special experimental techniques to characterize and investigate those defects and their impacts.

1.2 Dissertation Objectives

There are two primary facets to this dissertation. The first is to explore the “as-grown” defects and their manifestation at deep levels in novel materials such as GaN grown along non-standard crystal orientations (i.e., nonpolar (10-10) m-plane), and in materials grown by the emerging technique of ammonia-based molecular beam epitaxy (NH$_3$-MBE).
The way in which unconventional surface structures and new growth techniques impact the formation of electrically active defects, as well as the properties of these electronic defects in such materials, is largely unknown. Increased understanding of these issues is for continued growth optimizations and technological advances in these areas.

The objective of the second facet is to reveal how high energy particle radiation influences the presence and properties of deep level defects in GaN. Here we identified point defects induced by proton radiation in both n and p type GaN, and evaluated their thermal stabilities. This aspect of our research directly assesses the primary defects that cause degradation of irradiated devices and also generates approaches and designs to mitigate the impacts of such defects. As mentioned, the mitigation of these kinds of defects is essential for improving the reliability of GaN devices in space-based communication systems. The combination of these two research thrusts will advance the understanding of electrically active defects in GaN materials, electronic and optoelectronic devices, and future technologies based on GaN materials.

1.3 Dissertation Organization

Chapter 2 summarizes the current understanding of the issues related to this dissertation. After an overview of crystal defects and their manifestation as deep level states in materials and devices, the three major research topics of this dissertation are described. These topics are: defects in novel m-plane materials used for polarization engineering; defects in materials grown by emerging NH₃-MBE technology; and the impact of high energy particle irradiation on GaN based materials and devices. Chapter 3
describes the characterization techniques used, and how each reveals the aspects of deep states at different regions of the bandgap. Chapters 4 and 5 describe the systematic studies of deep states incorporated into the non-polar m-plane GaN, and reveal how crystal orientation and growth parameters such as III/V ratio may affect the formation of defects. Chapter 6 describes a comparative study of bandgap states (both dopant and traps) formed in p-type GaN grown by NH$_3$-MBE and by more mature metal organic vapor deposition (MOCVD). Chapters 7 - 9 describe defects induced by proton irradiation over the whole bandgap in n-type and p-type GaN, as well as their electrical properties and thermal stability. Chapter 10 presents the results of a comprehensive study of proton irradiation induced threshold voltage instability in AlGaN/GaN HEMT devices and heterostructures. Defect information obtained in earlier chapters is used, and both simulations and experimental investigations are performed, revealing the threshold voltage degradation in fact correlates with the deep compensating traps induced by proton irradiation in GaN buffer. Finally, Chapter 11 summarizes the defect taxonomy and conclusions reached in previous chapters, and presents suggestions for future study.
1.4 References

Chapter 2

Background

2.1 Introduction

This chapter provides a general description of the presence, detection and impact of crystal defects in GaN based materials and devices. It also includes background information for the three major research topics addressed in this dissertation. These topics are: a) polarization engineering and possible defects in materials grown along unconventional orientations; b) NH$_3$MBE as an emerging growth technique that is particularly promising for p-GaN growth; and c) the effects of radiation on GaN-based materials and devices.

2.2 Crystal Defects and Deep Level States

During the past two decades, a huge amount of effort has been devoted to reducing crystal defects in GaN-based materials for improving device performance. One of the main research fields is suppressing the extended defects, especially threading dislocations (TDs). TDs are typically of very high density in GaN due to the large lattice mismatch and thermal...
mismatch between the epi-layer and the commonly used sapphire substrate. [1-3] These TDs are not only structural defects themselves, but also capable of getting other electrically active defects that have detrimental effects on real devices. Fortunately, recent developments in buffer engineering and lateral epitaxial overgrowth (LEO) have made it possible to reduce TD density in GaN layers to $10^6 - 10^8$ cm$^{-2}$ (though standard cubic III-V materials like GaAs and InP have TD densities on the order of 100-1000 cm$^{-2}$). As a result, the availability of GaN templates and bulk GaN substrates for homoepitaxy has been greatly increased. Recently, even lower TD densities on the order of $10^4$ cm$^{-2}$ have been achieved for small area bulk GaN crystals, [4] meaning that, on average, there might be no more than one TD per 100×100 um$^2$ device area. These successes, as well as the amount of productive work in this field, have led to the belief that the impact of TD on the performance of GaN-based devices has already been substantially mitigated, and will be even less of a problem in the near future.

With resolution of TD problems in the next generation of advanced III-nitrides devices, the impact of point defects on material properties and device performance has now risen to the forefront. Possible point defects in GaN include native defects ($V_N$, $N_{Ga}$, $N_{i}$, $V_{Ga}$, $Ga_N$ and $Ga_i$, etc.), impurities ($Si$, $Mg$, $C$, $O$ and $H$, etc.), and complexes ($V_{Ga-H}$, $V_{Ga-O_N}$, $Mg_{Ga-V_N}$, etc.). Years of systematic studies have revealed that these point defects are often manifested as, or at least involved in the formation of, deep level states in the bandgap. For instance, density functional theory (DFT) calculations found that $V_{Ga}$ introduces multiple deep acceptor-like states in the lower half of the bandgap, while $V_N$ can act as donor-like states that possibly compensate p-GaN carriers. [5, 6] Moreover, by using a combination of Deep Level Transient/Optical Spectroscopes (DLTS/DLOS), the
incorporation of carbon was clearly revealed to be associated with the generation of multiple deep states in semi-insulating GaN. [7-9] In general, the presence of these deep level states is undesirable, as they may act as generation and recombination (G-R) centers, compensation centers, scattering centers, and leakage paths, thus alternating device parameters and/or reducing efficiency. Fortunately, the formation of these point defects during material growth is often sensitive to the growth details, such as growth technique, temperature, pressure, fluxes, contamination, and thus may be suppressed by appropriate growth optimization.

Figure 2.1 Major degradation mechanisms in GaN HEMT. [10]
In real devices, besides “pre-existing” as-grown traps, there are also additional traps created during device operation. These traps are attracting increasing attention because they may directly cause device instability and affect long term reliability, one of the major impediments to continued GaN development. As summarized in Fig. 2.1, [10] crystal defects in GaN-HEMTs induced during high frequency high power operations are believed to be actively involved in several major device degradations. While studies are continuing to confirm and explore these effects, there is already abundant evidence for direct and significant impacts of device operation/stress on device degradation through the formation of defect-related deep states. Figure 2.2 presents one such example. [11] Very high off-state voltage has been experimentally shown to create additional GaN buffer traps at the drain access region near the gate edge. These traps capture electrons from the channel, thereby severely degrading the output characteristics by drastically increasing dynamic on-resistance (R\textsubscript{ON}). Clearly, this kind of trapping effect must be fully understood and
substantially mitigated through proper design optimization before deploying the devices in real applications.

Figure 2.3 (a) High voltage off-state biasing of GaN HEMT induces $R_{ON}$ degradation through creating $E_C - 2.0$ eV trap; [11] (b) RF-stressing of GaN HEMT introduces $R_{ON}$ degradation through generating or modulating another trap at $E_C - 0.57$ eV. [12]

However, trapping effects in HEMTs is very complicated and subtle as the defects may be created through different mechanisms, at different physical locations, and have differential impacts on device parameters. For example, while the high voltage off-state biasing of GaN-HEMTs induces $R_{ON}$ degradation through generating a trap with activation energy of $E_C - 2.0$ eV, [11] RF-stressing of GaN-HEMT devices can lead to similar (but milder) degradation, by introducing and/or increasing the modulation of another trap with an activation energy of $E_C - 0.57$ eV (see Fig. 2.3). [12] It is also difficult to identify the physical locations of these traps, because of the rather complex structure of real HEMT devices, such as insulation, passivation and field plate, etc. Therefore, it is usually
impossible to reveal the detailed degradation mechanism, e.g., trap energy, concentration, origin, location and impact etc., solely based on HEMT characterizations. To this end, defect investigations at the materials level, the structure level and the device level, are often integrated to obtain comprehensive knowledge regarding these defects and to better identify the mechanism of “new” device degradation. Such an approach will be applied to the study of proton irradiation effects in GaN-HEMT later in the dissertation.

Although there have been both theoretical and experimental studies regarding these defects, the experimental characterization is of much greater significance now. It not only reveals the presence and properties of these defects, but it may also provide information on their behaviors as a function of varying growth parameters, a detail that can never be obtained by simplified theoretical calculations. In addition, experimental characterization is also the most direct approach for studying the trapping effects in real devices. A number of techniques – Transmission Electron Microscopy (TEM), Deep Level Transient/Optical Spectroscopes (DLTS/DLOS), Photoluminescence (PL), Cathodoluminescence (CL) and Positron Annihilation Spectroscopy (PAS), etc. – have been used in the experimental characterization of defects and related deep level states. Among these, only the combination of DLTS and DLOS provides quantitative characterization of traps throughout the wide band gap of III-Nitrides, and also allows the characterizations of electrically active defects in both materials and devices under operational conditions. In our research group at OSU, we have developed the basic methodology based on DLTS and DLOS to decipher the presence of traps in GaN materials, structures, and real devices, and investigate their responses to the changes in growth techniques, substrates and systematically varied growth conditions. Table 2.1 summarizes the energy positions and possible origins for deep levels
observed in c-plane n-type GaN by our group using DLTS/DLOS, which will be a good baseline for the studies described in this dissertation.
Table 2.1 Summary of the energy positions and possible origins for deep levels observed in c-plane n-type GaN using DLTS/DLOS.

<table>
<thead>
<tr>
<th>Energy position</th>
<th>Possible origin or configuration</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_C - 0.10-0.15$ eV</td>
<td>N vacancy related or Carbon on Ga site</td>
<td>Increase after high energy particle irradiation; matches theory; prominent in compensated GaN and p-GaN</td>
<td>8, 13-15</td>
</tr>
<tr>
<td>$E_C - 0.25$ eV</td>
<td>N vacancy related</td>
<td>Matches theory</td>
<td>14-17</td>
</tr>
<tr>
<td>$E_C - 0.40$ eV</td>
<td>Unknown</td>
<td>Trapping kinetics and hydrogen passivation suggest it probably a point defect cluster, but is also sensitive to dislocations and impurities (e.g., Fe); responsible for RF-stress induced HEMT degradation</td>
<td>16, 17</td>
</tr>
<tr>
<td>$E_C - 0.60$ eV</td>
<td>Unknown defect complex/cluster</td>
<td></td>
<td>18-20</td>
</tr>
<tr>
<td>$E_C - 0.72$ eV</td>
<td>Unknown</td>
<td>Increase after proton irradiation but not electron irradiation</td>
<td>14-16</td>
</tr>
<tr>
<td>$E_C - 0.91$ eV</td>
<td>Point defect cluster along dislocations</td>
<td>Matches theoretical trapping kinetics models</td>
<td>19</td>
</tr>
<tr>
<td>$E_C - 1.2-1.4$ eV</td>
<td>Possible interstitial carbon</td>
<td>Matches theory</td>
<td>7, 8, 14-17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Observable in C-doped semi-insulating GaN; responsible for high field induced HEMT degradation</td>
<td>21, 22</td>
</tr>
<tr>
<td>$E_C - 2.0$ eV</td>
<td>Possibly Carbon related</td>
<td></td>
<td>8, 11</td>
</tr>
<tr>
<td>$E_C - 2.4-2.7$ eV</td>
<td>$V_{Ga}$ and $V_{Ga}$-H complexes or Carbon related</td>
<td>Directly related to yellow luminescence; Observable in C-doped semi-insulating GaN</td>
<td>7-8, 14-18, 21</td>
</tr>
<tr>
<td>$E_C - 3.22$ eV</td>
<td>Residual Mg acceptor</td>
<td>Observed in MOCVD grown GaN</td>
<td>22</td>
</tr>
<tr>
<td>$E_C - 3.28$ eV</td>
<td>Substitutional Carbon</td>
<td>Matches theory; Scattering center</td>
<td>7-9, 14-18, 21-25</td>
</tr>
</tbody>
</table>
2.3 Novel Materials Grown Along Unconventional Crystal Orientations for Polarization Engineering

Polarization engineering is currently the one of the most dominant research fields in III-Nitrides. Polarization technology entails the growing of materials along different crystal orientations in order to engineer the polarization charge and field in device structures according to specific application requirements. Figure 2.4 illustrates several popular crystal orientations of wurtzite GaN. While traditional GaN epitaxy is performed on the c-plane, nowadays device structures are also grown along N-polar, non-polar (NP) and semi-polar (SP) orientations for achieving better device performance.

Figure 2.4 Illustration of several popular crystal orientations of wurtzite GaN.
In fact, polarization engineering is not an option for semiconductors like Si and GaAs, but it is particularly applicable for III-Nitrides, mainly because of the unique wurzite crystal structure of GaN-based materials. [26, 27] As shown in Fig. 2.5 (a), in the GaN unit cell, all the Ga and N atoms are tetrahedrally coordinated, and the two atom types individually form hexagonal, close-pack sublattices that are aligned with each other along the c-direction. Figure 2.5 (b) shows one Ga (or N) atom with its surrounding atoms. In an ideal tetrahedron structure, when all Ga-N bonds are of the same length ($c/a_0 = 1.6333$), the equilibrium position of the center cation (anion) atom coincides with the effective center of the surrounding anion (cation) atoms. However, the real atomic configuration often deviates from the ideal case, resulting in a displacement of the effective cation and anion centers. This displacement, combined with the ionic component of the Ga-N bond, creates a spontaneous polarization field in the c-direction. Different III-Nitrides, due to the differences in cation and crystal lattices, exhibit different spontaneous polarization fields, though all are oriented along the c-direction. Moreover, while the spontaneous polarization is associated with a relaxed crystal, applying external strain to the film would further
change the net dipole moment, causing an additional piezoelectric polarization effect. Generally, the materials grown along the c-plane only undergo an isotropic biaxial strain in the basal plane without a shear component, thus keeping the net dipole moment and the piezoelectric polarization field in the c-direction. The following paragraphs describe the polarization effects on structures grown along different orientations as well as their impacts on device operation.

Figure 2.6 (a) Atomic configuration of Ga-face GaN. (b-c) Polarization fields in Ga-polar AlGaN/GaN and InGaN/GaN heterostructures. (d) Calculated bounded interface charges of pseudomorphic Ga-polar alloys on relaxed GaN. [28]

In conventional Ga-polar (c-plane) GaN, the spontaneous polarization field points from the surface toward the substrate, as shown in Fig. 2.6 (a). Figures 2 (b) and 2 (c) show all the polarization fields in Ga-polar AlGaN/GaN and InGaN/GaN heterostructures. Here, piezoelectric fields only exist in the alloy layers, since in most GaN-based device structures, the GaN layer is fully relaxed whereas the pseudomorphic alloy layers are strained. Based on the lattice constants, AlGaN is tensile-strained, generating a piezoelectric field in the
same direction as the spontaneous polarization, while the InGaN layer is compressively strained, inducing a piezoelectric field in the opposite direction. The resultant polarization charge densities in these two structures are calculated as a function of alloy compositions and are shown in Fig. 2.6 (d). [28] As seen, a positive polarization charge is bounded at the AlGaN/GaN interface, while a negative polarization charge is fixed at InGaN/GaN interface.

![Figure 2.7](image)

Figure 2.7 (a) Band structure of Ga-polar Al0.3Ga0.7N/GaN heterostructure; [29] (b) GaN/InGaN/GaN quantum well. [28]

These high density polarization charges have significant impacts in real devices, which can be either beneficial or undesirable. Regarding the HEMT, the presence of the positive polarization charge at the Ga-polar AlGaN/GaN interface is advantageous, because it introduces two dimensional electron gas (2DEG) without intentional doping, as shown in Fig. 2.7 (a). [29] In contrast, the presence of a polarization field in Ga-polar...
InGaN/GaN LED quantum well (QW) results in a substantial quantum confined Stark effect (QCSE) that severely reduces internal quantum efficiency through separating electrons and holes. This effect is shown in Fig. 2.7 (b). [28] Furthermore, QCSE also imposes restrictions on the QW width in the state-of-the-art c-plane LEDs, which may lead to LED efficiency droop through current crowding and enhanced Auger recombination.

In N-polar GaN, the spontaneous polarization field is now pointing from the substrate toward the surface, as shown in Fig. 2.8 (a). Hence, for the same tensile-strained AlGaN on a relaxed GaN structure, the net polarization charge at the interface is now negative, as shown in Fig. 2.8 (b). Although in theory, this may attract holes and form two-dimensional hole gas (2DHG), in reality, hole accumulations are not observed, probably because they are fully compensated by positively charged donor-like trap states presenting at the same interface. In order to obtain a conductive channel, a different structure of N-polar GaN/AlGaN/GaN is proposed, as shown in Fig. 2.8 (c). Since the AlGaN is pseudomorphic, the top GaN layer can still be treated as relaxed. Therefore, a positive polarization charge will be induced at the top interface. The calculated spontaneous, piezoelectric and total polarization fields in such a structure are shown in Fig. 2.8 (d), as a function of Al composition. [29]
Figure 2.8 (a) Atomic configuration of N-polar GaN; (b-c) Polarization fields in N-polar AlGaN/GaN and GaN/AlGaN/GaN heterostructures; (d) Calculated bounded interface of N-polar material on relaxed GaN. [29]

Figure 2.9 Comparison of the band diagrams and 2DEG distribution of Ga-polar and N-polar HEMTs. [30]

Compared with Ga-polar structure, N-polar GaN/AlGaN/GaN provides a unique advantage for high frequency electronic applications. [30-32] As shown in Fig. 2.9, the AlGaN layer now acts as a heterojunction back-barrier in N-polar structure, enabling a
better 2DEG confinement, which is ideal for mitigating short channel effects. At the same
time, as the 2DEG density is now determined by the AlGaN underneath the channel, the
top GaN layer can be drastically scaled down to prompt modulation efficiency. In addition,
the N-polar structure also provides opportunity for substantially reducing the contact
resistance and parasitic delay, again favoring high speed device operation.

As can be expected, the polarization field in the non-polar structure is again
different from both Ga-polar and N-polar cases. Fig 2.10 shows that all the polarization
fields are now perpendicular to the growth direction. In other words, there are no
polarization fields along the InGaN/GaN QW structure. As a consequence, QCSE will be
minimal in such a structure, which also allows a thicker QW to be utilized for mitigating
current crowding in active region. [33, 34] The NP and SP materials have been shown to
substantially improve total quantum efficiency, and are thus the best candidates for
achieving high efficiency in the next generation of LED and LDs.
Despite of all of these advantages, growing high quality materials along these unconventional orientations is challenging. This is because the atomic configurations on these surfaces are completely different from those on c-plane surfaces, as illustrated clearly in Fig. 2.11. Viewing from the top, Ga- and N-polar surfaces each contain only one atom species: Ga atom for Ga-polar, and N atom for N-polar, and each possesses an in-plane hexagonal symmetry. In contrast, for non-polar m-plane surfaces, equal numbers of Ga and N atoms are found in a plane with reduced symmetry. Moreover, Ga-polar and N-polar structures both have Ga-N dipoles perpendicular to the surface, although in opposite directions, while the m-plane structure does not.

One immediate consequence of the reduced symmetry in the NP/SP growth plane is a scarcity of suitable substrates. For the early NP/SP studies, materials were all grown
on foreign substrates, e.g., (1-102) sapphire, (11-20) SiC, (100) LiAlO₂, and (100) MgAl₂O₄, where the large lattice mismatch constantly creates a high density of extended defects, mostly in the form of basal stacking faults (BSFs) and TDs. Recently, breakthroughs have been achieved in HVPE and ammonothermal growth of bulk GaN, which can be further sliced at certain directions to provide native GaN substrates in NP/SP orientations. These substrates enable homoepitaxy of NP/SP GaN with minimal BSFs and TDs, and thus have drastically improved NP/SP LED and LD performance. [36] However, these substrates are still very costly and limited in size, two significant obstacles to commercializing NP/SP devices.

Besides substrate availability, the difference in atomic configuration also manifests itself during epitaxial growth for these novel orientation materials, and it directly impacts defect generation and impurity incorporation through an atom absorption process. It has already been established experimentally that the incorporation of major impurities, like oxygen and carbon, is highly orientation-dependent. [37, 38] Models involving different bonding configurations at the growth surface have been proposed to explain these findings. For example, Fichtenbaum et al. suggested that O atoms impinging on group-V sites on the Ga-polar surface form only a single bond with Ga surface atoms, while they form three bonds when impinging on the N-polar surface. This causes a strong tendency of O atoms to bond to N-polar materials. [39, 40]

In addition to impurity incorporation, the atomic configuration of the surface also directly affects growth kinetics, especially the lateral diffusion of Ga and N atoms. [41] For example, theoretical calculations predict that the diffusion paths for Ga atoms are isotropic on both Ga-polar and N-polar surfaces, but with energy barriers of 0.32 eV and
0.85 eV, respectively. This suggests a larger diffusion length on the Ga-polar surface than the N-polar surface. In contrast, the diffusion path of Ga atoms on the m-plane surface is highly anisotropic, with energy barriers of 0.13 eV and 1.49 eV along the a- and c-directions, respectively. From this we can infer a longer growth step along the a-direction. These differences in diffusion behaviors contribute to the overall difference in the growth mechanism, and therefore to the differences in defect formation, for materials grown along different crystal orientations.

In conclusion, growing III-Nitrides along unconventional orientations enables polarization engineering, and provides unique opportunities for further advances in GaN-based device performance. However, the substantially different atomic surface configuration compared with c-plane GaN may also lead to a significant change growth kinetics and defect formation. Therefore, a systematic study of orientation-dependent defect generation is required to understand and optimize the growth of these novel materials.

### 2.4 Defect Formation in Materials Grown by Emerging NH₃-MBE Technology

Metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) are the two major techniques for growing high quality GaN-based structures and devices. While MOCVD has been the choice of the GaN industry because of its higher growth rate and throughput, the growth of GaN by MBE, particularly ammonia-based MBE (NH₃-MBE), is currently emerging with great potential and attracting more research interest. [42-45]
As shown in Table 2.2, there are many fundamental differences between MOCVD and MBE, and MBE growth indeed has some advantages over MOCVD in several respects. First, while MOCVD uses metal-organic precursors including trimethylgallium (TMGa), trimethylaluminum (TMAl) and trimethylindium (TMIn) with carrier gas (i.e., H₂ or N₂), MBE employs elemental metal sources, and may therefore significantly reduce the incorporation of carbon and hydrogen impurities into the films. Next, in contrast to the relatively higher pressures of gaseous conditions during MOCVD, MBE occurs under ultra-high vacuum. This enables better monitoring through reflection high energy electron diffraction (RHEED) and control of growth surface and atomic reconstruction, which yield highly abrupt interfaces that are desirable for devices such as HEMT. However, the growth of GaN by the more conventional plasma-assisted MBE (PAMBE) involves tightly controlled, low temperature Ga-rich conditions and a low growth rate which substantially limiting its applications.

Table 2.2 Fundamental differences between MOCVD and MBE.

<table>
<thead>
<tr>
<th></th>
<th>MOCVD</th>
<th>MBE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group III source</strong></td>
<td>Metal-organic</td>
<td>Elemental</td>
</tr>
<tr>
<td><strong>Group V source</strong></td>
<td>Ammonia</td>
<td>Nitrogen plasma (PAMBE) or ammonia (NH₃MBE)</td>
</tr>
<tr>
<td><strong>Carrier gas</strong></td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td><strong>Growth temperature</strong></td>
<td>High</td>
<td>Comparatively low</td>
</tr>
<tr>
<td><strong>Growth pressure</strong></td>
<td>Typically 15 to 750 Torr</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td><strong>Growth regime</strong></td>
<td>Near thermodynamic equilibrium</td>
<td>Non-equilibrium</td>
</tr>
</tbody>
</table>
Here, NH$_3$-MBE emerges as a unique alternative to PAMBE. While maintaining all of the advantages of MBE growth, NH$_3$-MBE, unlike PAMBE, introduces active nitrogen through NH$_3$ that is pyrolyzed at the hot substrate (PAMBE employs plasmatic nitrogen as a group V source). This change leads to an N-rich growth condition at relatively higher temperatures for NH$_3$-MBE growth of GaN, which is substantially different from PAMBE but indeed more similar to MOCVD. As a consequence, the growth rate of NH$_3$-MBE is significantly increased from that of PAMBE and even approaches that of MOCVD. At the same time, the N-rich condition also allows a larger optimization window, thus providing more opportunities for further development. With all these considered, NH$_3$-MBE technology might be a perfect choice for the GaN industry of the future.

![Figure 2.12 Comparison of deep level states in n-type GaN grown by different techniques.](image)

However, in addition to the growth characteristics, the fundamental differences between these growth techniques may also introduce differential crystal defect formations, which can be critical to device performance and require serious consideration. In fact, we
experimentally investigated this effect in an earlier study, in which a combination of DLTS and DLOS was used to characterize the distribution of defects throughout the bandgap of n-type GaN samples grown by different techniques. [46] As shown in Fig. 2.12, the overall defect distributions clearly differed in samples grown by MBE and MOCVD, as expected. Our study also showed that the total concentration of defects in samples grown by NH₃-MBE was much lower than those grown in MOCVD, a finding that again suggests NH₃-MBE is a promising technique for producing high quality materials. Interestingly, such an improvement of material quality may have already manifested itself in real devices, as NH₃-MBE-grown p-n diodes have achieved a lower ideality factor than the state-of-the-art p-n diodes grown by MOCVD. [43] In light of the fact that NH₃-MBE technology is still at its infancy compared with the much more mature MOCVD, further defect reduction and material improvements are expected. Here, quantitative characterization regarding defects and their dependences on growth conditions are of great significance, as it may provide guidelines for further growth optimizations and technological development.

Recently, MBE (both PAMBE and NH₃-MEB) has also shown great promise particularly for growing p-type GaN. [44, 47-49] Due to the substantial suppression of the hydrogen passivation effect during MBE, Mg doped samples showed p-type conductivity as grown. Therefore, the high temperature activation annealing required for MOCVD-grown samples is now unnecessary, adding flexibility to the process integration. Another important advantage for growing p-GaN with MBE is the absence of memory effect, which typically occurs in a MOCVD chamber. This provides great opportunities for design optimizations such as cascading LED structures that may circumvent efficiency droop. [48] In recent years, there have been an increased amount of efforts devoted to the growth of
high quality p-GaN materials by NH₃MBE and improving their electrical properties. For instance, E. C. H. Kyle et al. reported that growing p-GaN at lower temperatures with an In surfactant enhances p-type conductivity, possibly reducing the incidence of defect centers. [49] However, a proper understanding of this effect again requires a comprehensive investigation of the bandgap states and their properties. Unfortunately, to the best of our knowledge, this information does not exist. Therefore, this will be the topic of a separate chapter in this dissertation.

2.5 High Energy Particle Radiation Effects in GaN Materials and Devices

More recently, interest is increasing in the incorporation of GaN-based high frequency devices in space communication systems. [50, 51] Here, the excellent and continual improving device performance of GaN-HEMTs is of course the primarily reason, and the promise of being able to substantially reduce the size and weight of such systems is also a plus. However, besides these two factors, the tolerance to radiation of GaN devices must be carefully considered, because these devices will be operating under high radiation environments, and additional caution is needed for long term device reliability. Therefore, it is imperative that information be obtained on the impact of radiation to GaN devices and materials, as well as the ways to mitigate such impacts through design optimization.
The environment of space contains a variety of radiations, including high energy protons, electrons and neutrons trapped in Van Allen Belt (Fig. 2.13). [52] There are also heavy ions, gamma-rays, and x-rays, and so on. However, despite these many kinds of particles, radiation impacts on semiconductors are induced mainly through either
ionization or displacement. [51] In an ionization process, energy is transferred from radiation to valence band electrons. This energy generates electron-hole pairs in the device structure. The ionization damage is particularly pronounced in Si MOSFETs due to the presence of a semiconductor/oxide interface. As shown in Fig. 2.14, [53] for an n-channel MOS capacitor, irradiation-induced holes hop toward the Si/SiO$_2$ interface at positive bias, and are either trapped by the existing deep states near the interface, or create additional interface states. Both outcomes affect device performance. However, this would not be the case for compound semiconductor devices, because the formation of conductive channels does not necessarily require insulators, thereby a semiconductor/insulator interface. Consequently, these devices are not so severely affected by the ionization process. Indeed, it has been experimentally demonstrated that AlGaN/GaN HEMTs show little degradation after exposure to x-ray irradiation, suggesting that they are insensitive to ionization radiation damage. [51]

![Figure 2.15 Comparison of displacement threshold energy for GaN, Si and GaAs. [54]](image)
The second type of irradiation effect, displacement, occurs when high energy particles knock out the target atom from its normal lattice site, thereby creating crystal defects. Although this process does occur in all semiconductors, theoretical calculations predict that the displacement threshold energy is inversely proportional to bond length. This fact implies different degrees of impact for different materials. As shown in Fig. 2.15, GaN-based materials are predicted to have higher displacement thresholds than Si and GaAs, and therefore more resistant to displacement damage. [54] A great deal of empirical evidence supports this contention. As shown in Fig. 2.16, both LEDs and HEMTs generally show order of magnitude improvement in radiation tolerance when they incorporate GaN devices as compared to devices of other III-V based technologies. [55, 56] Overall, all these theories and experimental findings suggest that GaN based materials and devices are relatively radiation hard, and thus would be ideal candidates for space applications.

Figure 2.16 Comparison of radiation induced damage in (a) LED and (b) HEMT devices employing GaN and other compound semiconductor technologies. [55, 56]
Nevertheless, GaN-based devices still degrade after exposure to large doses of radiation. Significant degradation and shifts in GaN HEMTs (shown in Fig. 2.17) have been universally observed for key device parameters such as $I_{DS}$, $V_t$, $g_m$ and $R_s$ after irradiation by high energy protons. [50, 51, 57-61] The threshold radiation dose for such impacts is a fluence of $1 \times 10^{14}$ cm$^{-2}$ 2 MeV of proton irradiation, a quantity which is relatively high and probably equivalent to tens of years of total irradiation in space. [62-64] Even so, these effects have incited considerable interest from the whole research community. This is so not only because of the need for increasing radiation hardness for real applications, but also because it represents a special opportunity to investigate HEMT device degradation mechanisms and to explore complex correlations between the defect
generation at the materials level and performance degradation at device level. However, despite the fact that the radiation induced degradation has been widely reported for GaN-based HEMTs over the last decade, systematic investigation and modeling of these degradations has rarely been done. Consequently, no consensus has been reached regarding the details of these degradation mechanisms.

The difficulty in understanding the degradation of these devices is partly due to the difficulty of quantitatively characterizing radiation-induced defects at the materials level. Although it is well known that device degradation is attributable to materials defects, without quantitative defect details – energy position, charge state, introduction rate (the number of defects created by a single incident particle), etc. – it is impossible to establish reliable models to explain and predict these effects. This is so especially when different kinds of degradation interfere with each other at large doses, making the whole picture even more complicated. There have been several studies investigating the traps generated in GaN materials after irradiation with protons, electrons, neutrons, and gamma-rays. For instance, L. Polenta et al. showed that an $E_C - 0.07 \text{ eV}$ trap was generated in electron irradiated GaN, which they claimed was related to N-vacancy. [65] They correlated this trap with the mobility degradation of the material. [66] F. Auret and S. Goodman et al. observed proton-induced traps with similar activation energies, and characterized their creation as a function of post-radiation annealing temperature. [67] Besides those low activation energy traps, A. Polyakov et al. reported the induction of $E_C - 0.75 \text{ eV}$ and $E_C - 0.95 \text{ eV}$ traps by proton irradiation, and discussed their impact on electronic and optical material properties. [68] However, because all of these studies relied on thermal stimulation of the defects, they were limited by the fact they only observed trap induction
near the conduction band (within ~ 1 eV energy range), while a large portion of the 3.4 eV GaN band gap was left totally unexamined. This is unfortunate, because possible energy levels do exist in that part of the band gap and can be very important, as they can easily cause carrier compensation and mobility reduction. Hence, systematic characterization of irradiation-induced deep levels throughout the III-Nitride band gap, especially in the mid and lower band gap regions, will likely provide complete information for connecting GaN HEMT degradation pathways to their specific physical mechanisms for the first time.

Moreover, such investigation would also be beneficial for increasing our fundamental understanding of crystal defects in GaN. In theory, trap incorporation during high temperature growth is likely governed by the defect formation energy, whereas their generation during high energy irradiation at room temperature is not. [5] Thus, some defects that have high formation energies and are absent in as-grown samples may now appear after irradiation. Additionally, such studies can also shed light on the physical configuration and behavior of certain traps: since the total impurity concentration will not be affected by the irradiation under vacuum, those impurity-related traps should not change, unless they are in form of a complex with certain native defects or possibly involved in hydrogenation/dehydrogenation processes. [69]

In conclusion, GaN based devices have shown great promise for space electronics due to the unique combination of excellent device performance and relatively high radiation tolerance. However, GaN HEMTs still degrade at high radiation doses, and the detailed mechanisms for these radiation-induced degradations are not yet fully understood. Quantitative characterization of radiation induced deep levels throughout the GaN bandgap
may provide key information for understanding the device degradation, as well as the formation and properties of the defect itself.
2.6 References


3.1 Overview

This chapter describes the experimental techniques that were used in this dissertation to quantitatively characterize the electrically active defect states in semiconductor materials. In fact, these techniques are not only applicable to the detection of deep traps in the bandgap, but may also provide unique perspectives on investigating dopant levels in certain cases, especially for those novel materials including ultra-wide bandgap semiconductors, where effective shallow dopants have yet be well developed. Since all these techniques rely on characterizing either thermally or optically stimulated emission (or capture) processes from (or to) these bandgap states, the basic physics associated with crystal defects (mostly point defects) and these processes (both thermal and optical) will be discussed first. This knowledge will provide the context for understanding the proper characterization technique for a specific defect state, as well as the way to interpret the results of the characterization. Next, the knowledge regarding defects and their behaviors will be incorporated into capacitance characteristics of simple
Schottky diodes and p-n diodes. Special attention will be given to the changes of depletion capacitance signals as a function of voltage, frequency and temperature, which can be used to monitor dopant properties, and capacitance transients measured as a function of temperature and optical excitation, which enables deep defect state characterizations. The combination of capacitance-frequency (and capacitance-temperature), DLTS, and DLOS measurements provides full coverage of the deep states throughout the wide bandgap of novel III-Nitride semiconductors, which cannot be achieved by conventional technologies.

3.2 Physics of Bandgap States

3.2.1 Emission and Capture Processes

Figure 3.1 The processes possible for a bandgap state involving transitions to or from a band: (a) electron capture from conduction band; (b) electron emission to conduction band; (c) hole capture from valence band; (d) hole emission to valence band. [1]
Crystal defects may manifest as electrically active bandgap states depending on the charge state and occupancy. [1, 2] The Schockley-Read-Hall model describes four major generation and recombination processes through which these bandgap states may change their occupancies. As shown in Fig. 3.1, these processes are: (a) electron capture from conduction band; (b) electron emission to conduction band; (c) hole capture from valence band; (d) hole emission to valence band. [1] With all these four processes considered, the rate at which the bandgap state changes its occupancy should be:

\[
\frac{\partial n_T}{\partial t} = (c_n n_T e_n n_T) - (c_p p_T e_p p_T)
\]

(3.1)

where \(n_T\) and \(p_T\) are the concentrations of occupied and empty bandgap states, \(n\) and \(p\) are carrier concentrations, \(e_n\) and \(e_p\) are the emission rates for electrons and holes, and \(c_n\) and \(c_p\) are the capture coefficients for electrons and holes, respectively. Because these processes can be stimulated either thermally or optically, different parameters should be used for different types of processes.

Equation (3.1) is a general equation that directly determines the bandgap state occupancy as a function of time in all measurements. For purposes of characterization, an emission process would be preferred, as it depends only on the occupied bandgap states. In contrast, the capture process is also affected by the carrier density in the conduction (or valence) band, and this is a difficult process to quantify under measurement conditions.

3.2.2 Thermal Emission

Now we first consider the thermal emission process. In fact, the thermal emission rates and capture coefficients are correlated. From the perspective of detailed balance for
traps, the capture and emission of electrons to the conduction band may be expressed as follows:

\[ e_n = c_n N_C \exp\left(\frac{E_T - E_C}{kT}\right) \]  

(3.2)

where \( N_C \) is the effective density of states in conduction band, and \( E_T \) is the bandgap energy position. The thermal capture coefficient \( c_n \), may be defined as follows:

\[ c_n \equiv \sigma_n \nu_{th} \]  

(3.3)

where \( \sigma_n \) is the thermal capture cross section, and \( \nu_{th} \) is the thermal velocity. The parameter \( \sigma_n \) describes the possibility of a carrier being captured by the bandgap state, and has units of \( \text{cm}^2 \). Thermal velocity is defined as:

\[ \nu_{th} \equiv \left(\frac{3kT}{m_n}\right)^{1/2} \]  

(3.4)

where \( m_n \) is the electron effective mass. In addition, the effective density of states in the conduction band can be expressed as:

\[ N_C = 2\left(\frac{2\pi m_n kT}{\hbar^2}\right)^{3/2} \]  

(3.5)

Substituting Equations (3.3) through (3.5) into Equation (3.2), the electron thermal emission rate becomes:

\[ e_n = 3.25 \times 10^{21} \frac{m_n}{m_0} \sigma_n T^2 \exp\left(\frac{(E_T - E_C)}{kT}\right) \]  

(3.6)

The corresponding thermal emission time constant \( \tau_n = 1/e_n \) thus becomes:

\[ \tau_n T^2 = \frac{\exp\left(\frac{(E_C - E_T)}{kT}\right)}{\sigma_n 3.25 \times 10^{21} \frac{m_n}{m_0}} \]  

(3.7)

For hole emission processes relative to the valence band, the equations are nearly identical, except for the substitution of effective hole mass \( m_p \) for \( m_n \), and, because energy position is now relative to valence band maximum, \( E_T - E_V \) replaces for \( E_C - E_T \). Equations (3.6)
and (3.7) describe all thermal emission processes of bandgap states. They are the bases of an Arrhenius analysis for extracting trap energy positions and thermal capture cross sections.

Figure 3.2 Thermal emission rates and time constants for bandgap states as a function of temperature. A carrier capture cross section of $1 \times 10^{-16}$ cm$^2$ is assumed for all states.

Figure 3.2 depicts Equations (3.6) and (3.7) by plotting emission rates and time constants as functions of temperature for bandgap states at energy positions of $E_C - 0.01$ eV, 0.1 eV, 0.2 eV, 0.6 eV and 1.0 eV. For all these states, a capture cross section of $10^{-16}$ cm$^2$ is assumed. This kind of plot will be used several times in this chapter, as it is the key for understanding the different regimes to which different techniques would be best applied.
Here, one can first reveal some general trends of thermal emission: at a certain temperature, the emission process of deeper states occurs at a smaller rate (larger time constant); while at a fixed frequency (time constant), deeper state emits at a higher temperature. It can also be seen that the emission time constant for states over \( \sim 1.0 \) eV away from the conduction band edge can be very long even at elevated temperatures. Therefore, it is necessary to study the optically stimulated emission process to characterize those deep traps.

3.2.3 Optical Emission

For optical emission process, the emission rate is defined as:

\[
e_n^o \equiv \Phi(h\gamma)\sigma_n^o(h\gamma)
\]  

where \( \Phi \) is the incident photon flux, and \( \sigma_n^o \) is the electron optical cross section. Both of these parameters are functions of incident photon energy. While \( \Phi \) is an experimental parameter, \( \sigma_n^o \) is indeed a unique property of bandgap state, which describes the probability of a photon being absorbed by this state. It has a unit of cm\(^2\).

In the most simplified case, the optical emission from a bandgap state is a pure electronic excitation (absorption) process, and can therefore be analyzed within the electronic subsystem using an \( E-k \) diagram. The emission/absorption probability (optical cross section) depends on the transition energy, and the densities of initial and final states.

Lucovsky formulated the following simple analytic model to describe it: [3]

\[
\sigma_n^o(h\gamma) \propto \frac{E_T^{1/2}(h\gamma-E_T)^{3/2}}{(h\gamma)^3}
\]  

This model is particularly appropriate for hydrogenic traps, which are often relatively “shallow and delocalized” states close to conduction (or valence) band edge. [4] According
to Eq. (3.9), for pure electronic excitation, a sharp onset will occur in the $\sigma_n^o$ spectrum at the trap (thermal activation) energy position $E_T$. This behavior has been experimentally observed for many traps and a variety of materials. [3, 5, 6]

Figure 3.3 Schematic illustration of the recombination of a localized hole with a free electron. [7]

However, in many cases optical transition from or to deep states (typically localized deep states) is accompanied by strong electron-phonon coupling. Figure 3.3 illustrates one such example. [7] A deep acceptor with localized hole wavefunction (bound hole) can induce a large lattice distortion because the center atom is displaced from equilibrium position. When the bonded hole recombines with a free electron, a photon is emitted immediately, but the lattice atoms will “slowly” relax to equilibrium configuration afterwards, emitting phonons to release additional vibration energy in the system. Similarly, for excitation processes, additional energy may be initially absorbed by the optical process
and then released through phonon emission. With multiple phonon states involved, such an effect can result in phonon replicas or a broad spectrum around the optical ionization energy $E_o$. Because of this, lattice vibration energy as well as the electronic subsystem must be taken into account together. Such optical transition processes need to be considered in the configuration coordination (CC) diagram. [8]

![Figure 3.4 Configuration coordination diagram accounting for both electronic energy and lattice potential energy. $V_C$, $V_v$ and $V_{il}$ are the conduction band, valence band and defect ground state, respectively. $Q$ represents the atomic displacement due to lattice relaxation.](image)

As shown in Fig. 3.4, [9] due to lattice distortion around the defect, the minimum of the defect ground state ($V_{il}$) is horizontally displaced from the minimum of the conduction band ($V_C$), and the Franck-Condon energy $D$ quantifies such an effect. During a thermal process where phonons are directly involved, the transition occurs between the
minima of $V_{ti}$ and $V_c$, regardless of the atomic displacement. Thus, the thermal activation energy $E_T$ equals the trap energy position with respect to $E_C$. However, for optical emission processes, the transition can only occur vertically in CC diagram because the optical excitations are always much faster than thermal relaxations through phonons. [10] At the same time, the transient matrix strongly depends on the distribution of initial states (the final states are spatially uniform as conduction band states are all empty). As a result, when the distribution of initial states (on $V_{ti}$) peaks at $Q_{ti}$ (due to the parabolic shape of $V_{ti}$), the optical ionization energy is greater than the defect thermal activation energy $E_T$ by $D$. However, it is worth noting that the optical ionization energy only corresponds to the “most probable” transition energy, and not to the threshold (lowest) energy for optical transition. Additional details on this relationship will be provided later at the end of the chapter, where different defect characterization techniques are compared.

Over the last four decades, several models have been proposed to describe the $\sigma^0$ spectrum accounting for the lattice relaxation effects. For example, Chantre et al. developed an analytic model correlating defect wavefunction localization with lattice relaxation. [4] The equation describing this correlation is:

$$\sigma_n^0(h\gamma) \propto \frac{1}{4k_BTDh\gamma} \int dE_k \frac{E_k^{3/2}}{(E_k+m)^2} \exp\left(-\frac{(h\gamma-E_k-E_T-D)^2}{4k_BT_D}\right)$$ (3.10)

Here, $m$ can be expressed as:

$$m \propto \frac{h^2\alpha^2}{2m_T(E_T+D)}$$ (3.11)

where, $\alpha$ describes the extent of defect state potential well. More recently, Passler developed a model utilizing the concept of effective phonon energy ($\epsilon$), as shown below: [9]
\[ \sigma_n^0(h\gamma) \propto \frac{1}{h\gamma} \frac{1}{\sqrt{2\pi D \coth(\frac{\varepsilon}{2k_B T})}} \int dE_k \frac{E_k^{3/2}}{(E_k+E_T)^2} \exp\left(-\frac{(h\gamma-E_k-E_T-D)^2}{2D \coth(\frac{\varepsilon}{2k_B T})}\right) \]  

(3.12)

These models can be used for simulating the broad \( \sigma^0 \) spectrum observed in DLOS measurements, therefore, reveal the trap energy and Franck-Condon energy for deep level states.

3.3 Capacitance-based Measurement for Quantitative Characterization

With the defect physics discussed above, we now describe how to experimentally monitor/characterize these processes. The most direct approach is to use capacitance-based measurements, because they focus on the electrically active fixed charge in depletion region. To measure a capacitance, a small ac voltage signal \( dV \) at certain sampling frequency is first applied to the sample, and the corresponding charge modulation \( dQ \) is measured. The small signal capacitance is thusly defined as:

\[ C = \left| \frac{dQ}{dV} \right| \]  

(3.13)

As will be discussed later, sampling frequency is a very important feature as it determines whether a bandgap state (dopant or trap) responds to this ac modulation, manifesting in the capacitance signal; or its emission does not follow the ac modulation, thus manifesting as a capacitance transient.
Figure 3.5 Typical Schottky diode and p-n diode structures for study n-type GaN through capacitance-based measurements.

The simplest structures for performing such capacitance-based characterizations are Schottky or p-n diodes, where depletion regions are ready formed and can be easily modulated by external bias. For p-n diodes, abrupt one-sided p-n junctions are preferred so that most of the depletion region is in the lightly doped layer, and capacitance (and capacitance transient) signals will be mostly sensitive to this region. Figure 3.5 presents the typical structures for studying the n-type lightly doped layer. In both cases, the highly doped layer beneath the layer of interest is for forming Ohmic contact with low series resistance, whereas the semitransparent top contacts are for enabling optical measurements.

The depletion capacitance at a given depletion depth \( W \) is expressed as follows:

\[
C = \frac{\varepsilon A}{W} \tag{3.14}
\]

where \( \varepsilon \) is the dielectric constant, and \( A \) is diode area. For the depletion region where the space charge is uniformly distributed, the depletion capacitance as a function of applied dc bias \( (V) \) can be derived using Poisson’s equation, and is expressed as:

\[
C = \varepsilon A \left[ \frac{q N_{SCR}}{2 \varepsilon (V_{th} - V)} \right]^{1/2} \tag{3.15}
\]
Here, $V_{bi}$ is the build-in voltage, and $N_{SCR}$ is the averaged space charge including both dopant and electrically active defect states.

In addition, $C-V$ measurements can also be analyzed by applying the concept of charge modulation at the depletion edge. In this case, the net fixed charge density at the depletion edge is expressed as:

$$N_{SCR}(W) = \frac{C^3}{q\varepsilon A^2 \left(\frac{dC}{dV}\right)}$$

This local net fixed charge may also include both dopant and electrically active defect states, depending on their charge states and responses to the modulation. Equation (3.16) is typically used for profiling fixed charge density in materials.
3.4 Capacitance-frequency \((C-f)\) and Capacitance-temperature \((C-T)\) Methods

![Diagram showing capacitance-frequency and capacitance-temperature methods.]

Figure 3.6 Illustration of deep state response to capacitance sampling frequency.

Capacitance-frequency \((C-f)\) and capacitance-temperature \((C-T)\) methods that investigate bandgap state thermal emission are special tools for studying deep dopant levels. As seen in Equation (3.13), capacitance measurements rely on the signal response: an ac signal first provides carriers to be captured by the bandgap states, then the states emit carriers back to generate the modulation signal for calculating capacitance. Thus, whether or not a bandgap state responds to the ac sampling frequency may directly impact the capacitance signal. To illustrate this effect better, Fig. 3.6 plots a typical thermal emission rate curve. As seen, in the region above the thermal emission rate curve, the bandgap state
will not follow the sampling frequencies, resulting in a lower capacitance value; below the curve, it can follow and yield a higher capacitance value. If this bandgap state is in fact a dopant state that is typically of a high concentration, the change in capacitance signal due to different responses can be significant. More importantly, since these changes all occur at conditions along the emission rate curve, the thermal emissions rate curve can be mapped by $C$-$f$ scans at different temperatures, or $C$-$T$ scans at different sampling frequencies, as highlighted in Fig. 3.6. Therefore, $C$-$f$ and $C$-$T$ characterizations may provide information regarding the energy position and capture cross section of the dopant state.

In reality, the application of these techniques depends on the relative position of the emission rate curve with respect to the practical temperature and frequency domains. The typical range of ac sampling frequencies for capacitance measurements is between 100 Hz and about 2 MHz (i.e. Agilent E49980 LCR meter). Typical temperature scans are from 77 K to 400~500 K. Together, these bounds form a “detection window” of $C$-$f$ and $C$-$T$ methods. For Si doped n-type GaN, since the Si dopant is very close to the conduction band edge ($E_C - 12$ meV), [11] its thermal emission rate curve is always above this “detection window” (see Fig. 3.2). Therefore, the $Si_{Ga}$ state in GaN cannot be detected through this approach. However, for p-type GaN, since the activation energy for $Mg_{Ga}$ acceptor is much larger (around $E_V + 200$ meV), [12] the emission rate curve is within the detection window, allowing this dopant level to be well characterized by these techniques.
Figure 3.7 (a) $C-f$ curves measured at different temperatures at 0 V bias in p-type GaN. (b) $C-V$ characteristics obtained at 110 K with sampling frequencies of 1 kHz and 1 MHz, respectively.

As an example, Fig. 3.7 presents the $C-f$ measurement results for a p-type GaN. These measurements were performed between 1 kHz ~ 1 MHz sample frequency range at different temperatures. Large frequency dispersions are clearly observed, where the capacitance roll-off frequency corresponds to the lowest frequency to which that defect state cannot respond. [13] This “roll-off frequency” increases with temperature, consistent with the emission rate behavior for the bandgap state. Furthermore, $C-V$ measurements performed at different frequencies also confirm this attribution. At low frequencies (e.g., 1 kHz), dopant states can respond to the ac sampling signal, thus behaving as normal dopants and exhibiting standard $C-V$ characteristics. At high frequencies (e.g., 1 MHz), on the other hand, they cannot follow the ac signal, and are thus not detectable by the capacitance meter, resulting in a low fixed charge density and a total depletion for the layer of interest.
Figure 3.8 (a) $G/\omega$ vs. $f$ plot for a p-GaN sample; (b) Arrhenius analysis for obtaining the dopant activation energy and capture cross section.

To further analyze this effect, either $dC/df$ or conductance-based approaches can be used. Here, we show the conductance method (also known as admittance spectroscopy) as an example. As seen in Fig. 3.8, $G/\omega$ is plotted as a function of sampling frequency ($G$ as conductance), where peak features can be found at frequencies corresponding to the capacitance “roll-off”. [14] An Arrhenius analysis of these peaks (based on Equation (3.6)) provides the dopant energy position and capture cross section. The dopant concentration can be obtained from the doping profile of 1 kHz $C-V$ measurements.

In fact, besides the dopant emission process as discussed above, large series resistance ($R_s$) may also introduce significant $C-f$ dispersion. [1, 13] This is because the measured capacitance ($C_M$) is determined by the real capacitance $C$, frequency ($\omega = 2\pi f$), and $R_s$, as expressed in the following equation:

$$C_M = \frac{C}{1+(\omega R_s C)^2} \quad (3.17)$$
Thus, when $R_S$ is large, increasing $\omega$ may lead to smaller $C_M$. However, such an effect can often be distinguished from the dopant emission effect: according to Equation (3.17), the measured capacitance will ultimately drop down nearly to zero at high frequency, if it is due to the $R_S$ effect; while, though dopant effect will lead to a total depletion for the layer of interest, high frequency capacitance remains a reasonably large value, as the depletion depth is always finite.

After all, $C$-$f$ and $C$-$T$ methods provide a unique perspective to investigate the dopant thermal emission process. Although Hall measurements are more often used for obtaining the dopant activation energy, information regarding the dopant capture process and cross section, which may shine light on the defect configuration, is accessible only through such $C$-$f$ and $C$-$T$ techniques.

### 3.5 DLTS

DLTS is a conventional technique for characterizing the thermal emission of bandgap states that are too deep to be detected by $C$-$f$ and $C$-$T$ methods. [15] As the emission rates of these deeper states are often below the typical capacitance sampling frequency, they do not directly contribute to the capacitance signal, manifesting instead as a function of time (as a capacitance transient). DLTS monitors and analyzes this transient as a function of temperature, so as to reveal the defect emission characteristics and defect concentration.
Figure 3.9 (a-c) Schematic diagrams of trap modulation in n-type Schottky diode; (d) Timing diagram of applied voltage and capacitance signals.

Capacitance transient occurs due to defect modulation. However, unlike \( C-f \) or \( C-T \) methods, which modulate the bandgap states by ac sampling signal, here it is achieved by moving the quasi-Fermi level across these deep states when applying quiescent and filling bias. [2] To illustrate this, we take an n-type GaN Schottky diode for example. Figure 3.9 (a-c) shows the schematic diagrams of defect modulation, and Fig. 3.9 (d) illustrates the timing diagrams of voltage and capacitance signals. At reverse biased quiescent condition, the deep states within the depletion region are mostly emptied. An electrical pulse at 0 V quickly shrinks the depletion region, thus filling the traps between the two depletion edges. When the reverse bias is applied again, the carriers retract, while the filled traps will be above quasi Fermi level and start to thermally emit electrons, generating a
capacitance transient. The positive transient is due to the emission of majority carriers (to a majority carrier band), whereas the negative transient is the result of minority carrier emission (to minority carrier band).

Now we consider using Equation (3.1) to derive an analytical expression for the capacitance transient. Due to the presence of the depletion region, there are no carriers in either the conduction band or the valance band, so the two capture processes can be neglected. In addition, for a defect that is above the middle of the bandgap $E_i$, $e_p$ is most likely negligible relative to $e_n$, especially for wide bandgap semiconductors. Therefore, Equation (3.1) reduces to:

$$\frac{\partial n_T}{\partial t} = -e_n n_T$$  \hspace{1cm} (3.18)

By solving this equation, the filled defect states as a function of time can be expressed as:

$$n_T(t) = n_T(0) \exp(-e_n t)$$  \hspace{1cm} (3.19)

Now we assume the traps are uniformly distributed and modulated within the depletion region, and at $t = 0$, the defect state is fully filled, thus making $n_T(0) = N_T$. Replacing $N_{SCR}$ in Equation (3.15) with the positively charged doping density $N_D$ and the density of trapped electrons $n_T(t)$, the capacitance transient can be written as:

$$C(t) = \varepsilon A \left[ \frac{q(N_D - N_T \exp(-e_n t))}{2\varepsilon(V_{bi} - V)} \right]^{1/2}$$  \hspace{1cm} (3.20)

When the defect concentration is much smaller than doping density, Equation (3.20) can be further simplified to:

$$C(t) = \varepsilon A \left[ \frac{q}{2\varepsilon(V_{bi} - V)} \right]^{1/2} \left( N_D - \frac{1}{2} N_T \exp(-e_n t) \right) = C_\infty \left( 1 - \frac{N_T \exp(-e_n t)}{2N_D} \right)$$  \hspace{1cm} (3.21)

Hence, the capacitance transient now directly correlates with its emission process as well as the defect density.
During real measurements, all capacitance transients are digitally acquired at high resolution as a function of DLTS scan temperatures ranging from 77 K to 400 K. These capacitance transients are analyzed using the conventional double boxcar method. While the details of double boxcar methods can be found in ref. 12, Fig. 3.10 (a) highlights its key concept: at a given “rate window” $1/(t_2-t_1)$, the temperature-dependent defect emission process results in a peak feature, and the capacitance transient signal peaks at a temperature when trap emission rate equals the value of the rate window. Figure 3.10 (b) presents an example of DLTS spectra and an Arrhenius analysis for an n-type GaN sample. [6] As seen, a set of rate windows are applied in the analysis, and these DLTS peaks are used to construct Arrhenius plots. The Arrhenius plots, based on Equation (3.7), allow the defect activation energy and capture cross sections to be extracted via the slope and y-intercept, respectively. In addition, the defect concentration can also be roughly calculated from the peak height as follows:
\[ N_T = 6.14N_D \left( \frac{\Delta C}{C_\infty} \right) \quad (3.22) \]

when \( \beta = \frac{t_2}{t_1} \) is kept at 2.5 for all rate windows in the double boxcar method.

It should be noted that Equation (3.22) is based on Equations (3.20) and (3.21), which are derived for the oversimplified case in which trap modulation is uniform within the depletion region. In reality, this is never the case, due to the so-called “Lambda effect,” and to the Fermi level crossing defect level at different positions under different bias.
conditions (shown in Fig. 3.11). When these effects are accounted for, a more accurate calculation of trap concentration would be: [2]

\[ N_T = 6.14N_D \left( \frac{\Delta C_0}{C_\infty} \right) \left[ \frac{x_d^2}{(x_d-\lambda)^2-(x_0-\lambda)^2} \right] \] (3.23)

where, \( x_0 \) and \( x_d \) are the depletion depths at filling and quiescent bias conditions. \( \lambda \) for each trap is defined as:

\[ \lambda = \left[ \frac{2\epsilon \epsilon_0 q^2}{N_D} (E_F - E_T) \right]^{1/2} \] (3.24)

Although DLTS is a well-established technique that enables quantitative characterizations of deep states, its thermal emission rates (as shown in Fig. 3.2) limit its application for detecting traps within about 1.0 eV from the conduction (or valance) band edge in n-type (or p-type) materials. However, for wide band gap semiconductors such as GaN, a significant portion of the bandgap is left unexplored by either \( C-f/C-T \) or DLTS. Therefore, optically stimulated emission must be employed to reveal deep levels and their properties in those energy ranges.

3.6 DLOS

Similar to the deep level thermal emission that monitored in DLTS, the optical emission of deep states is also slower than the capacitance ac sampling signal, therefore again producing a capacitance transient. DLOS measurement characterizes this transient as a function of incident light energy, so as to reveal the defect energy position, concentration as well as the lattice relaxation effect associated with the optical process.
Figure 3.12 illustrates the modulation and timing diagrams for DLOS measurements. The similarities and differences between DLOS and DLTS can be clearly revealed when Fig. 3.12 is compared to Fig. 3.9. First, the electrical filling process in DLOS is similar to that in DLTS, except that the pulse duration in DLOS is 10 s while in DLTS it is 10 ms. Next, in DLOS, it is now the optical transient (since the shutter opening) that is recorded and analyzed, instead of the thermal transient (since the end of filling pulse) in DLTS. In addition, an interval that is long enough to saturate most of the thermal transient is added in DLOS measurements before the shutter opens, so that the influence of thermal emission on optical transient analysis is minimal. Finally, while DLTS is performed with a temperature scan, DLOS can be done at a fixed temperature. All the DLOS measurements presented in this study were done at room temperature. The optical transients were recorded since the moment of shutter opening up to several hundreds of seconds when the optical emission process reaches “steady-state”. The light from Xe and QTH lamps is dispersed through high resolution monochromators, providing monochromatic optical excitations.
from 0.5 eV to ~ 6.0 eV in 0.02 eV steps. Therefore, DLOS enables the detection of deep states in the energy range that cannot be probed through either $C-f (C-T)$ or DLTS.

The capacitance optical transient is still expressed by Equation (3.21), except that now the thermal emission rate is replaced by the optical emission rate, which is defined in Equation (3.8). Consequently, the sign of the optical transient is again indicative of the transient type: positive transients are due to the emission of majority carriers (to the majority carrier band), whereas negative transients are the result of minority carrier emission (to the minority carrier band). Analysis of DLOS mainly focuses on both ends of the optical transient. The initial portion of the transient is used for obtaining the optical cross section spectrum, so as to determine the defect energy position and lattice relaxation effect. The derivative of Equation (3.21) results in: [4, 6]

$$\frac{dC(t)}{dt} \bigg|_{t=0} = -\frac{C_\infty N_T}{2N_D} \frac{d\sigma_n^0(t)}{dt} \bigg|_{t=0}$$

(3.25)

assuming $\sigma_n^0(t) \times t < 0.1$. Hence, the optical cross section can now be expressed as:

$$\sigma_n^0 = \frac{2N_D}{\Phi(h\nu)N_T C_\infty} \frac{dC(t)}{dt} \bigg|_{t=0}$$

(3.26)

The $\sigma_n^0$ spectrum can then be analyzed using different models as discussed in before.

On the other end, the steady state photocapacitance (SSPC) plotted as a function of incident energy can be used to estimate deep state energy position and concentration. The difference in trap energy obtained from SSPC and the $\sigma_n^0$ spectrum will be discussed later in this section. Regarding the trap concentration, according to Equation (3.21), if $t = 0$ and steady state condition ($t = \infty$) obtains, one can get:

$$N_T = 2N_D \left( \frac{\Delta C}{C_\infty} \right)$$

(3.27)

where, $\Delta C = C(\infty) - C(0)$, the total magnitude of the capacitance optical transient.
Figure 3.13 Illustration of possible competition between electron emission and hole emission processes during DLOS measurements.

However, it is important to note that DLOS only provides the lower limit of trap concentration, especially for traps in the lower half of the band gap. This effect is illustrated in Fig. 3.13. As seen, when the incident energy ($h\nu_2$) is large enough to excite electrons from a deep state below the mid of the bandgap to the conduction band, the same photon may also provide enough energy for emitting a hole from this state to the valence band (that can also be viewed as emit a valence band electron to this state). In this case, the measured capacitance transient is indeed a net effect of two opposite processes, and Equation (3.27) clearly underestimates defect concentration. [6] Unfortunately, the way to correct such an underestimate has not yet been determined.
Figure 3.14 SSPC spectrum and optical cross section analysis for investigating the deep states in m-plane n-type GaN. The solid line is a fit to the Lucovsky model while the dashed line is a fit to the Passler model.

Figure 3.14 shows the DLOS results of m-plane n-type GaN as an example. Two positive onsets are clearly observed in both $\sigma_n^0$ and SSPC spectra, suggesting the presences of two electron traps in this portion of the bandgap. The more accurate trap energies are determined to be $E_C - 2.50$ eV and $E_C - 3.30$ eV through optical cross section analysis, which also reveals that the $E_C - 2.50$ eV trap is associated with a large lattice relaxation effect by fitting to the Passler model. [9] Trap concentrations are obtained using the heights of the corresponding step-like feature in the SSPC spectrum. For the $E_C - 2.50$ eV and $E_C - 3.30$ eV traps shown, the concentrations are $2.6 \times 10^{16}$ cm$^{-3}$ and $2.8 \times 10^{16}$ cm$^{-3}$, respectively.
3.7 Correspondence of DLTS, DLOS and Photoluminescence (PL) in Terms of a Configuration-Coordination Model

As mentioned, the optical processes involving deep localized states are often associated with strong electron-phonon coupling. In fact, this effect not only manifests in DLOS, but also affects many other optical measurements, including PL, absorption, and so on. Because different characterization techniques, or even a different analyses for the same technique, may reveal different aspects of the process, it is necessary to understand the mechanisms of lattice relaxation affecting optical transitions and the correspondence among these techniques.

Figure 3.15 Optical excitation of a defect in CC diagram.
Figure 3.15 shows the one dimensional CC diagram of a defect with large lattice relaxation. Here, the CC diagram represents the total potential energy of the electronic and lattice vibration subsystems. First, we consider the effect of each individual subsystem. Within the electronic subsystem, the minima of ground state and excited state are vertically displaced by the trap thermal energy ($E_T$). Regarding the lattice vibration subsystem, under the adiabatic approximation, [9, 10] both ground state and excited state bands are parabolic, each consisting of multiple phonon states that are equally spaced by the phonon energy of that band (labeled as $v$, $v' = 0, 1, 2 \ldots$ etc.). Assuming the phonon energies for ground state and excited state are identical, the spacing among their individual phonon states will be the same, resulting in identical bands for ground state and excited state. Next, considering the interaction between these two subsystems, a typical and important assumption is that electrons and phonons linearly interact with each other. As a result, in the CC diagram, the minima of both bands are horizontally displaced. It can be seen from Fig. 3.14 that this displacement can translate into phonon quantity within the parabolic band, and be quantified by Franck-Condon energy ($D$). Besides the energy bands, another important feature of the CC diagram is that the pathways for optical transition and thermal transition are different: during optical transition, photon emission or absorption occurs instantly and vertically, while thermal transition is a comparatively slower process and can occur laterally through phonon emission and absorption, depending on the change in phonon state before and after transition.

We first consider the absorption process shown in Fig. 3.15, when electrons transit from ground state to excited state. The probability of such a transition is indeed governed by the initial state distribution, as the final states are spatially uniform because conduction
band states are all empty. Since the distribution of initial states (ν=0 on ground state) peaks at $Q_{II}$, the majority of the transition occurs at $Q_{II}$ (illustrated by the thick arrow), corresponding to an optical ionization energy of $E_O$. As can be seen, $E_O = E_T + D$. At the same time, this transition also causes a phonon state change from $ν = 0$ to $ν’ = 2$ ($D = 2\hbar \omega_p$, where $\omega_p$ is phonon energy). Thus, after the photon is absorbed, two phonons will be “slowly” released through the lattice relaxation effect, and the electron relaxes to the bottom of the excited state band at $Q_C$. However, it should be noted that this only describes the most probable transition. In fact, the transition between $ν = 0$ and $ν’ = 0$ states may also occur (illustrated by the thin arrow), but with a much smaller probability due to their small lateral overlap. In other words, once the photon energy is larger than $E_T$, it is possible that the electrons in the ground state are excited. With all of this explained, we can now differentiate the results obtained from different techniques and analyses. Clearly, DLOS optical cross section analysis models the optical ionization energy $E_O$ with $D$, while the threshold energy $E_T$ will likely manifest in SSPC and absorption as a spectrum onset. However, since the transition without phonon ($ν = 0$ and $ν’ = 0$) may have a very low rate, the observable onset in SSPC and other absorption spectra can be indeed larger than $E_T$. 


Next, we consider the process shown in Fig. 3.16, in which electrons relax from excited state to ground state and emit a photon. Similarly, as the distribution of initial states ($v' = 0$ on excited state) peaks at $Q_C$, the major transition (illustrated by the thick arrow) emits photons at an energy of $E_T - D$. This transition also causes a phonon state change from $v' = 0$ to $v = 2$, thus, after the photon is emitted, two phonons are “slowly” released through the lattice relaxation effect, and the electron finally relaxes to the bottom of the ground state band at $Q_{tl}$. Here, the transition between $v = 0$ and $v' = 0$ states that emit $E_T$ photons may still occur (illustrated by the thin arrow), but at a much lower rate. These photon emission processes can be monitored by Photoluminescence (PL), another widely used deep level characterization tool. In PL spectrum, emission peak energy corresponds to $E_T - D$, the full-width-half-maximum (FWHM) of the peak equals $D$, and the high

Figure 3.16 Photon emission process of defect states in CC diagram.
energy bound of the peak feature is close to $E_T$, which is often referred to as zero-phonon-line (ZPL).

Finally, unlike all the optical characterizations described above, the lattice relaxation effect does not manifest in thermally stimulated DLTS measurements. [8] Therefore, DLTS detects either $E_T$ or $E'_T$, depending on the material conductivity type and sample structures. As will be seen in the next chapter, such information is essential for resolving complex optical characterization results.
3.8 Summary

Figure 3.17 Illustration of how different characterization techniques should be used for probing deep states at different region of the bandgap. A carrier capture cross section of $1 \times 10^{-16}$ cm$^2$ is assumed for all states.

Both thermal and optical emission processes can be used to investigate electrically active defect states. Several capacitance-based characterizations are described, and each of them is suitable for detecting bandgap states in a certain energy range. As summarized in Fig. 3.17, $C-f$ and $C-T$ can be used to study states that have high concentration but are relatively shallow in the bandgap; DLTS monitors the capacitance transient during temperature scan, enabling quantifications of deep level states within $0.1 \sim 1.0$ eV from the conduction band edge; and DLOS detects the optical emission from the deep states as a
function of incident light energy to characterize traps in the rest of the bandgap. The combination of these three techniques provides a full coverage of the deep states throughout the bandgap of novel III-Nitride semiconductors.
3.9 Reference


Chapter 4

Impact of Crystal Orientation on Deep Level States in NH$_3$MBE grown GaN

4.1 Introduction

III-Nitride multi-quantum-well structures grown along non-polar orientations, i.e., m-plane [1-100] and a-plane [11-20], have been attracting extensive interests during the last decade. [1-4] This is mainly due to their unique properties that favor optoelectronic applications such as LEDs and LDs. In emitters employing these non-polar structures, the Quantum Confine Stark Effect (QCSE) is greatly suppressed, resulting in substantially improved internal quantum efficiency, as compared with that of conventional structures grown along c-plane polar directions. [1] However, due to the novelty of these materials, their epitaxial growth is far from being fully optimized as is the case for the well-developed c-plane materials. Particularly, the high density of crystal defect (both extended and point defects) remains as a huge challenge for the further application of these materials. Recently, the emerging bulk non-polar GaN substrates enable substantial reduction of extended defect density in device structures. However, regarding the point defects, knowledge of their formation and mitigation has yet been established and even sparsely reported. Hence, in this chapter, we start with a quantitative characterization and systematic comparison of
m-plane vs. c-plane GaN to assess the influence of crystal orientation on deep traps formation. Part of this work has been published in *Appl. Phys. Lett.* 100, 052114 (2012).

### 4.2 Experimental Details

In order to isolate the impact of growth orientation on defect formation, both m-plane GaN substrate and c-plane GaN template, with TD density of \(~5\times10^6\) cm\(^2\) and \(~\text{mid} 10^8\) cm\(^2\) respectively, were co-loaded for simultaneous growth. During the NH\(_3\)-MBE growth, conditions optimized for achieving high quality high mobility c-plane n-type GaN was used [5]: the substrate temperature was kept at 780 °C, the chamber pressure was at 1×10\(^{-4}\) Torr, Ga beam equivalent pressure was at 2×10\(^{-7}\) Torr and ammonia flux was at 200 sccm (yielding V/III ratio of 1000). The final growth structure (shown in Fig. 4.1) consisted of a 300 nm-thick GaN:Si (3×10\(^{18}\) cm\(^{-3}\)) highly doped layer, topped by a 500 nm-thick GaN:Si (1×10\(^{17}\) cm\(^{-3}\)) low doped layer. All samples were then fabricated into 300×300 \(\mu\)m\(^2\).
Schottky diodes, using electron-beam evaporation to deposit 8 nm-thick semitransparent Ni gate electrode on top and 500 nm-thick Ti/Al/Ni/Au Ohmic contacts on the n⁺-GaN layer exposed through reactive-ion-etching.

Capacitance-based DLTS was performed between 77 K and 400 K to explore deep levels within about 1 eV below the conduction band edge, while DLOS probed the remainder of the GaN band gap using a Xe-lamp filtered through a 0.25 m monochromator to provide monochromatic optical excitation from 1.2 eV to 3.6 eV at a step of 0.02 eV. A quiescent bias of -0.5 V and a filling bias of 0 V were used for both DLTS and DLOS measurements, while the filling pulse durations were 10 ms and 10 s for DLTS and DLOS, respectively. The details of DLOS/DLTS measurements can be found in the prior chapter. In addition, room temperature PL measurements were performed on unprocessed as-grown samples, using a separate Xe-lamp coupled with a monochromator to provide an excitation wavelength of 300 nm at a power level of 3.7 µW.
4.3 Correlating Impurity Incorporation and Background Doping

![SIMS concentration profiles of silicon, oxygen and carbon in both m-plane and c-plane GaN. The square markers indicate the measured effective doping concentration from C-V analysis.](image)

Before characterizing deep level states, secondary ion mass spectrometry (SIMS) measurements were first performed on unprocessed pieces to monitor the impurity incorporation in each sample. As summarized in Fig. 4.2, while the intentional Si dopant concentrations are similar in both samples at $1 \times 10^{17}$ cm$^{-3}$, the m-plane sample does exhibit $\sim 50\times$ and $\sim 10\times$ higher concentrations for oxygen and carbon, as compared with the c-plane sample: in m-plane GaN, both oxygen and carbon density are at mid-low $10^{16}$ cm$^{-3}$ (note that the detection limit of SIMS is $\sim$ low $10^{16}$ cm$^{-3}$), whereas in m-plane sample,
oxygen has a concentration of $\sim 1 \times 10^{18}$ cm$^{-3}$ and carbon has a concentration of $\sim 3 \times 10^{17}$ cm$^{-3}$ (note that the low concentration depth dependence for the c-plane data is attributable to sputtering artifacts). [6] These large oxygen and carbon concentration differences between the m-plane and c-plane material cannot be explained by differences in sputter rates, which were determined to be similar for both samples. [6] In fact, as these two samples were grown simultaneously on the same sample block, these differences strongly suggest very different impurity incorporation mechanisms and/or rates for the two different growth surfaces.

Room temperature 1 MHz $C-V$ measurements were then performed on the processed Schottky diodes, with the obtained n-type net doping profile plotted in Fig. 4.2 as well. By comparing the SIMS results and doping profiles, it is clearly seen that: in the m-plane GaN, $n_s$ closely follows the oxygen concentration, and is well above the intentional Si doping concentration; while in the c-plane sample where oxygen content is much lower, $n_s$ is dictated by the Si doping. This is in fact consistent with theoretical calculation that predicts substitutional $\text{O}_N$ to be a shallow donor that directly contributes to the background doping. [7] On the other hand, with respect to carbon, though it is known to predominantly form $\text{C}_N$ acceptor-like states in n-type GaN, [8] due to its relatively smaller concentration as compared with oxygen, its compensation effect is probably obscured by the excess oxygen donor in the m-plane sample. Unfortunately, $\text{O}_N$ donor state cannot be further characterized by $C-f$ or $C-T$ methods, as it has been associated with a small activation energy around 30 meV, [9] thus far out of the “characterization window” of $C-f$ and $C-T$ techniques.
Figure 4.3 (a) DLTS spectra of m-plane and c-plane GaN for the 80 s\(^{-1}\) rate window revealing much higher trap concentration for the m-plane GaN material. (b) Arrhenius plots for the different deep levels corresponding to the peaks from each rate windows.
Table 4.1 Concentrations for deep level states in c-plane and m-plane GaN detected by DLTS and DLOS. Trap concentration in cm$^{-3}$.

<table>
<thead>
<tr>
<th>$E_c$ (eV)</th>
<th>0.14</th>
<th>0.20</th>
<th>0.25</th>
<th>0.40</th>
<th>0.63</th>
<th>0.66</th>
<th>1.30</th>
<th>2.50</th>
<th>3.27</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-plane</td>
<td>-</td>
<td>-</td>
<td>4.7×10$^{12}$</td>
<td>2.8×10$^{12}$</td>
<td>2.0×10$^{13}$</td>
<td>6.4×10$^{13}$</td>
<td>1.0×10$^{14}$</td>
<td>1.1×10$^{15}$</td>
<td>1.5×10$^{15}$</td>
</tr>
<tr>
<td>m-plane</td>
<td>4.2×10$^{14}$</td>
<td>5.7×10$^{14}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.2×10$^{14}$</td>
<td>9.0×10$^{14}$</td>
<td>2.6×10$^{16}$</td>
<td>2.8×10$^{16}$</td>
</tr>
</tbody>
</table>

In this section, we focus on the quantitative characterization of deep level states throughout the whole GaN bandgap, which is achieved by the combination of DLTS and DLOS. First, the presence of deep level defects within ~1.0 eV from the GaN conduction band edge was explored by DLTS. The spectra for both m-plane and c-plane samples are shown in Fig. 4.3 (a) and the associated Arrhenius analysis results are presented in Fig. 4.3 (b). As seen, in the baseline c-plane sample, four electron traps at $E_c$ - 0.25 eV, $E_c$ - 0.40 eV, $E_c$ - 0.63 eV and $E_c$ - 0.66 eV are detected, all with relatively low trap concentrations of 10$^{12}$ cm$^{-3}$ ~ mid-10$^{13}$ cm$^{-3}$ (detailed trap concentration values are listed in Table 4.1, with Lambda effect considered), [10] consistent with prior deep level studies of NH$_3$MBE-grown n-type GaN samples. [11] However, the m-plane GaN sample reveals a DLTS spectrum that is substantially different from the one obtained in c-plane GaN: not have only the defect concentrations been greatly increased for the m-plane sample (the total concentration is now in the ~ mid-high 10$^{14}$ cm$^{-3}$ range accounting for the Lambda effect), but also the defects observed in m-plane GaN are indeed different from the ones probed in c-plane GaN. For example, the traps at $E_c$ - 0.14 eV and $E_c$ - 0.20 eV in m-plane GaN are not evident in the c-plane material. In addition, regarding the $E_c$ - 0.66 eV electron trap detected in m-plane GaN, though its activation energy matches the $E_c$ - 0.66 eV trap in c-
plane GaN, it actually possesses a much larger capture cross section value \(8.9 \times 10^{-13} \text{ cm}^2\) vs. \(1.1 \times 10^{-15} \text{ cm}^2\), which is responsible for the large relative shift in the Arrhenius plot and DLTS spectra. The very different capture cross section may be suggestive of an entirely different physical source or a different physical defect configuration for the same defect. [12, 13] Also worth noting is that the high background doping for the m-plane sample might obscure other low concentration traps, such as the \(E_C - 0.25 \text{ eV}\) and \(E_C - 0.40 \text{ eV}\) states. More details regarding the potential physical sources and defect configurations of each specific trap in m-plane GaN will be discussed in the next chapter when comparing the trap formations at different growth conditions.

Figure 4.4 Steady state photo-capacitance spectra of m-plane and c-plane GaN. Inset shows the optical cross section spectra for m-plane and c-plane GaN. Solid lines are fits to the Lucovsky model, whereas dashed line is a fit to the Passler model.
Next, DLOS measurements were employed to facilitate investigation of traps deeper in the bandgap. The steady state photocapacitance (SSPC) spectra are shown in Fig. 4.4, with the optical cross section spectra present in the inset. Two major electron traps with positive SSPC onsets near $E_C - 2.50$ eV and $E_C - 3.27/3.30$ eV are observed in both samples. Precise energy positions and lattice relaxation effects for these traps are calculated by fitting to the Lucovsky and the Passler models as shown in the inset. [14, 15] It is found that while the close to valance band state at $E_C - 3.27/3.30$ eV exhibits negligible Franck-Condon energy, the other deeper trap at $E_C - 2.50$ eV is associated with a sizable $D_{FC}$ of $\sim 0.35$ eV ($E_O = E_T + D = \sim 2.85$ eV). More details of this $E_C - 2.50$ eV trap and its manifestations in optical transitions will be discussed later in this chapter. Besides these two traps, there is also evidence of positive onsets near $E_C - 1.30$ eV in SSPC spectra in both samples. However, as those emissions are typically very slow (more than 300 s), finding proper rate windows to perform accurate optical cross section analysis is difficult, thus we adopt their SSPC onset energies as the trap energy levels. Overall, unlike DLTS, similar traps are observed in both m-plane and c-plane GaN in this energy range probed by DLOS.

With the trap energies being determined, we can now compare their concentrations to reveal the impact of growth orientation. As can be clearly seen in Fig. 4.4, changing the growth orientation from c-plane to m-plane induces drastic increase in concentration of major DLOS-detected traps. In Table 4.1, the concentration increases are at least one order of magnitude for all three traps. In fact, the $E_C - 3.27/3.30$ eV and $E_C - 1.30$ eV states have been previously attributed to acceptor-like C$_N$ substitutional defect and interstitial C$_I$ state, respectively, thus their increases in concentration are consistent with the carbon impurity
increase as detected by SIMS. With regarding the $E_C - 2.50$ eV trap, its energy level matches the widely reported $V_{Ga}$-related states that appear between $E_C - 2.4 \sim 2.7$ eV, [16-18] however, we notice that traps at similar energy range have also been previously associated with carbon in semi-insulating GaN. [8] Unfortunately, with the current information, nothing conclusive can yet be claimed on the origin of this trap. After all, these DLTS/DLOS studies have revealed that growth orientation directly impacts defects associated with incorporated carbon impurity, and it is also possible that the formation of native crystal defects (if $E_C - 2.50$ eV trap is $V_{Ga}$ related) are affected by the growth orientation as well.

4.5 Photoluminescence

Figure 4.5 (a) Room temperature PL spectra for unprocessed m-plane and c-plane GaN samples, plotted in logarithmic scale. (b) PL spectra of unprocessed m-plane GaN, plotted in linear scale.
Next, room temperature PL measurements were performed on the unprocessed samples to further investigate these bandgap states and their behaviors in a photon emission process (DLOS is essentially a photon absorption process). Figure 4.5 (a) shows the PL spectra for these two samples, both are normalized to the 3.4 eV near band emission (NBE) peaks, respectively. As seen, besides NBE, these two spectra share a strong emission peak centered ~ 2.2 eV, with the m-plane sample showing much higher emission intensity than the c-plane GaN. In fact, this feature, often referred to as yellow luminescence (YL), has been widely observed in n-type GaN and extensively studied both theoretically and experimentally. [18, 19] It is generally accepted that this emission process is associated with the $E_C - 2.50$ eV trap in GaN. [19] Therefore, the much enhanced YL in m-plane sample is indeed consistent with the DLOS results that $E_C - 2.50$ eV trap forms with a much higher concentration in m-plane GaN as compared with c-plane sample. In addition, we noted that the full width at half maximum (FWHM) of this YL peak is ~ 0.4 eV, as can be seen in Fig. 4.5 (b) where PL spectrum for m-plane sample is plotted in linear scale. Such broadness is suggestive of strong electron-phonon coupling effect for this defect, again consistent with the result of DLOS capture cross section analysis.

4.6 A Detailed Investigation of $E_C - 2.50$ eV Trap

Now we investigate this $E_C - 2.50$ eV trap in m-plane GaN in a greater detail. This trap not only has a relatively high concentration, and also has been actively involved in different kinds of optical processes, thus could substantially affect the material optical properties and the performance of optoelectronic devices. Here, confirming the defect
energy position is the most imperative, and especially necessary in this case, since the
DLOS spectra have only been fitted to a rather simplified model. To this end, a specially
devised minority carrier injection DLTS measurement was performed to independently
characterize the energy position for this trap.

![Figure 4.6 Structure for m-plane GaN pn-junction diode.](image)

As mentioned in the prior chapter, DLTS characterizes the thermal process and is
not affected by $D_{FC}$, and thus may enable an accurate determination of defect energy
position. [7] However, in a Schottky structure, DLTS can only measure carrier emissions
from deep states within $\sim 1 \text{ eV}$ from the majority carrier band (conduction band in this case)
and is insensitive to this $\sim E_C - 2.50 \text{ eV}$ trap. Therefore, a separate pn-junction diode is
employed, as it may offer opportunity to probe this defect as a minority carrier trap $\sim 1 \text{eV}$
away from the valence band edge. [20] Figure 4.6 shows the structure of the m-plane pn-
diode. As seen, the doping density of the top p-type layer is so high that even considering
the $1 \times 10^{18} \text{ cm}^{-3}$ n-type background doping, majority of the depletion region would still be
in the n-type region, thus DLTS would be mostly sensitive to defects in n-type material. The growth conditions for the n-GaN region were identical to the ones used in Schottky structure growth, therefore similar defect distributions would be expected. Unlike regular DLTS that is performed with a 0 V filling bias, a forward filling bias at 1.5 V was employed in this study so that the defects was able to capture the holes that injected from p-type region at forward bias condition.

Figure 4.7 (a) DLTS spectra of m-plane GaN pn-diode performed with a filling bias of 1.5 V. (b) Arrhenius plot for the major minority carrier trap observed in DLTS.

The results of the minority carrier injection DLTS are presented in Fig. 4.7. As seen, instead of positive peak features that are usually observed in DLTS performed on Schottky diodes, a strong negative peak dominates the whole spectrum. This is suggestive of the detection of a minority carrier trap, whose concentration is much higher than the majority carrier traps emit in the same temperature range. Arrhenius analysis unambiguously reveals that the activation energy for the minority carrier trap is $E_V + 0.90 \text{ eV}$ (that is $E_C - 2.50 \text{ eV}$),
exactly matching the SSPC onset and DLOS fitting results. Furthermore, the dominance of this trap over the other majority carrier traps is also consistent with the DLTS and DLOS results obtained from Schottky diode as listed in Table 4.1: this $E_v + 0.90 \text{ eV} \,(E_C - 2.50 \text{ eV})$ trap has a much higher concentration than the $E_C - 0.67 \text{ eV}$ trap that would appear in the same temperature range, thus only negative DLTS signals were observed here.

Figure 4.8 CC diagram of $E_C - 2.50 \text{ eV}$ trap in GaN and the correspondences of the results obtained by different characterization techniques.

With the exact defect energy level confirmed, the correspondence of the defect manifestations in different processes can now be understood in the CC diagram, as shown in Fig. 4.8. First, the minority carrier injection DLTS measured the defect energy position with respect to the valence band edge, i.e., $E'_{T,\text{DLTS}} = 0.90 \text{ eV}$. Second, SSPC onset is very close
to (or a bit larger than) the defect energy position with respect to the conduction band edge, i.e., $E_T \sim 2.50$ eV. Third, due to the lattice relaxation effect, the optical ionization energy $E_O$, which represents the most probable transition from ground state to excited state and is obtained through optical capture cross section analysis, is greater than $E_T$ by the amount of Franck-condon energy, i.e., $D \sim 0.35$ eV. Fourth, during the emission process, the PL spectrum peaks at 2.20 eV, corresponding to the dominating transition occurring at $Q_{CV}$, whose energy equals $E_T - D$. Finally, the FWHM of the PL peak is also a result of electron-phonon coupling, and the measured FWHM of 0.4 eV agrees reasonably well with $D \sim 0.35$ eV.

### 4.7 Summary

In this study, strong relationships between both intrinsic and extrinsic defect formation and crystal growth orientations for NH$_3$-MBE grown GaN were experimentally revealed. Taking the entirety of the deep level data together suggests that the growth dynamics at the m-plane growth surface may play a role in incorporating carbon and oxygen impurities, and probably sourcing $V_{Ga}$ defects as well. The comprehensive investigation of the $E_C$ - 2.50 eV trap using DLTS, DLOS and PL reveals that a strong lattice relaxation effect is associated with this defect. Finally, the fact that this $E_C$ - 2.50 eV trap is actively involved in different optical processes implies the importance of reducing concentrations of these deep levels for further optimizing device performance.
4.8 References


Chapter 5

Impact of V/III ratio on Deep Level States
in NH₃MBE Grown m-plane GaN

5.1 Introduction

The prior chapter has clearly demonstrated that the growth surface orientation does directly impact the impurity incorporation and deep level formation during NH₃MBE growth of GaN. Building from that study, we now investigate how the growth conditions may further affect the formation of those states in m-plane GaN. Although such influences have been extensively studied for deep defects in c-plane GaN, it is still an interesting and less explored topic for non-polar materials, especially as now “new” traps are involved, and even for the same defects, their dependences on growth parameters are likely to differ from the c-plane case due to the impact from the growth surface as well as corresponding formation mechanisms. Moreover, such information is important for technology developments as it may shed light on growth optimizations that allow for improved material quality and enhanced device performance. In this chapter, we describe the results of a systematic investigation of deep state distributions in NH₃MBE-grown m-plane GaN as a function of carefully controlled V/III flux ratio. Similar to the prior study, DLTS and
DLOS facilitate the quantitative characterization of deep states throughout the bandgap, and the measurement results are further correlated with SIMS and PL analysis to explore potential physical sources and optical properties of specific traps. Part of this work has been published in *Appl. Phys. Lett.* 101, 152104 (2012).

### 5.2 Experimental details

Figure 5.1 M-plane n-type Schottky diodes grown with different V/III ratios.

Figure 5.1 presents the structures of n-type m-plane GaN samples studied here. Totally three samples were grown on free standing m-plane (1-100) GaN substrates as used in the prior study. All three samples were grown under identical N-rich NH₃MBE growth conditions, except that the ammonia flux values were systematically adjusted from 80 sccm to 200 sccm and 500 sccm, yielding three different nominal V/III flux ratios of 400, 1000, and 2500, respectively. In order to support capacitance-based characterizations, the
samples were processed into n-type Schottky diodes, following earlier procedures. The measurement details are also identical to the prior study.

5.3 Correlation between Impurity and Background Doping

Figure 5.2 Impurity concentrations detected by SIMS in m-plane GaN samples grown under different V/III ratios plotted along with the net n-type doping concentration measured by C-V analysis (square symbols).

First, the impact of V/III ratio on impurity incorporations was evaluated. Figure 5.2 summarizes the concentrations for common impurities, i.e., silicon, carbon and oxygen, in each sample, which were detected by SIMS and averaged over the layer thickness. As seen,
in stark contrast to silicon and carbon, whose concentrations do not show any clear trend, the oxygen concentration displays a strong monotonic decrease from $\sim 2.1 \times 10^{18} \text{ cm}^{-3}$ to $\sim 3.5 \times 10^{17} \text{ cm}^{-3}$ as the V/III ratio is increased from 400 to 2500. At the same time, room temperature 1 MHz $C-V$ measurements reveal that the oxygen again dictates the background n-type doping in all these growth conditions, as the net n-type doping profile matches closely to the SIMS-detected oxygen profile, and both are well above the $1 \times 10^{17} \text{ cm}^{-3}$ intentional silicon doping level. This, together with the previous comparison between c-/m-plane GaN, is consistent with theoretical and prior experimental reports, confirming that the incorporated oxygen predominantly forms substitutional shallow donor $\text{O}_N$ in these NH$_3$MBE grown m-plane GaN, and is responsible for the high concentration of background n-type doping. [1-2]
Figure 5.3 DLTS spectra of the 80 s⁻¹ rate window for m-plane GaN samples grown with V/III ratios of 400, 1000 and 2500. The DLTS peak around 120 K in the highest V/III ratio sample is fit by two electron traps.
Figure 5.4 Arrhenius analysis for deep levels observed in all three m-plane GaN samples.

Table 5.1 Summary of SIMS result and deep level concentrations in m-plane GaN grown with different V/III ratios. All impurity and trap concentrations are given in cm$^{-3}$.

<table>
<thead>
<tr>
<th>V/III ratio</th>
<th>Impurity</th>
<th>Deep level energy position</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[O]</td>
<td>[C]</td>
</tr>
<tr>
<td>400</td>
<td>2.1×10^{18}</td>
<td>1.4×10^{16}</td>
</tr>
<tr>
<td>1000</td>
<td>1.0×10^{18}</td>
<td>2.1×10^{16}</td>
</tr>
<tr>
<td>2500</td>
<td>3.5×10^{17}</td>
<td>8.0×10^{13}</td>
</tr>
</tbody>
</table>

The DLTS trap spectra for each sample at the 80 s$^{-1}$ rate window and full Arrhenius plots based on a wide range of rate windows for each trap are shown in Fig. 5.3 and Fig. 5.4. The activation energies and concentrations for these traps in each sample are listed.
with DLOS and relevant SIMS results in Table 5.1. In Fig. 5.3, the similarities, differences and trends among the DLTS spectra are immediately apparent. First, each V/III ratio sample reveals the presence of the same electron traps at $E_c - 0.21$ eV, $0.67$ eV and possibly at $E_c - 0.14$ eV (clearly evident for the lower two V/III ratios and slightly perceptible for the highest V/III ratio), all unique to NH$_3$MBE grown m-plane GaN. Second, the relative dominances among these trap features are clearly different for each flux ratio. For instance, the $E_c - 0.67$ eV level is the dominant trap at a V/III ratio of 400, whereas at the largest V/III ratio of 2500, it becomes much less significant while the shallow $E_c - 0.26$ eV state is now dominant, and for the intermediate V/III ratio of 1000, all three DLTS traps seem to exhibit similar concentrations.

![Figure 5.5 Concentrations of the traps present at $E_C - 0.14$ eV, $E_C - 0.21$ eV and $E_C - 0.67$ eV as a function of oxygen impurity concentration measured by SIMS.](image)

Figure 5.5 Concentrations of the traps present at $E_C - 0.14$ eV, $E_C - 0.21$ eV and $E_C - 0.67$ eV as a function of oxygen impurity concentration measured by SIMS.
The third key finding from the DLTS spectra is that the individual dependence of the concentration on V/III ratio (and therefore oxygen content) is different for each trap. As further summarized in Fig. 5.5, the concentrations of $E_c - 0.14$ eV and $0.67$ eV traps not only vary monotonically with V/III ratio, and also exhibit almost linearly relations with the oxygen content. This suggests a strong linkage of growth conditions and/or oxygen incorporation with respect to the physical sources for these two trap levels. However, whether these two traps are indeed oxygen-related still requires further experimental confirmation. In stark contrast, the concentration of $E_c - 0.21$ eV trap remains almost constant in these samples, suggesting it is likely due to a unique physical source different from the former two traps.

Apart from the three traps mentioned above, there are two other traps with activation energies of $E_c - 0.26$ eV and $0.62$ eV that are also present in the DLTS spectra. Unfortunately, since they were observed only one sample (i.e., in the highest V/III ratio sample), meaningful evaluation of how they may change as a function of V/III ratio, or identification of possible physical sources, are only speculative.
Figure 5.6 Room temperature steady state photocapacitance spectra of m-plane GaN grown with different V/III ratios.

Figure 5.7 DLOS detected trap concentrations for $E_C - 2.50$ eV and $E_C - 3.28$ eV state and SIMS measured carbon density as a function of V-III ratio.
Next, room temperature DLOS were performed on all three samples, and SSPC results are now shown in Fig. 5.6, with detected defect concentrations listed in Table 5.1. Unlike the traps in the upper region of the GaN bandgap detected by DLTS, there is no evidence of new types of defect states being introduced due to the growth variations in the DLOS measurements, nor is there any clear dependence of deep trap concentrations on V/III ratio or oxygen content. The slightly higher defect densities for traps observed in the intermediate V/III ratio 1000 sample are more likely due to minor run-run growth variations. Even so, the dependence of $E_C - 3.28$ eV trap concentration as a function of V/III ratio closely follows the carbon density measured by SIMS, as shown in Fig. 5.7. This not only is consistent with the assertion of the C$_N$ related nature of this trap, [3] and also demonstrates the sensitivity of DLOS as a quantitative characterization technique. The other major trap at $E_C - 2.50$ eV has been commonly observed in GaN and attributed to either gallium vacancies ($V_{Ga}$) or carbon-related defects. [1, 4-6] Regarding the $V_{Ga}$ attribution, there have been reports claiming that $V_{Ga}$-O$_N$ defect complex possesses a similar activation energy and is energetically more favorable in m-plane GaN, [7, 8] however the fact that there is no obvious dependence of the $E_C - 2.50$ eV level on oxygen content in this sample likely excludes such a possibility ($V_{Ga}$-O$_N$ complex). Regarding the carbon attribution, it indeed seems possible as in these samples the concentration of $E_C - 2.50$ eV level does generally follow the carbon density as seen in Fig. 5.7. However, we note that “carbon-related” $E_C - 2.50$ eV trap has only been observed in carbon-doped semi-insulating GaN samples, [5] and whether this trap present in these $\sim$10$^{18}$ cm$^{-3}$ unintentionally doped n-type GaN is associated with the same origin needs further investigation and confirmation.
5.5 Photoluminescence

![Figure 5.8 Room temperature PL for unprocessed m-plane and c-plane GaN samples.](image)

**Figure 5.8** Room temperature PL for unprocessed m-plane and c-plane GaN samples.

![Figure 5.9 DLOS detected trap concentration for $E_C - 2.50$ eV state and SIMS measured carbon density as a function of V-III ratio.](image)

**Figure 5.9** DLOS detected trap concentration for $E_C - 2.50$ eV state and SIMS measured carbon density as a function of V-III ratio.
Room temperature PL spectra of these three samples are shown in Fig. 5.8. For all three cases, the YL peak is prominent, though there may also be evidence of eA transition at \( \sim 3.25 \) eV, [9] possibly correlated with \( E_C - 3.28 \) eV trap. However, similar to DLOS, no obvious dependence can be observed for YL either. With that been said, it is still interesting to note that the YL peak intensity correlates very well with the DLOS detected trap concentration for \( E_C - 2.50 \) eV trap (see Fig. 5.9), again suggesting that DLOS and PL measure different optical processes involving the same trap, and both are very sensitive to small changes, even if they are likely due to run-to-run variations.

5.6 Summary

In summary, the impact of V/III growth flux ratio on deep state incorporation in NH\(_3\)-based MBE grown m-plane GaN was systematically studied by DLTS and DLOS. Overall, there is a non-uniform effect on the trends for individual traps as a function of varying V/III ratio. This is suggestive of different sources for each state. The trap concentrations of \( E_C - 0.14 \) eV and \( 0.67 \) eV states exhibited drastic decreases with increasing V/III ratio and may correlate with a systematic reduction in background oxygen impurity concentration measured via SIMS, suggestive that their physical sources include an oxygen-related defect. DLOS revealed that very deep states in mid-bandgap and near valance band regime do not display a strong dependence on V/III ratio. Interestingly, overall, the total sum of traps integrated across the bandgap is relatively unchanged, it is just the distribution of those traps across the bandgap (i.e. changing of the dominant electrically active defects) that is substantially altered with growth conditions for the m-
plane material. Current work is focused on enabling the identification of these sources since depending on where the dominant levels lie in the bandgap, the behavior of subsequent devices can vary greatly in terms of recombination-generation currents, carrier scattering and lifetimes.
5.7 Reference


Chapter 6

Comparison of Deep Level States in p-GaN
grown by NH₃MBE and MOCVD

6.1 Introduction

While the previous two chapters investigate the deep levels in the novel m-plane III-Nitride materials, this chapter studies the distribution of bandgap states in state-of-the-art, widely used Mg-doped p-type GaN, and particularly focuses on the impact of growth technique on the deep state formation. In fact, though p-type GaN and alloys are essential component layers in nearly all GaN-based optoelectronic devices (e.g., light emitting diodes, laser diodes) as well as several electronic devices (e.g., vertical pn-diodes, gate injection transistors and hetero-junction bipolar transistors etc.), [1-6] the electrically active defects in p-GaN have been sparsely studied in general. [7-11] On the other hand, NH₃MBE is an emerging growth technology that has already shown great promise as compared with conventional MOCVD in p-GaN growth, e.g., as-grown p-type conductivity and less contamination at a comparable growth rate, [2, 12, 13] however, a comparison of the bandgap states formed in these two materials, which would be beneficial for further differentiating these two growth techniques and their applications, is still
lacking. To this end, we here report a comprehensive and comparative study of the bandgap states in NH$_3$MBE and MOCVD grown p-GaN. Such information is especially important for the relatively less matured NH$_3$MBE growth, as it may serve as a baseline and provide guidance for future growth optimizations and technology advances.

6.2 Sample Structure and Experimental Details

![Diagrams of test structures for capacitance-based characterizations of p-type GaN](image)

Figure 6.1 Test structures for performing capacitance-based characterizations of p-type GaN (a) conventional p-/p+ Schottky diode; (b) Schottky diode formed on p+ layer; (c) p+/p-/n+ diode; (d) a comparison of C-f dispersion measured in structure (a) and (c).
One major challenge for performing capacitance-based DLTS and DLOS measurements of p-type GaN is the ability to achieve both high signal sensitivity and low series resistance using conventional p-GaN Schottky diodes. [8, 14] As shown in Fig. 6.1 (a), in a conventional p’/p+ Schottky diode structure, p-type Ohmic contacts need to be formed on the etched surface, which, however, has experimentally proven difficult. [15] Even if a “quasi-Ohmic” contact can be obtained, it may lead to large series resistance that requires all capacitance-based characterizations to be performed at low frequencies with more noise and lower sensitivity. [8] One alternative approach is depositing both Schottky and Ohmic contacts on the un-etched surface, as illustrated in Fig. 6.1 (b). However, the high doping density ideal for the Ohmic contact formation not only renders low characterization sensitivity but also leads to poor Schottky contact quality.

In this study, a p’/p/n+ test structure as shown in Fig. 6.1 (c) was specially devised. The p- and n-type Ohmic contacts are both deposited on highly doped layers, ensuring a low series resistance to mitigate the capacitance-frequency dispersion. A direct comparison of the C-f characteristics for structure (a) and (c) is presented in Fig. 6 (d). While the Schottky diode only responds to the capacitance sampling frequencies near 1 KHz, the p’/p/n+ diode is responsive to a wide range of frequencies, enabling the high frequency (1 MHz) capacitance measurements that are facilitated with high accuracy low noise characterization instruments. In addition, since the doping concentration in the p’-layer is approximately a factor of 100 lower than that of the n’-layer, the depletion region resides almost completely in the p’-GaN layer, therefore, the capacitance-based DLOS and DLTS measurements will be predominantly sensitive to traps in the light doped p’GaN layer, achieving a significantly enhanced measurement sensitivity, e.g., \(10^5 \times N_A \sim 10^{13} \text{ cm}^{-3}\). [16]
NH₃MBE and MOCVD grown samples studied here contain similar p+/p−/n+ structures for probing traps in the p−-GaN layer as shown in Fig. 6.2. Both structures were grown on GaN on sapphire templates with threading dislocation density of mid 10⁸ cm⁻², at standard conditions for each growth technique. The NH₃MBE growth of the p−-GaN (nominal Mg doping ~ 1×10¹⁸ cm⁻³) layer was performed at 780 °C with a Ga beam equivalent pressure (BEP) of 5×10⁸ Torr and NH₃ flow rate of 200 sccm. [2] During the MOCVD growth, the p−-GaN (nominal Mg doping ~ 1×10¹⁸ cm⁻³) epitaxy was performed at 1050 °C with TMGa flow rate of 12.6 umol/min and NH₃ flow rate of 3200 sccm. Due to the well-known H passivation effect for MOCVD grown p-GaN, an additional 15 minutes Mg activation annealing at 600 °C in ambient (N₂/O₂) was performed for the MOCVD grown sample. In contrast, the NH₃MBE grown GaN:Mg shows p-type conductivity as-grown, thus no activation annealing was performed.
The as-grown NH₃MBE and the annealed MOCVD samples were fabricated into 300×300 μm² square mesas using a chlorine-based reactive ion etching (RIE) process. Subsequently, Ohmic contacts were formed by electron beam evaporation. The n⁺-GaN Ohmic contact consisted of a 500 nm thick Ti/Al/Ni/Au stack, and the p⁺-GaN Ohmic contact was a 10 nm thick semitransparent Pd/Au structure to allow optical measurements.

At temperatures beyond 200 K, the C-f dispersions were small in both samples, thus 1 MHz capacitance-based DLTS and DLOS were applied for characterizing deep state distributions associated with different types of growth. DLOS and DLTS were measured at identical depletion depth of ~ 90 nm in both samples, ensuring same volume of the materials was probed and a direct comparison of the defect concentrations can be achieved. At temperatures lower than 200 K, when capacitance-frequency dispersions were significant, C-f measurements were performed as a function of temperature to characterize the major acceptor levels in these two materials.
6.3 Basic Capacitance Characteristics

Figure 6.3 (a) Room temperature capacitance-based characterizations (C-V, C-f) of NH$_3$MBE and MOCVD grown p-GaN; (b) Net p-type doping profiles for both samples extracted from 1 MHz C-V measurements.
Prior to any defect characterizations, room temperature capacitance-based measurements were first carried out to verify the device design and extract basic diode characteristics. Fig. 6.3 (a) inset presents the results of $C-f$ measurements performed at a gate bias of 0 V. As seen, the NH$_3$MBE grown sample exhibits a nearly constant capacitance value between 1 kHz ~ 1 MHz, and only a slight dispersion (<10%) can be observed in MOCVD grown sample, validating the use of 1 MHz capacitance-based characterizations in both diodes. $C-V$ curves measured at 1 MHz (shown in Fig. 6.3 (a)), clearly reveal p-type conductivities for both samples, though one experienced an activation annealing while the other was as-grown. Figure 6.3 (b) presents the p-type net doping profiles extracted from the $C-V$ characteristics. Uniform doping profiles are obtained in both samples, with net doping densities of $1.5 \times 10^{18}$ cm$^{-3}$ and $6 \times 10^{17}$ cm$^{-3}$ for the MOCVD and NH$_3$MBE grown samples, respectively. These concentrations agree reasonably well with the intentionally doped Mg concentration (nominally $\sim 1 \times 10^{18}$ cm$^{-3}$) in the p$^-$-GaN layer, confirming the p$^-$-GaN layers were being characterized, as designed.
6.4 Characterizing Deep Acceptor States

Figure 6.4 (a-b) $C-f$ characteristics for the two samples at low temperatures. (c-d) Corresponding $G/\omega$ plots for investigating the emission processes of major acceptors in both samples.
Since different processes (e.g., annealing vs. no-annealing) were involved in achieving p-type conductivity, it is of great interest to explore the properties for acceptor states in these two materials. Here, $C_f$ characterization provides a unique approach for such investigation as described earlier. [9-11] Although the capacitances for both samples are nearly frequency independent at room temperature, at low temperatures (below 200 K) they do exhibit significant dispersions. As shown in Fig. 6.4 (a-b), the capacitances drastically reduce with increasing sampling frequency in both MOCVD and NH$_3$MBE grown samples. The fact that these capacitance “roll-offs” shift toward high frequency at elevated temperature suggests that these are thermally-assisted phenomena. Additionally, the high frequency capacitance stabilizing at ~ 20 pF, corresponding to a depletion depth of ~ 300 nm that is generally consistent with the designed p-layer thickness, excludes the
series resistance as the major reason for these effects, because that would result in a near zero capacitance at the high frequency bound. [17] With these considered, the observed capacitance dispersion is most likely associated with the thermal emission/response of acceptor states with respect to the capacitance sampling frequency.

To analyze these acceptor states involved, conductance methods were applied. Fig. 6.4 (c-d) plot $G/\omega$ as a function of frequency at each temperature, where the peak frequency corresponds to the acceptor emission rate at that temperature. [11] Subsequent Arrhenius analysis reveals that these major acceptor states in the MOCVD and NH$_3$MBE grown samples are indeed identical, as their manifestations almost overlap with each other in the Arrhenius plots (shown in Fig. 6.5). Such a close correlation confirms that though the active acceptor state in the MOCVD growth p-GaN experienced additional H-passivation and thermal activation annealing, its properties remains the same to the one that was directly formed in NH$_3$MBE-grown p-GaN. The activation energy for these acceptors is calculated to be 0.16 eV, matching very well with widely reported values for Mg$_{Ga}$ acceptor obtained through Hall measurements. [2] However, we note that though the capture cross section of $2 \times 10^{-14}$ cm$^2$ is in theory typical for such a point defect (i.e., Mg$_{Ga}$ acceptor) in semiconductor, it is in fact much larger (~ 6 orders of magnitude) than the ones characterized by similar methods in conventional Schottky diode structures (both MBE and MOCVD grown). [9-11] Whether such a huge difference is a result of the differences in growth conditions or test structures is still unclear at this point, and additional experiments are now being designed to investigate this effect.
6.5 Deep level state characterization

Figure 6.6 (a) Optical cross section spectra for NH$_3$MBE and MOCVD grown p-GaN; (b) SSPC spectra obtained at the same depletion depth in the two samples.
The DLOS measurement results, including optical cross section spectra and SSPC spectra, are now described. First of all, as seen in Fig. 6.6 (a), the optical cross section spectra for these two samples are very similar, suggesting that materials grown by these two techniques at rather different conditions indeed share common traps in the energy range detected by DLOS. Second, as in p-type materials, positive and negative features in DLOS spectrum correspond to the emission of hole traps and electron traps, respectively, [8] the three positive features observed in Fig. 6.6 (a) are indicative of the presences of three hole traps (energy position with respect to \( E_V \)). Next, while the onset near \( E_C \) is sharp in spectrum, suggestive of negligible lattice relaxation effect, the other two traps deeper in the bandgap are very broad in spectrum, typical for localized deep states whose optical transitions are associated with strong electron-phonon coupling. [18-21] Therefore, different optical ionization models developed by Lucovsky and Passler et al. are used for fitting these two types of features, respectively. [18, 19] The three defects are thusly determined to be at \( E_V + 1.50 \text{ eV} \) (with \( D_{FC} \sim 0.4 \text{ eV} \)), \( E_V + 2.42 \text{ eV} \) (with \( D_{FC} \sim 0.4 \text{ eV} \)) and \( E_V + 3.26 \text{ eV} \) (with negligible \( D_{FC} \)), respectively.

In fact, these three hole traps also manifest as onsets in SSPC spectra, where the step heights for these features are used for estimating the trap concentrations. As seen in Fig. 6.6 (b) and the inset, unlike the optical capture cross section spectra, the two samples characterized here reveal substantially different SSPC spectra, indicative of significant differences in both overall distribution and individual defect concentrations. First, the total concentration for all traps (corresponding to the peak amplitude of SSPC spectrum) in NH\(_3\)MBE grown p-GaN is \( \sim 4.3 \times 10^{15} \text{ cm}^{-3} \), much less than that of \( 2.2 \times 10^{16} \text{ cm}^{-3} \) in MOCVD grown sample. Next, the impact of growth method is clearly different for
By changing from MOCVD to NH$_3$MBE growth, the $E_V + 2.42$ eV trap reduces by $20\times$ in concentration, while the $E_V + 3.26$ eV state reduces by $3\times$, and the deep level at $E_V + 1.50$ eV even increases by $2\times$. A direct consequence of such behaviors is the different dominances among traps between the two growth methods, e.g., the $E_V + 2.42$ eV trap is the most dominant state in MOCVD grown p-GaN, whereas the major traps in NH$_3$MBE grown p-GaN become the ones at $E_V + 1.50$ eV and $E_V + 3.28$ eV.

Next, DLTS was performed to characterize defect states in the lower portion of the bandgap (within ~ 1 eV from valence band edge). Figure 6.7 presents the DLTS spectra for both samples at a measurement rate window of 10 s$^{-1}$. Clearly, the DLTS spectra for...
these two materials are substantially different, again indicative of different defect distribution in the probed energy range. As seen, while the emission spectrum of NH$_3$MBE sample seems to consist of multiple broad features (possibly peaking at 220 K, 300 K and 365 K, respectively) with similar amplitudes, the DLTS spectrum for MOCVD grown sample is mostly dominated by a broad emission feature peaking at ~ 350 K. In fact, the DLTS feature at 365 K in NH$_3$MBE sample and 350 K in MOCVD sample may be associated with the same defect, as they are very close in Arrhenius plots, sharing similar activation energy $\sim E_V + 0.74$ eV and capture cross section of $1\times10^{-15}$ cm$^2$. Similar to all DLOS-detected traps, the growth technique clearly has an impact on the formation of this trap, as its concentration is $\sim 2\times$ smaller in NH$_3$MBE grown sample than MOCVD grown p-GaN. Apart from these, additional efforts, including multi-peak fitting and DLTS measurements at different bias conditions, are needed to further resolve the other DLTS features. Fortunately, the concentrations for all these DLTS-detected traps are on the order of mid $10^{14}$ cm$^{-3}$ $\sim$ low $10^{15}$ cm$^{-3}$, much smaller than those dominating DLOS-detected defect states, thus they would probably have a less significant impact on material properties and device operations.
6.6 Summary

In this chapter, the presences and distributions of deep states throughout the bandgap in MOCVD and NH₃MBE grown p-GaN are fully characterized, and summarized in Fig. 6.8. While the MgGa acceptors are found to be identical in both samples despite of different activation processes, the growth method does significantly impact on the formations of almost all the other deep states. Unfortunately, this initial study was not designed for revealing the physical origins for any of those traps; thus no further comments can be made regarding their formation mechanisms at this point. However, these different trap distributions detected by DLOS/DLTS can have consequences on the characteristics of devices grown by both methods depending on the device structure and application. And while NH₃MBE is far less mature than MOCVD, the overall lower trap concentration for
NH₃MBE p-GaN suggests that significant performance and/or functional advantages for p-GaN containing devices grown by NH₃MBE might be possible. Continual work focuses on the specifics of how each trap is influenced by growth parameters (e.g. growth temperature, surfactant etc.) is on-going, and the origins for several of the traps observed here will be discussed later in Chapter 9, where proton irradiation induced states in p-GaN are studied.
6.7 Reference

Chapter 7

Impact of Proton Irradiation on Deep Level States in n-GaN

7.1 Introduction

Unlike the previous chapters that describe the formation of as-grown traps in GaN-based materials, the following chapters explore the defects that are induced by high-energy particle irradiation in GaN-based materials and devices. III-Nitrides have been considered as ideal candidates for device applications in space electronics due to their unique combination of excellent transport properties and superior radiation hardness as compared with Si and GaAs-based semiconductor technologies. [1-5] However, despite their radiation resistance, GaN devices nevertheless do degrade upon large radiation exposure. As is the case for semiconductors having undergone high energy particle radiation, such degradations are generally attributed to the creation of defects, which act as bandgap states that can compensate free carriers, increase carrier scattering, and increase device leakage currents, among other mechanisms. [1-10] Nowadays, with the application of GaN devices in space electronics growing in scope and circuit complexity, obtaining quantitative information regarding the irradiation induced defects in GaN-based materials and revealing
the degradation mechanisms in devices become imperative, as they are essential for predicting device performance over operational lifetime and mitigating major degradations through design optimization.

Although the degradation features in GaN-based materials and devices have been widely observed and reported, there have been only a few studies on the actual defects created by radiation damage in GaN. [11, 12] In most of those studies, thermally based DLTS technology was used to characterize and demonstrate the existence of proton irradiation induced traps within approximately 1 eV of the conduction band edge for n-type GaN. However, as DLTS relies on the thermal emission process, their ability to observe very deep traps is limited by slower thermal carrier emission rates, thus, it does not allow for probing of the majority of the GaN bandgap where deeper bandgap states are known to exist. To this end, DLOS measurement, by replacing the thermally-stimulated emission with much faster optically-excited photoemission, would enable probing of states deeper in the rest of 3.4 eV GaN bandgap.

In this chapter, we present the results of a systematic study of 1.8 MeV proton irradiation induced deep level defects in n-type GaN. The combination of DLTS and DLOS provides a complete and quantitative characterization of trap energies, cross sections and concentrations and how their properties evolve with radiation fluence. In addition, by using spectrally-resolved lighted capacitance voltage (\(L-CV\)) measurements, specific traps are identified as being the source of proton radiation-induced carrier removal in n-GaN. The information obtained in here will serve as the baseline for further investigations of thermal stability, Fermi level impact on irradiation induced defects in GaN materials and radiation
induced device level degradation, which are presented in the next three chapters. Part of this work has been published in *Appl. Phys. Lett.* 103, 042102 (2013).

### 7.2 Experimental Details

![Figure 7.1 Structure for n-type Schottky diodes used in this study.](image)

The GaN samples used in this study were grown by NH$_3$-MBE on a c-plane GaN template, at growth conditions optimized for c-plane n-type GaN to yield high as-grown crystal quality. [13] As shown in Fig. 7.1, the final growth structure, from the substrate up, consisted of a 300 nm GaN:Si ([Si] $\sim 3\times10^{18}$ cm$^{-3}$) conduction layer and then a 500 nm GaN:Si ([Si] $\sim 3\times10^{16}$ cm$^{-3}$) layer that was probed in subsequent measurements. After growth, the sample was processed into 300×300 μm$^2$ square Schottky diodes, following procedures described in Ref. 14-18.
After processing, multiple Schottky diodes across an entire wafer were characterized using $I-V$, $C-V$, DLTS and DLOS measurements to verify initial diode uniformity and explore the defect distribution before irradiation. In both DLTS and DLOS measurements, a quiescent reverse bias of -0.5 V and a filling bias of 0 V were used, while the filling pulse durations were 10 ms and 10 s for DLTS and DLOS, respectively. After pre-rad characterizations, the wafer was diced into four pieces, and each of them were exposed to different proton fluences of $1.0 \times 10^{12}$ cm$^{-2}$, $3.9 \times 10^{12}$ cm$^{-2}$, $7.2 \times 10^{12}$ cm$^{-2}$ and $1.1 \times 10^{13}$ cm$^{-2}$, so that by comparing the pre-rad and each post-rad defect spectrum, the effects of proton irradiation on deep level states can be revealed as a function of radiation dose. Proton irradiation was performed at 1.8 MeV in ultra-high-vacuum at 300 K using a Van de Graaff particle accelerator, yielding a penetration depth of $\sim 20$ μm in GaN according to Stopping and Range of Ion in Matter (SRIM) simulations. These conditions are identical to those used in prior work in order to maintain consistency within a larger systematic study of proton radiation effects in GaN. [2, 9] It should also be noted that the equivalent displacement damage doses in this study are high (typically $\sim 3\text{-}30$ times larger), compared with most realistic space environments. [19-22] Thus, it is reasonable to expect devices built in these technologies to function well in most space applications.
7.3 Basic $I-V$ $C-V$ Characteristics

Prior to deep level characterizations, room temperature $I-V$ and $C-V$ measurements were first performed on post-radiation samples to reveal the basic electrical characteristics for Schottky diodes. As shown in Fig. 7.2, strong rectification behaviors were observed for all radiation conditions, suggestive of decent diode quality even after proton irradiation. In addition, leakage currents were below detection limits at a reverse bias value of -0.5 V, where DLTS/DLOS measurements were performed for all values of proton fluencies, assuring high sensitivity capacitance-based characterizations can be performed.

Figure 7.2 Room temperature $I-V$ characteristics of GaN samples exposed to different proton fluences.
Figure 7.3 Room temperature 1 MHz $C$-$V$ curves of GaN samples exposed to different proton fluences. The inset shows the evolution of extracted n-type doping concentration at a reverse bias of -0.5 V for each proton fluence.

Figure 7.3 presents the $C$-$V$ measurement results on these samples. All $C$-$V$ measurements were performed with a sampling frequency of 1 MHz at room temperature, and were done in the dark to prevent possible trap emission assisted by the environment light. As shown, the post-irradiation $C$-$V$ curves started to deviate from the pre-irradiation case beyond the $3.9 \times 10^{12}$ cm$^{-2}$ proton fluence, and carrier removal was clearly evident. The net doping density, i.e., $N_D^+ - N_A^-$, exhibits a monotonic decrease as a function of increasing fluence, with the carrier reduction reaching the maximum of $4.0 \pm 1.0 \times 10^{15}$ cm$^{-3}$ at the proton fluence of $1.1 \times 10^{13}$ cm$^{-2}$. According to the extensive studies of many other irradiated semiconductors, such a carrier reduction likely suggests increased carrier...
compensation due to the creation of radiation-induced deep states in GaN, [7, 23] which were subsequently investigated by the deep level spectroscopy characterizations, discussed next.
7.4 Deep Level State Characterization

Figure 7.4 (a) DLTS spectra of rate window 80 s$^{-1}$ for GaN samples exposed to different proton fluences. (b) Arrhenius analyses for deep levels in n-type GaN before and after proton irradiation. The dashed lines represent the fitting results.
Table 7.1 Summary of deep level states and their concentrations in proton irradiated NH$_3$-MBE grown n-GaN. Trap concentrations are given in cm$^{-3}$.

<table>
<thead>
<tr>
<th>Proton-fluence</th>
<th>$E_C$-0.13eV</th>
<th>$E_C$-0.16eV</th>
<th>$E_C$-0.25eV</th>
<th>$E_C$-0.60eV</th>
<th>$E_C$-0.72eV</th>
<th>$E_C$-1.25eV</th>
<th>$E_C$-2.50eV</th>
<th>$E_C$-3.25eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-rad</td>
<td>-</td>
<td>-</td>
<td>1.7×10$^{14}$</td>
<td>2.8×10$^{14}$</td>
<td>6.2×10$^{14}$</td>
<td>3.9×10$^{14}$</td>
<td>3.2×10$^{14}$</td>
<td>9.8×10$^{14}$</td>
</tr>
<tr>
<td>$1.0\times10^{12}$ cm$^{-2}$</td>
<td>2.9×10$^{14}$</td>
<td>2.5×10$^{14}$</td>
<td>2.7×10$^{14}$</td>
<td>3.0×10$^{15}$</td>
<td>1.0×10$^{15}$</td>
<td>5.1×10$^{14}$</td>
<td>3.4×10$^{14}$</td>
<td>1.1×10$^{15}$</td>
</tr>
<tr>
<td>$3.9\times10^{12}$ cm$^{-2}$</td>
<td>9.0×10$^{14}$</td>
<td>1.0×10$^{15}$</td>
<td>5.4×10$^{14}$</td>
<td>3.7×10$^{15}$</td>
<td>2.3×10$^{15}$</td>
<td>5.9×10$^{14}$</td>
<td>4.1×10$^{14}$</td>
<td>1.6×10$^{15}$</td>
</tr>
<tr>
<td>$7.2\times10^{12}$ cm$^{-2}$</td>
<td>1.7×10$^{15}$</td>
<td>1.5×10$^{15}$</td>
<td>6.9×10$^{14}$</td>
<td>4.0×10$^{15}$</td>
<td>2.4×10$^{15}$</td>
<td>7.1×10$^{14}$</td>
<td>4.2×10$^{14}$</td>
<td>1.8×10$^{15}$</td>
</tr>
<tr>
<td>$1.1\times10^{13}$ cm$^{-2}$</td>
<td>2.5×10$^{15}$</td>
<td>3.0×10$^{15}$</td>
<td>1.3×10$^{15}$</td>
<td>3.6×10$^{15}$</td>
<td>3.9×10$^{15}$</td>
<td>7.7×10$^{14}$</td>
<td>4.3×10$^{14}$</td>
<td>2.1×10$^{15}$</td>
</tr>
</tbody>
</table>

First, DLTS was applied to all these samples to explore the effect of high-energy proton irradiation on traps in the upper part of the GaN bandgap. Figure 7.4 (a) presents the evolution of trap spectra at 80 s$^{-1}$ rate window for all pre- and post-irradiation samples, while Fig. 7.4 (b) shows the Arrhenius plots for each detected trap covering a wide range of rate windows from 4 to 2000 s$^{-1}$. An effective mass of 0.2 $m_0$ for GaN electrons was assumed for Arrhenius analysis. The trap activation energies and concentrations from the DLTS data are summarized in Table 7.1. As seen in Fig. 7.4 (a), three as-grown deep states were detected by DLTS with activation energies of $E_C$ - 0.25 eV, 0.60 eV and 0.72 eV. Each of these traps has been previously reported and studied in detail for NH$_3$-MBE grown n-GaN. The $E_C$ - 0.25 eV trap has been attributed to a nitrogen vacancy-related origin [16]; the $E_C$ - 0.60 eV trap has been suggested to be related to point defect complexes possibly decorating threading dislocations [24]; and the $E_C$ - 0.72 eV trap has yet to be associated with a particular defect configuration. After irradiation, dramatic changes occur in the
DLTS spectra as a function of proton irradiation fluence: two additional traps with activation energies of $E_C$-0.13 eV and 0.16 eV were clearly introduced at ~ 100 K and 120 K, respectively; a general increase in concentrations of the as-grown traps were also evident. The energy levels and Arrhenius data of the two shallow electron traps match earlier reports for the so-called ER1 and ER2 traps observed after 2 MeV proton irradiation, and similar to the so-called ED1 and ED2 traps introduced after 1 MeV electron irradiation. [11, 25, 26] All of these states were proposed to be nitrogen vacancy-related defects. In fact, observing such correlations with prior irradiation studies made on MOCVD-grown GaN is encouraging, as this suggests that similar defect formations may be occurring regardless of irradiation conditions and growth method, which is indeed expected for these radiation induced traps. However, this result alone does not allow for making meaningful comments regarding the physical sources for these deep levels. Nevertheless, the evolution of DLTS peak heights, which translates to the tabulation of trap concentrations given in Table 7.1, is still revealing. There are clearly differential effects of protons on the individual trap types that are possibly associated with the specific defect origins and introduction mechanisms, and understanding these will be the objective for the next chapter, where their thermal stabilities are investigated.
We now turn to DLOS in order to assess the impact of proton radiation on defect states in the rest of the GaN bandgap. The DLOS SSPC spectra for all samples are shown in Fig. 7.5. The corresponding trap concentrations are listed in Table 7.1. Unlike DLTS that detected the creation of two new traps, DLOS revealed three electron traps that are present both before and after proton irradiation. These three traps, i.e., $E_C - 1.25 \text{ eV}$, $2.50 \text{ eV}$ and $3.25 \text{ eV}$, closely match frequently observed defect states in n-GaN, which through extensive studies have been associated with C$_i$, V$_{Ga}$ and C$_N$ defects, respectively. [14-17, 27, 28] Regarding the trap concentration, it should be noted that the DLOS-determined concentration is an average value over the whole depletion region, and it often provides a lower bound of concentrations due to model simplification and possible competition with
hole emission for the states existing below mid-gap in n-type sample. [29] However, their trends as a function of radiation fluence are still clearly revealed, and similar to DLTS-detected states, each of these traps increases in concentration as a function of increasing radiation fluence.

Since the proton bombardment energy of 1.8 MeV greatly exceeds the 20.8 eV atomic displacement energy for Ga atoms in the GaN lattice, formation of additional V$_{Ga}$ defects, [3, 10, 26] and hence an increase in the $E_C - 2.50$ eV V$_{Ga}$ trap concentration, is reasonable. In contrast, the reason for the increase of C$_N$-related $E_C - 3.25$ eV level with proton fluence is less obvious. However, we notice that the formation of this level requires nitrogen vacancies. Based on the Transport of Ions in Matter (TRIM) simulations, the displacement of N atoms during the 1.8 MeV proton irradiation is also anticipated. [3, 10] Thus, one plausible explanation for the increased concentration of the $E_C - 3.25$ eV level is that proton irradiation creates more group V vacancies for carbon incorporation. In fact, this is supported by first principle calculations showing it is energetically favorable to form C$_N$ defects in n-GaN. [30] Another possible mechanism for such an increase could involve dehydrogenation of pre-existing defect complexes that were passivated by hydrogen atoms before proton irradiation. [31] The creation of the other trap at $E_C - 1.25$ eV may be due to the displacement of C atoms, as this defect has been associated with interstitial carbon. However, further experimental and theoretical investigation is needed to confirm these attributions.
Figure 7.6 (a) DLTS detected 1.8 MeV proton irradiation-induced trap concentration as a function of proton fluence. (b) DLOS detected 1.8 MeV proton irradiation induced trap concentration as a function of proton fluence.
Table 7.2 Apparent introduction rates for 1.8 MeV proton irradiation induced states. *DLOS only detects the lower limit of introduction rates for traps in the lower half of the bandgap.

<table>
<thead>
<tr>
<th>Trap energy ($E_C$)</th>
<th>0.13eV</th>
<th>0.16eV</th>
<th>0.25eV</th>
<th>0.60eV</th>
<th>0.72eV</th>
<th>1.25eV</th>
<th>2.50eV*</th>
<th>3.25eV*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction rate (cm$^{-1}$)</td>
<td>229</td>
<td>207</td>
<td>73</td>
<td>-</td>
<td>210</td>
<td>32</td>
<td>14</td>
<td>86</td>
</tr>
</tbody>
</table>

In addition to the formation mechanism, the introduction behavior, e.g., introduction rate for each trap, is another important aspect for radiation study. To better reveal this, another n-GaN sample with higher n-type doping at $1 \times 10^{17}$ cm$^{-3}$ was irradiated by protons at the same conditions, but higher total fluences of $1 \times 10^{13}$, $3 \times 10^{13}$ and $1 \times 10^{14}$ cm$^{-2}$. Pre-rad and post-rad DLTS/DLOS characterizations revealed that the identical traps were created in that sample, but at a higher concentrations. This not only confirms the results as presented above, but also allows for investigation the trap introduction over a larger proton fluence range. Plotting the proton irradiation-induced trap concentrations (i.e., subtracting pre-rad trap concentration from the total post-rad trap concentration) for all the samples, as shown in Fig. 7.6 (a-b), the introduction for all the traps except $E_C$ - 0.60 eV state are revealed to be almost linear as a function of proton fluence, which is indeed expected as these traps are created through a physical displacement process. Apparent introduction rates obtained for these traps are listed in Table 7.2. It is clearly that the introduction rates are differential for individual traps, which is due to different generation mechanisms depending on their physical origins. Note that DLOS often underestimates the
concentration for defects in the lower half of the bandgap, thus the apparent introduction rates for the \( E_C - 2.50 \) eV and \( E_C - 3.25 \) eV trap only presents the lower limits.

### 7.5 Correlating Carrier Removal and Radiation Induced Traps

![Graph showing net doping concentrations at -0.5 V from lighted C-V measurements.](image)

Figure 7.7 Extracted net doping concentrations at - 0.5 V from lighted C-V measurements. Different illumination conditions, i.e. no light, 1.24 eV, 2.48 eV, 3.24 eV and 3.38 eV are presented from left to right, while the unirradiated control sample and the two samples experienced large proton fluence.

With the proton irradiation induced trap levels and their evolutions as a function of proton fluence having been revealed by DLTS and DLOS, attempts were made to connect these results to carrier removal, as observed in Fig. 7.3 inset, and explore which levels are
responsible for the carrier removal effect. Here, we employed the lighted C-V measurements at room temperature, where the net doping density changes due to depopulating each defect state can be clearly revealed. [32] The same experiments were performed on all samples, but only three representative samples are shown here, i.e., the as-grown sample, and the two samples experienced $3.9 \times 10^{12}$ cm$^{-2}$ and $1.1 \times 10^{13}$ cm$^{-2}$ proton fluences. The extracted net ionized doping concentrations at -0.5 V with no light, under saturating 1.24 eV, 2.48 eV, 3.24 eV and 3.38 eV illumination energies, are shown in Fig. 7.7. These energies were chosen to photo-ionize each detected level one by one. Looking from left to right one can see how the carrier recovery occurs for each sample, while the carrier removal comparison is also presented for each illumination conditions. First, in full darkness, when all the traps are at thermal equilibrium, the carrier removal is prominent and increases with increasing proton fluence. Then, the 1.24 eV illumination allows the trapped electrons on all the DLTS-detected traps (i.e., those with activation energies less than $E_C - 1.24$ eV) to be emitted while all the deeper DLOS-detected traps are unaffected (filled). As seen, the net doping concentrations remain the same to those measured at dark in all samples, indicating that those DLTS-detected traps are likely not contributing to the carrier removal effect. However, the 2.48 eV illumination that selectively empties the DLOS-detected $E_C - 1.25$ eV traps while keeping the deeper traps at $E_C - 2.50$ eV and 3.25 eV filled, indeed leads to observable increases for the irradiated samples, revealing the compensating nature of the $E_C - 1.25$ eV trap. There is no apparent change observed in the non-irradiated sample, and that is probably due to the smaller trap concentration. Similar compensation behaviors were observed for the $E_C - 2.50$ eV and 3.25 eV traps under illuminations of 3.24 eV and 3.38 eV, respectively. Even for the as-grown control sample,
the carrier compensation effect is now evident, indicating the importance of these two states for non-irradiated applications from the perspective of doping efficiency. Finally, under the 3.38 eV illumination whose energy is just below the GaN bandgap and enough to ionize all three DLOS-probed traps, the net doping concentrations for the two irradiated samples are nearly restored to the as-grown case. Such a carrier recovery through ionizing the $E_C - 1.25$ eV, 2.50 eV and 3.25 eV states unambiguously revealed their roles in dictating proton irradiation-induced carrier removal for n-type GaN.

7.6 Summary

In this chapter, the presence of 1.8 MeV proton irradiation induced traps were characterized by DLOS and DLTS measurements. Two “new” traps at $E_C - 0.13$ eV and 0.16 eV were created in proton irradiated NH$_3$-MBE grown n-GaN. In addition, general concentration increases for almost all the pre-existing traps were evident, though the introduction rates are substantially different for different types of traps. The deep levels at $E_C - 1.25$ eV, 2.50 eV and 3.25 eV were identified as compensating centers that are responsible for the carrier removal in proton-damaged n-GaN.
7.7 Reference


Chapter 8

Thermal Stability of Proton Irradiation Induced Deep Traps in n-GaN

8.1 Introduction

The last chapter reveals the presence of high-energy proton irradiation-induced deep levels within the n-GaN bandgap. However, still very little is understood about the physical defect configurations associated with these states from that study alone. To this end, we now perform a post-radiation thermal annealing study, which is a widely used approach to elucidate the behavior of such defects and gain deeper insights into their natures, because analysis of the defect annealing kinetics can reveal details of defect migration, defect reactions and reconfigurations, as well as how the presence of specific states directly affect electronic transport. [1-9] In fact, several studies of thermal annealing effects on irradiation-induced traps in n-type GaN have been performed after high-energy proton, electron and $^{60}$Co gamma radiation using DLTS. [5, 8, 10] For all cases, the concentrations of the detected trap states near the conduction band edge ($E_C$) decreased even after annealing at temperatures of 200 °C to 300 °C, which was attributed to the recombination of nitrogen vacancy-nitrogen interstitial Frenkel pairs ($V_N-N_i$). [5, 8] However, as mentioned before, the thermal-based DLTS is insensitive to much of the large
bandgap, [11, 12] where deeper bandgap states have been not only demonstrated to exist, but also revealed to play an important role in affecting material electrical properties. [13-15] In fact, it is the defect states at $E_C - 1.25$ eV, $2.50$ eV and $3.25$ eV, rather than the DLTS-detected levels in the upper part of the bandgap, that are directly responsible for carrier removal effects through trap-specific carrier compensation. [16] Therefore, in this chapter, we use the combination of DLTS and DLOS to investigate the proton irradiation induced defect states throughout the bandgap, and systematically explore their thermal stabilities and annealing kinetics. Distinct thermal sensitivities have been revealed for individual traps, which are consistent with their different physical sources. Moreover, by tracking the recovery of bulk degradation phenomena, especially carrier removal, with the annealing behavior of the individual traps, we have been able to identify the specific defects that completely control this key degradation pathway and its recovery. This work has been published in *J. Appl. Phys.*, 118, 155701 (2015).

### 8.2 Experimental details

The n-GaN sample used in this thermal annealing study was identical to the one studied in the last chapter. Following the pre-rad characterizations, the sample was diced into two pieces: one was maintained as a “non-irradiated” control sample, while the other one was exposed to 1.8 MeV proton irradiation at a fluence of $1 \times 10^{13}$ cm$^{-2}$ using a Pelletron particle accelerator. The sample for irradiation was kept under vacuum at room temperature throughout the radiation process. After irradiation, DLTS and DLOS measurements were performed on irradiated devices (denoted as post-rad) to reveal the introduction of
irradiation-induced deep levels. To explore the effects of annealing on these traps, particularly the impact from annealing temperature, the post-rad sample was further diced into multiple pieces; each experienced a separate 10 minute anneal at a specific temperature between 200 °C to 400 °C in an N₂ ambient. Each post-rad annealed sample was then characterized so that by comparing samples the evolution of each trap as a function of annealing temperature could be revealed. In parallel, the non-irradiated control sample was also annealed at 400 °C for 10 minutes so that the thermal stability of the as-grown traps could also be assessed. Well-behaved I-V and C-V diode characteristics were obtained for all radiation and annealing conditions, ensuring that high sensitivity DLTS/DLOS measurements can be performed. Figure 8.1 shows room temperature 1 MHz C-V characteristics for n-GaN samples before irradiation, after irradiation and after annealing at different temperatures. Note that the steady evolution of the C-V characteristics as a function of post-radiation annealing temperature indicates a slight increase in the net doping concentration back toward its as-grown, pre-irradiation value, since the annealing lowers the concentration of the radiation-induced defects that otherwise compensate the background doping via carrier removal. This is described later in the chapter.
Figure 8.1 Room temperature 1 MHz $C$-$V$ characteristics for n-GaN samples before irradiation, after irradiation and after annealing at different temperatures.
8.3 Deep Level Characterization

Figure 8.2 DLTS spectra (80 s\(^{-1}\) rate window) for n-GaN samples before irradiation, after irradiation and after annealing at different temperatures.
Figure 8.3 Multi-peak fitting of DLTS spectra for samples at all conditions. The dashed lines are the total fitting results.
Figure 8.4 Arrhenius plots for DLTS-detected traps (a) in pre-rad and post-rad samples without annealing, and (b) post-rad samples annealed at different conditions. The dashed lines are fitting results.
We start by applying DLTS to characterize defect states in the upper GaN bandgap (within ~ 1 eV from \(E_c\)). Figure 8.2 shows the DLTS spectra for all the samples, with the data plotted for the 80 s\(^{-1}\) rate window. First, by comparing the pre-rad and post-rad spectra, the presence of proton irradiation-induced deep states are clearly revealed. Two “new” traps are apparent with peaks near 100 K to 120 K. All pre-existing traps increase in concentration after irradiation, consistent with earlier reports. [10, 16] Next, we follow the DLTS spectra as a function of post-rad annealing temperature to explore the influence of thermal annealing. The responses of the low temperature portion (77 K to 250 K) and the high temperature portion (250 K to 400 K) of these DLTS spectra are substantially different. While the DLTS spectral intensity in the high temperature range decreases monotonically as the annealing temperature increases, suggestive of a continuous reduction in trap concentration, the evolution of the low temperature trap spectra is quite complex. Comparing the control, post-irradiation and post-irradiation plus 400 °C annealed samples, very shallow traps (peaks at temperatures lower than the as-grown peak at 150 K) created by the irradiation are completely removed after 400 °C annealing, whereas the traps existing prior to irradiation ultimately increase in concentration after a 400 °C anneal. To elucidate the evolution of traps (determine their energies and concentrations) that compose the complex spectrum as a function of annealing, a multi-peak fitting procedure of the DLTS spectra was performed. During fitting, each individual trap feature was fit by a Gaussian distribution with a fixed full width at half maximum in all rate windows, and only the peak position and amplitude were allowed to be adjusted. Figure 8.3 shows the fitting results at a single rate window, where excellent fitting of the DLTS spectrum was achieved for each condition. By performing the fits as a function of all experimentally used rate windows,
individual trap activation energies were determined by analyzing Arrhenius plots for each trap. Figure 8.4 (a) shows Arrhenius plots for the non-irradiated and post-irradiation sample with no anneal, and Fig. 8.4 (b) shows a collection of Arrhenius data for the post-irradiation sample with no anneal and for all annealing conditions. An electron effective mass of $0.2m_0$ was used for fitting. The resultant energy positions and capture cross sections for all of the DLTS-detected traps are summarized in Table 8.1, and the concentrations for these traps at all conditions are compiled in Table 8.2. Also shown is a summary of traps detected by DLOS that will be discussed in a later section.

Overall, a total of six electron traps were detected by DLTS. For the as-grown control sample, three electron traps were found at $E_C - 0.25$ eV, 0.60 eV and 0.72 eV. These traps have each been well documented in n-type GaN. [17-20] After irradiation, each of these pre-irradiation traps were still detected along with three new traps that appear at $E_C - 0.13$ eV, 0.16 eV and 0.20 eV. Though closely spaced in energy, these irradiation-induced traps are clearly distinct in both the raw DLTS data and also in their respective Arrhenius results. Regarding the trap feature that appears at the higher temperature range of the DLTS spectrum, this feature has been observed before and it was been attributed to a state near $~ E_C - 0.9$ eV, [17] but here the broad data do not provide for a useful fit. Recently performed iso-thermal DLTS, which allows us to explore a wider range of time constants, however, has confirmed this to be the energy level associated with that trap.
Figure 8.5 DLTS spectra (80 s\(^{-1}\) rate window) for the unirradiated control sample before and after 400 °C annealing.
Figure 8.6: (a) The remaining concentrations for irradiation-induced traps at $E_C - 0.13$ eV, $E_C - 0.16$ eV, $E_C - 0.20$ eV and $E_C - 0.25$ eV, as a function of annealing temperature. The solid lines are fitting results for traps at $E_C - 0.13$ eV and $E_C - 0.16$ eV using the first-order reaction model as described in Section IV. The behavior of the traps at $E_C - 0.20$ eV and $0.25$ eV do not fit this model and only the raw data is shown. (b) The remaining concentrations for irradiation-induced traps at $E_C - 0.60$ eV and $E_C - 0.72$ eV as a function of annealing temperature.
Table 8.2 Concentrations of deep levels in n-GaN samples before irradiation, after irradiation, and after post-irradiation annealing at different temperatures. The trap concentrations are the averaged values from multiple measurements.

<table>
<thead>
<tr>
<th>Deep level energy (E&lt;sub&gt;C&lt;/sub&gt;)</th>
<th>0.13eV</th>
<th>0.16eV</th>
<th>0.20eV</th>
<th>0.25eV</th>
<th>0.60eV</th>
<th>0.72eV</th>
<th>1.25eV</th>
<th>2.50eV</th>
<th>3.25eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-rad/Unirradiated</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>28</td>
<td>6.0</td>
<td>4.6</td>
<td>3.1</td>
<td>12</td>
</tr>
<tr>
<td>Post-rad</td>
<td>42</td>
<td>40</td>
<td>15</td>
<td>10</td>
<td>42</td>
<td>45</td>
<td>8.3</td>
<td>5.0</td>
<td>30</td>
</tr>
<tr>
<td>Post-rad 200ºC anneal</td>
<td>40</td>
<td>36</td>
<td>15</td>
<td>11</td>
<td>40</td>
<td>35</td>
<td>8.0</td>
<td>4.9</td>
<td>29</td>
</tr>
<tr>
<td>Post-rad 250ºC anneal</td>
<td>37</td>
<td>44</td>
<td>17</td>
<td>11</td>
<td>37</td>
<td>35</td>
<td>7.4</td>
<td>4.8</td>
<td>27</td>
</tr>
<tr>
<td>Post-rad 300ºC anneal</td>
<td>7.5</td>
<td>22</td>
<td>26</td>
<td>10</td>
<td>41</td>
<td>23</td>
<td>6.4</td>
<td>4.4</td>
<td>21</td>
</tr>
<tr>
<td>Post-rad 350ºC anneal</td>
<td>1.1</td>
<td>2.0</td>
<td>11</td>
<td>24</td>
<td>36</td>
<td>13</td>
<td>6.2</td>
<td>3.4</td>
<td>19</td>
</tr>
<tr>
<td>Post-rad 400ºC anneal</td>
<td>0.6</td>
<td>0.4</td>
<td>5.5</td>
<td>24</td>
<td>36</td>
<td>11</td>
<td>5.4</td>
<td>3.2</td>
<td>17</td>
</tr>
</tbody>
</table>

With the trap activation energies determined, we now turn toward analysis of the individual trap concentrations as a function of irradiation and annealing conditions. Note that each individual trap concentration provided in Table 8.2 is the sum of the as-grown and post-irradiation/annealing concentrations. Thus, to unambiguously evaluate the annealing behaviors of only the concentration of each trap that was created by the irradiation (irradiation induced traps), it is necessary to evaluate the effect of annealing on the concentration of defects present for samples that were not exposed to radiation(as-grown traps), so that this value can be subtracted from the combined total. To accomplish this deconvolution, DLTS was performed on the as-grown sample subjected to the same 400 ºC annealing conditions, but with no irradiation. As shown in Fig. 8.5, there was no
measurable change in the spectrum before and after annealing, confirming that (a) the anneal itself does not appear to create new traps, and (b) the annealing conditions used here have no measurable effects on the as-grown defect behavior. This is reasonable since the short anneal at 400 °C is well below the much higher (and longer duration) 800 °C growth temperature of the GaN layers. With this information, we can assume that there is no change in the concentration of grown-in traps due to annealing by itself and that all changes are attributed to the irradiation process and subsequent removal of the irradiation-induced traps. Figure 8.6 shows plots of the individual, irradiation-induced trap concentrations detected by DLTS, $N_{T, \text{rad}}$, after subtraction of the appropriate as-grown trap concentrations, as a function of annealing temperature. Clearly, substantially different trends of $N_{T, \text{rad}}$ are observed for different traps. First we consider the trap concentrations corresponding to the low temperature DLTS peaks in Fig. 8.6 (a). Two of the new, irradiation-induced traps, at $E_C - 0.13$ eV and $E_C - 0.16$ eV are dominant after irradiation and up to post-irradiation annealing temperatures of ~ 250 °C, subsequently decreasing in concentration after annealing between 250 °C and 350 °C, and are totally removed to below detection limits by annealing beyond 350 °C (these behaviors are analyzed in the next section). In contrast, the third trap that was newly introduced by irradiation, at $E_C - 0.20$ eV, has a relatively low concentration after irradiation, weakly increases in concentration with annealing temperatures between 200 °C ~ 300 °C, but later decreases in concentration for anneals between 300 °C and 400°C, and is nearly completely removed by annealing at 400 °C. The other low temperature trap at $E_C - 0.25$ eV is the only one in this range that is present in the as-grown sample. Its concentration remains almost constant until 300 °C, after which the trap concentration increases with rising annealing temperature, and finally saturates and
becomes the dominant trap in the low temperature range of the DLTS spectrum after the
400 °C anneal has effectively removed the other traps corresponding to the low temperature
DLTS peaks.

We now consider the DLTS peaks near and above 300 K. The responses of the $E_C$
- 0.60 eV and 0.72 eV traps are mapped as a function of post-irradiation annealing in Fig.
8.6 (b). Each of these traps exists in the as-grown sample, but the figure shows the
concentrations of traps after the as-grown concentrations have been subtracted out.
Therefore, although both traps are nearly equivalent in terms of DLTS peak magnitude
after irradiation in Fig. 8.3, the concentration for the irradiation-induced $E_C$ - 0.72 eV state
is more than 2× higher than that of the $E_C$ - 0.60 eV state, due to the lower concentration
for as-grown $E_C$ - 0.72 eV traps. The concentration of the $E_C$ - 0.72 eV state monotonically
decreases with annealing temperature, whereas the $E_C$ - 0.60 eV trap remains virtually
constant. These different behaviors are suggestive of different recovery/introduction
processes for these states, and as such could be linked to differences in their physical
origins and introduction mechanisms. These questions are discussed later in this chapter.
Figure 8.7 Room temperature DLOS SSPC spectra for n-GaN samples before irradiation, after irradiation and subsequently annealed at different temperatures.
Figure 8.8 DLOS optical cross section spectra analysis for n-GaN samples (a) before and after irradiation, and (b) post-irradiation and subsequently annealed at different temperatures.
We have applied DLOS to explore the irradiation-induced deep levels in the mid- and lower-portion of the GaN bandgap. Figure 8.7 shows the DLOS SSPC spectra for pre-rad and post-rad samples. Even without detailed analysis, the impact of proton irradiation and post-rad annealing on these much deeper bandgap states are already evident: the peak amplitude of the SSPC spectrum at 3.4 eV, which represents the total concentration of all DLOS-detected traps, first increased after proton irradiation, and then monotonically decreased as a function of annealing temperature. Three states are detected in the as-grown condition. Figure 8.8 shows the detailed optical cross section spectra. As see, the near valence band state was determined to be at $E_C$ - 3.28 eV with negligible lattice relaxation effect, whereas the trap exhibiting a broad onset was revealed at $E_C$ - 2.50 eV with Franck-Condon energy ($D_{FC}$) of 0.20 eV, indicative of large lattice relaxation associating with its optical transitions. Regarding the other trap that is prominent in the QTH SSPC spectrum as shown in the inset of Fig. 8.7, its energy position was determined to be $E_C$ - 1.25 eV according to the SSPC onset. These three traps are commonly detected states in MBE-grown n-GaN, whose origins have been connected to carbon interstitials ($C_I$), gallium vacancies ($V_{Ga}$) and $C_N$ substitutional defects, respectively, as shown elsewhere. [13, 14, 18-22]
Figure 8.9 DLOS SSPC spectra for the unirradiated sample before and after annealing.

Figure 8.10 The remaining concentrations for irradiation-induced traps at $E_C - 1.25$ eV, $E_C - 2.50$ eV and $E_C - 3.25$ eV as a function of annealing temperature. The solid line is the fitting result of the $E_C - 2.50$ eV state using equation described in section 8.4.
As can be seen in Fig. 8.7 and Fig. 8.8, after irradiation, no new energy levels were detected. The only effect of both irradiation and annealing is on the concentrations of these states, which are listed in Table 8.2 for all sample conditions. Similar to the as-grown DLTS trap behavior, the pre-existing traps seen by DLOS are not affected by annealing at 400 °C, as shown in Fig. 8.9. Therefore, the concentrations for the irradiation-induced traps at different annealing conditions ($N_{T, \text{rad}}$) can be obtained by subtracting the as-grown trap concentrations from the total trap concentrations. The resultant $N_{T, \text{rad}}$ for each state is plotted as a function of annealing temperature in Fig. 8.10. Before any annealing (post-rad), the trap at $E_C - 3.28$ eV (likely corresponding to the $E_C - 3.25$ eV trap in our earlier reports) [16] dominates the DLOS SSPC spectrum, while the other two traps at $E_C - 1.25$ eV and $E_C - 2.50$ eV exhibit much smaller concentrations, consistent with previous studies. [16] The subsequent post-irradiation annealing reduces the concentrations of all three DLOS-detected traps. The concentration of the state at $E_C - 3.28$ eV reduces monotonically and gradually with annealing temperature. After 400 °C annealing, the remaining trap concentration reduces to as low as ~30% of the post-irradiation value. Similar behavior is observed for the irradiation-induced trap at $E_C - 1.25$ eV, but at much smaller concentrations. The behavior of the irradiation-induced traps at $E_C - 2.50$ eV, however, is very different. The concentration of this trap remains nearly constant up to an annealing temperature of ~ 250 °C, rapidly reduces for higher temperatures, and ultimately anneals out to below DLOS detection beyond 350 °C.
8.4 Annealing Kinetics of Proton Irradiation-induced Defect States

The different behavior seen for traps throughout the entire GaN bandgap suggests that there are different thermal stability and recovery processes for individual traps. In this section, the annealing behaviors for each DLOS and DLTS detected trap are discussed in an effort to reveal their specific annealing kinetics where possible. As described below, the dependence on annealing temperature for all nine traps can be divided into four general categories.

Regarding the first grouping, the traps at $E_C - 0.13$ eV, $E_C - 0.16$ eV and $E_C - 2.50$ eV all undergo sharp reductions in concentration within a relatively narrow annealing temperature range, i.e., between $250 \sim 350$ °C. This kind of reduction has been previously observed and described by the first-order reaction model: [4, 5, 7, 8]

$$N_T = N_0 \times \exp\left\{-\nu \Delta t \exp\left(-\frac{qE_{TA}}{k_BT}\right)\right\} \quad (8.1)$$

where $N_0$ is the starting irradiation-induced defect concentration, $N_T$ is the remaining concentration for those traps after being annealed at temperature $T$ (200 °C to 400 °C) for a length of time $\Delta t$ (600 seconds in this work), $\nu$ is a frequency factor (commonly assumed to be $10^{13} \text{s}^{-1}$), [7, 8] and $E_{TA}$ is the activation energy for the process. As seen in Fig. 8.6 (a) and Fig. 8.10, this model reasonably explains the individual evolutions of $E_C - 0.13$ eV, $E_C - 0.16$ eV and $E_C - 2.50$ eV traps by assuming a single activation energy for each trap, 1.7 eV, 1.8 eV and 1.8 eV, respectively. Regarding the $E_C - 0.13$ eV and $E_C - 0.16$ eV traps, both are commonly reported for irradiated n-type GaN and have been associated with nitrogen vacancies ($V_N$). [5, 6, 8, 23] Although the activation energies (1.7 eV, 1.8 eV) obtained here are much smaller than the theoretically predicted 2.6 eV diffusion barrier for
VN, [8, 24] they actually match reasonably well with the 1.6 eV diffusion barrier for nitrogen interstitial (NI); therefore, the observed reductions in trap concentration might be explained by the VN-NI Frenkel-pair recombination as a result of NI diffusing to the less mobile VN defect sites during annealing. Regarding the $E_C - 2.50$ eV trap that has been correlated with the $V_{Ga}$ defect, the 1.8 eV activation energy matches well with the theoretically predicted 1.9 eV diffusion barrier for $V_{Ga}$, [24] thus such a trap reduction is probably due to the migration of $V_{Ga}$ defect by itself. [8, 24]

The traps at $E_C - 0.72$ eV, $E_C - 1.25$ eV and $E_C - 3.28$ eV constitute the second grouping. Here the trap concentrations each decrease in a more gradual manner over a large annealing temperature range (more than 200 °C). Clearly, their responses cannot be well-described by any first-order reaction model with a single activation energy, such as the first grouping, suggestive of totally different reduction mechanisms. However, similar gradual reductions in irradiation-induced trap concentrations during annealing have been observed in other material systems, where complicated models assuming multiple annealing stages/processes to account for recovery from different defect configurations were proposed. [1, 4, 5, 8] Since the characteristics of these trap reductions have yet to be determined, the detailed mechanisms, and how the possible physical origins of each state (i.e., the $E_C - 1.25$ eV trap has been correlated with carbon interstitial defects, the $E_C - 3.28$ eV state has been linked to $C_N$ defects, while $E_C - 0.72$ eV trap origin remains unknown) [13, 18] may impact the reductions are not clear. Further investigations, including iso-thermal annealing experiments that may better reveal the annealing kinetics and theoretical modeling of how defect configurations may impact diffusion, are still on-going. [1, 4]
The third grouping, consisting of the states at $E_C - 0.20$ eV and $E_C - 0.25$ eV, is entirely different, as both increase in concentration at certain annealing conditions prior to decreasing. Similar responses have been reported for irradiated induced traps in other materials and structures (e.g., Si, GaAs, InP, Si/SiO$_2$ interface) and attributed to defect reconfiguration and/or defect complex formation processes. [1-3, 25-27] For example, the increase of the $E_C - 0.25$ eV trap and the reduction of the $E_C - 0.20$ eV trap not only occur concurrently (between 300 °C and 400 °C), but are of similar concentrations. Such a correlation might suggest that the $E_C - 0.20$ eV trap may act as an intermediate defect state that forms between 200 °C and 300 °C, which converts to an $E_C - 0.25$ eV trap for annealing temperatures above 300 °C. This defect reconfiguration model is also supported by the previous reports that linked both traps to a V$_N$ origin. [6, 10, 16] Nevertheless, further investigation is needed to confirm this possible reconfiguration model.

The final, fourth group consists solely of the irradiation-induced $E_C - 0.60$ eV trap, which remains almost unchanged for all the annealing temperatures, indicative of a relatively large barrier for defect reduction.

8.5 Annealing of Irradiation-induced Traps and Carrier Recovery

In an earlier report, it was shown by using lighted $C$-$V$ measurements that the irradiation-induced deep traps at $E_C - 1.25$ eV, $E_C - 2.50$ eV and $E_C - 3.25$ eV are the states primarily responsible for carrier removal in proton irradiated n-GaN. [16] With the thermal stability of these and all bandgap states now measured, it is of interest to investigate the
correlation of carrier concentration, compensation and their recovery with specific defect states as a function of post-irradiation annealing.

The net doping \((N_D^+-N_A^-)\) concentration for each sample condition obtained from \(C-V\) measurements is shown in Fig. 8.11 (a), at the identical depletion depth of \(\sim 0.22 \mu\text{m}\), corresponding to a reverse bias \(\sim -0.5\) V where DLTS and DLOS measurements were performed. The irradiation-removed net doping density clearly recovers for annealing temperatures beyond 250 °C, and monotonically but gradually increases with increasing anneal temperature. The states at \(E_C - 0.13\) eV, \(E_C - 0.16\) eV, \(E_C - 0.20\) eV, \(E_C - 0.25\) eV, \(E_C - 0.60\) eV and \(E_C - 2.50\) eV can be ruled out as the dominant defect responsible for carrier removal, as their annealing dependencies are substantially different from that of the net doping concentration. Among the remaining traps at \(E_C - 0.72\) eV, \(E_C - 1.25\) eV and \(E_C - 3.28\) eV, only the states at \(E_C - 1.25\) eV and \(E_C - 3.28\) eV (likely corresponding to the \(E_C - 3.25\) eV trap in the earlier report) were identified as compensating centers, as shown previously. [16] Considering DLOS only provides a lower limit of the actual trap concentration for states in the lower half of the bandgap, [16, 18] Fig. 8.11 (b) plots the normalized evolution for the concentrations of the states at \(E_C - 1.25\) eV and \(E_C - 3.28\) eV against the remaining carrier removal effect. The close correlations between these three curves strongly suggest the carrier removal/recovery effect is mostly dictated by the radiation-induced \(E_C - 1.25\) eV and \(E_C - 3.28\) eV states. Building such a linkage is important as it assists further device reliability modeling and directs future research to understanding the introduction/recovery of these two defect states.

168
Figure 8.11 (a) Effective n-type doping density \((N_D^+ - N_A^-)\) of irradiated samples before and after annealing, extracted from room temperature 1 MHz \(C-V\) measurements. (b) A comparison of the carrier removal effect and the evolution of irradiation-induced \(E_C - 3.25\) eV and \(E_C - 1.25\) eV traps/
8.6 Summary

Isochronal annealing with temperatures up to 400 °C was performed on 1.8 MeV proton irradiated n-GaN. DLTS/DLOS characterization reveals significant annealing of irradiation induced defect states throughout the GaN bandgap, though the individual responses are highly non-uniform. Sharp reductions in trap concentration as a function of annealing temperature are revealed for trap states at $E_C - 0.13$ eV, $E_C - 0.16$ eV, and $E_C - 2.50$ eV, which are all ultimately annealed out at 400 °C. In contrast, more gradual reductions are observed for traps at $E_C - 0.72$ eV, $E_C - 1.25$ eV and $E_C - 3.28$ eV. Traps at $E_C - 0.20$ eV and $E_C - 0.25$ eV increase in concentration during annealing. These differential responses suggest different introduction/reduction mechanisms linked to individual defect origins. Finally, a 70% recovery of removed carriers due to irradiation can be achieved by annealing the sample at 400 °C, which is correlated with the reduced concentrations of traps at $E_C - 1.25$ eV and $E_C - 3.28$ eV, which act as compensating centers.
8.7 Reference

Chapter 9

Impact of Proton Irradiation on Deep Level States in p-GaN

9.1 Introduction

While Chapter 7 and 8 describe the presence and behaviors of proton irradiation induced traps in n-type GaN, this chapter will study the proton irradiation induced traps in p-type GaN material. As mentioned in Chapter 6, Mg-doped p-type GaN and related alloys present in almost all GaN-based optoelectronic devices and several advanced electronic devices. [1, 2] With the epitaxial growth of p-type III-Nitrides continually improving over the years, high quality p-type layers are attracting increasing interests for applications in high performance radio-frequency (RF) and power electronic devices, as it may enable advantageous designs and provide additional flexibilities. [3-6] For instance, a p-AlGaN cap integrated to the conventional AlGaN/GaN heterostructure forms a gate-injection transistor (GIT) that can operate in enhancement-mode, desirable for power conversion systems. [3] Since many system applications for these high performance devices require exposure to high energy particle irradiation, knowledge regarding the radiation-induced deep level energies, concentrations and overall dependence on the irradiation conditions for each component layer, including the p-GaN layer, is essential to understand degradation
mechanisms and to build predictive models of reliability in the long term. While there exists a growing body of literature on the behavior of standard AlGaN/GaN high electron mobility transistors (HEMTs) after such exposure, [7-12] and also some early work on n-type GaN (as presented in Chapter 7 and 8), [13-17] comparatively little has been reported to date on the effects of high-energy particle irradiation on p-type GaN:Mg in general, [18-20] and even less is known about the traps in p-GaN due to exposure to high-energy particle irradiation.

To this end, we investigate the deep level defects induced by high-energy proton irradiation as a function of proton fluence in p-type GaN. Deep level energies, trap concentrations and their dependencies on proton fluence are characterized using a combination of capacitance-based DLTS and DLOS performed. In fact, in addition to the practical interest for predicting the behaviors of p-GaN containing devices for high radiation applications, such a study is also of fundamental importance as it may shed light to the physical origins for deep states in p-GaN, which is discussed later in this chapter. This work has been published in *Appl. Phys. Lett.* 106, 022104 (2015).
9.2 Experimental Details

Figure 9.1 Schematic diagram of the p+/p-/n+ diode structure used in the measurements.

To facilitate capacitance-based characterizations in p-GaN, p+/p/n+ diodes as shown in Fig. 9.1 is used here. The advantageous for such a structure has been described in Chapter 6. The sample was grown by NH₃-MBE on a semi-insulating GaN:Fe template with a threading dislocation density in the mid 10⁸ cm⁻² range. The p⁻ and p⁺ layers were grown at 780 °C and the n⁺ contact layer was grown at 840 °C. The detailed growth parameters and procedures can be found in Ref. 2. After growth, the sample was fabricated into 300×300 μm² square following the process as described earlier. The resulting diodes exhibited good rectification with a low series resistance of 60 Ω and minimal capacitance dispersion in the range of 1 kHz to ~ 1 MHz, validating the use of 1 MHz capacitance-based measurements in this study. To reveal the impact of proton irradiation, the fully processed sample was diced into a set of three pieces, with one used as the pre-irradiation control sample and the other two exposed to proton irradiation. Similar to the proton irradiations used in n-GaN study, 1.8 MeV protons generated by a Pelletron particle
accelerator irradiate the sample at 300 K in vacuum. One sample received a proton dose of $1 \times 10^{13} \text{ cm}^{-2}$ and the other was radiated up to a proton dose of $3 \times 10^{13} \text{ cm}^{-2}$. For DLTS and DLOS, a quiescent reverse bias of -0.5 V and filling bias of +0.5 V are used for both pre- and post-radiation measurements. Multiple diodes were characterized for all sample pieces, revealing small (~10%) diode-to-diode variation within each piece.

9.3 Basic $C-V$ characteristics

![Graph showing C-V characteristics](image)

Figure 9.2 Room temperature 1 MHz $C-V$ characteristics for diodes exposed to different proton fluences.

Figure 9.2 shows the p-type ionized doping profiles extracted from room temperature 1 MHz $C-V$ measurements for diodes on the three sample pieces. As seen, the
net doping concentration (i.e. $N_A^- - N_D^+$) in the GaN:Mg test layer is nearly unchanged before and after radiation. Although one might expect carrier compensation after radiating with $1 \times 10^{13}$ cm$^{-2}$ proton fluence as we have seen for n-type GaN:Si, here the background net doping concentration, even though low ($N_A^- - N_D^+ \sim 2 \times 10^{17}$ cm$^{-3}$) for p-type GaN:Mg, is nevertheless large compared with the n-type radiation studies that had test layers with background doping on the order of $10^{16}$ cm$^{-3}$ for which compensation was observed. Thus, if radiation-induced states are being formed, their concentration is not high enough to add noticeable carrier compensation that can compete with the high doping ($\sim 2 \times 10^{17}$ cm$^{-3}$). As a result, simple studies of carrier compensation are not applicable here as the effect is masked by the large intentional acceptor concentration, and high sensitivity DLTS and DLOS characterizations are needed to reveal the radiation impacts.
9.4 Deep Level State Characterization

![Graph showing DLTS spectra](image)

Figure 9.3 Comparison of the DLTS spectra at 10 s\(^{-1}\) rate window for samples exposed to different proton fluences. The inset shows the Arrhenius plot of the dominant irradiation induced trap. An effective hole mass of 0.9 \(m_o\) was used in the calculations.

Table 9.1 Summary of deep level states and corresponding concentrations in NH\(_3\)-MBE grown p-GaN exposed to different proton fluences. Trap concentrations are given in cm\(^{-3}\).

<table>
<thead>
<tr>
<th>Rad-fluence</th>
<th>(E_V + 0.48) eV</th>
<th>(E_V + 1.02) eV</th>
<th>(E_V + 1.50) eV</th>
<th>(E_V + 2.42) eV</th>
<th>(E_V + 3.00) eV</th>
<th>(E_V + 3.28) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td>low 10(^{13})</td>
<td>-</td>
<td>8.0\times10(^{14})</td>
<td>1.4\times10(^{15})</td>
<td>1.3\times10(^{15})</td>
<td>1.8\times10(^{15})</td>
</tr>
<tr>
<td>1\times10(^{13}) cm(^{-2})</td>
<td>3.8\times10(^{14})</td>
<td>8.0\times10(^{13})</td>
<td>8.7\times10(^{14})</td>
<td>2.0\times10(^{15})</td>
<td>1.2\times10(^{15})</td>
<td>2.7\times10(^{15})</td>
</tr>
<tr>
<td>3\times10(^{13}) cm(^{-2})</td>
<td>6.4\times10(^{14})</td>
<td>3.0\times10(^{14})</td>
<td>8.0\times10(^{14})</td>
<td>4.4\times10(^{15})</td>
<td>2.5\times10(^{15})</td>
<td>3.4\times10(^{15})</td>
</tr>
</tbody>
</table>
To investigate the effect of proton irradiation on the deep level distribution in the lower portion of the bandgap (for p-type material, this is within ~ 1 eV from valence band edge), DLTS was first performed. Figure 9.3 shows a representative set of DLTS data for a measurement rate window of 10 s⁻¹. Prior to any irradiation, two weak but distinct features centered near ~ 275 K and 360 K, whose characteristics are indicative of hole trapping, can be observed in the DLTS spectrum. Estimated from the value of the DLTS signal at the maximum of each peak, the concentrations for both two traps are on the order of low 10¹³ cm⁻³, which is close to the DLTS detection limit of 10⁻⁴− 10⁻⁵×background doping, confirming the as-grown p-GaN material is of high crystal quality. Irradiation with 1.8 MeV proton clearly enhances the hole trapping feature ~ 275 K, whose concentration monotonically increases as a function of proton fluence. Now the higher DLTS signal and improved signal-to-noise after irradiation allows excellent Arrhenius analysis to be achieved (shown in the Fig. 9.3 inset), from which an activation energy of $E_V + 0.48$ eV and a hole capture cross section of $3.2 \times 10^{-17}$ cm² are determined. Very precise calculation of the trap concentration requires full accounting for the volume of the depletion region within which the $E_V + 0.48$ eV traps are modulated by the measurement voltages used here (i.e., DLTS “lambda effect” correction), [21-22] and the resultant concentrations for this trap after being irradiated with proton fluences of $1 \times 10^{13}$ cm⁻² and $3 \times 10^{13}$ cm⁻² are $3.8 \times 10^{14}$ cm⁻³ and $6.4 \times 10^{14}$ cm⁻³, respectively. It is noted that the full width at half maximum (FWHM) of this DLTS feature is approximately 50 K, yielding a FWHM/peak temperature ($T_p$) ratio of ~ 0.18. Such a value is larger than the theoretically ideal value of FWHM/$T_p$ = 0.1 for a simple point defect. [23-24] This may suggest the participation of other, lower concentration traps with similar emission rates that are closely spaced in energy or possibly
implies that the $E_V + 0.48$ eV defect might not a simple point defect. However, further experiments including capture kinetics and DLTS at different bias conditions are required to confirm this attribution. Unlike the defect state(s) at $E_V + 0.48$ eV, the behavior of the other pre-existing trap feature at $\sim 360$ K as a function of proton fluence remains unclear due to its relatively weak signal after irradiation, especially in the sample exposed to $3 \times 10^{13}$ cm$^2$ proton fluence. In fact, this is mainly because the feature at 360 K is completely overwhelmed by the emergence of a newly created and much more dominant trap that peaks at a higher temperature near our DLTS measurement apparatus temperature limit. Although it is difficult to obtain a definitive energy level for this newly generated trap, its emission rate (DLTS peak temperature) implies it to be somewhat higher than $E_V + 0.9$ eV. Fortunately, this trap can be fully determined using DLOS as discussed in the following paragraphs.
Figure 9.4 (a) Room temperature DLOS steady state photocapacitance spectra for samples exposed to different proton fluences. (b) Optical cross sections obtained from the photocapacitance transient data. The fits to the data (solid line) were generated using Lucovsky model.
Figure 9.4 (a) shows DLOS steady state photocapacitance (SSPC) results between the energy ranges from \( E_V + 0.5 \text{ eV} \) to \( E_V + 3.6 \text{ eV} \) for the same set of samples. For p-type GaN, positive and negative onsets of the SSPC spectrum correspond to the presences of hole traps and electron traps, respectively. [26] The onset energies indicate the deep level energy position with respect to the specific band edge, i.e., valence band edge for hole traps and conduction band edge for electron traps. In the as-grown control sample, denoted by the black line in Fig. 9.4 (a), three positive onsets are observed at \( E_V + 1.50 \text{ eV} \), \( E_V + 2.42 \text{ eV} \) and \( E_V + 3.04 \text{ eV} \). Further analysis of optical cross section spectra in Fig. 9.4 (b) using the Lucovksy model reveals the feature at \( E_V + 3.04 \text{ eV} \) is actually composed of two hole traps at \( E_V + 3.00 \text{ eV} \) and \( E_V + 3.28 \text{ eV} \). [25] Here, the traps at \( E_V + 1.50 \text{ eV} \), \( E_V + 2.42 \text{ eV} \) and \( E_V + 3.28 \text{ eV} \) match earlier investigation of as-grown traps in NH\(_3\)MBE grown p-GaN samples as described in Chapter 6, whereas the \( E_V + 3.00 \text{ eV} \) trap is not observed in the prior study, suggesting its formation is possibly sensitive to specific growth conditions. The concentration of each DLOS-detected level is calculated by the SSPC step heights and listed in Table 9.1. As seen, the concentrations are all on the order of \( 10^{15} \text{ cm}^{-3} \) even before irradiation, much higher than those observed in the lower portion of the bandgap by DLTS.

Subsequent proton irradiation brings significant changes to the SSPC spectrum, where both substantial increases in trap concentrations of existing defects and the introduction of a new trap are clearly revealed. First, we consider the effects of proton irradiation on the pre-existing traps. As seen in Fig. 9.4 (a) and Table 9.1, the most prominent change due to irradiation is the monotonic increase of the as-grown trap at \( E_V + 2.42 \text{ eV} \), whose concentration reaches \( 4.4\times10^{15} \text{ cm}^{-3} \) at a fluence of \( 3\times10^{15} \text{ cm}^{-2} \), corresponding to a \( 3.0\times10^{15} \text{ cm}^{-3} \) increase. Similarly large irradiation effects are also
observed for the states at $E_V + 3.00$ eV and $E_V + 3.28$ eV, whose concentrations, after exposure to $3 \times 10^{13}$ cm$^{-2}$ protons, increase by $1.2 \times 10^{15}$ cm$^{-3}$ and $1.6 \times 10^{15}$ cm$^{-3}$, respectively. In stark contrast to those three states, the concentration for the $E_V + 1.50$ eV pre-existing trap is constant for all conditions, within the 10% diode-to-diode variation, and thus we conclude that this trap is insensitive to 1.8 MeV proton irradiation.

The post-irradiation results also reveal the creation of a new deep level that only is apparent after exposure to high energy protons, as shown by the SSPC onset at $E_V + 1.02$ eV in the Fig. 9.4 (a) inset. This trap becomes especially noticeable at the higher fluence of $3 \times 10^{13}$ cm$^{-2}$, where it exhibits a concentration of $3.0 \times 10^{14}$ cm$^{-3}$. Recalling the DLTS discussion above, this trap is likely to be responsible for the hole emission near the high temperature DLTS limit that was difficult to resolve by that measurement. In fact the trends of these two trap features also match, with the concentrations becoming large only after exposure to the higher proton fluence and are not observable for the as-grown control sample. Although with limited data sets (2 fluence values plus the as-grown sample), the introduction rate (defined as irradiation-induced trap concentration $\Delta n_T$ divided by proton fluence $\Phi$) [27] for this trap is approximately $10 \times$ lower than that of the irradiation induced $E_V + 2.42$ eV state. Such a significant difference upon identical proton irradiation reveals trap-specific sensitivities to proton irradiation, and is suggestive of different physical origins and/or physical defect configurations for each state, but far more detailed work beyond these first findings of irradiation-induced deep levels in p-GaN is needed for complete identification.
9.5 Discussion

Figure 9.5 Summary of proton irradiation induced traps in p-GaN.

Figure 9.6 Theoretically calculated formation energies as a function of Fermi level for native point defects in GaN. [28]
The distribution of 1.8 MeV proton irradiation induced traps in p-GaN is summarized in Fig. 9.5. In spite of the very sparse reports on defect levels in any form of p-type GaN to date, there are theoretical work and experimental studies in n-type GaN that can be compared to, [28-34] thus preliminary connections to potential physical sources is possible. For instance, previous theoretical studies based on density functional theory (DFT) calculations (as shown in Fig. 9.6) have predicted that the nitrogen vacancy (\(V_N\)) 3+/+ transition may correspond to a bandgap state at \(E_V + 0.47\) eV in p-type GaN, [29] which is very close to the \(E_V + 0.48\) eV trap energy measured here by DLTS. Additionally, the 1.8 MeV proton energy is also sufficient to displace nitrogen atoms (with an average threshold displacement energy of 32 eV in GaN) [30] and the proton irradiation can thus be expected to create significant concentrations of \(V_N\)-related defects. Hence, it is reasonable to tentatively assign the \(E_V + 0.48\) eV hole trap to a nitrogen vacancy related origin. Next, we note that the energy position in the bandgap for the newly generated trap at \(E_V + 1.02\) eV is very close to the widely observed gallium vacancy (\(V_{Ga}\)) related state in n-type GaN at \(\sim E_C - 2.5\) eV / \(E_V + 0.9\) eV. [28, 31, 32] The presence of this trap only after proton irradiation in p-type GaN is also consistent with the accepted view of gallium vacancies in GaN since it is not observed for the as-grown p-GaN, which is as expected due to the high formation energy of \(V_{Ga}\) in p-GaN, and is not even perceptible for the lower proton fluence irradiation condition (see Fig. 9.4 (a) inset). [28] Only after the higher proton fluence of \(3 \times 10^{13}\) cm\(^{-2}\) is the state seen, and considering that the average threshold displacement energy for Ga atoms in GaN is reported to be 73 eV, [30] the damage associate with the 1.8 MeV proton flux might well manifest in \(V_{Ga}\) creation, even for p-type GaN. Regarding the trap at \(E_V + 2.42\) eV, its energy position is similar to those observed in electron and
neutron irradiated GaN samples at $E_C - 0.8 \sim 1.0$ eV, which have been associated with either Ga or N interstitial defects (Ga$_I$ or N$_I$), as shown in Fig. 9.6. [28, 33] Typically, displacement damage generates Frenkel pairs that have equal numbers of vacancies and interstitials, therefore, in these samples, as the introduction rate for this $E_V + 2.42$ eV trap is much higher than the irradiation induced $V_{Ga}$-related trap at $E_V + 1.02$ eV, we consider it more likely a N$_I$ defect rather than Ga$_I$. In fact, this tentative assignment is further supported by the fact that the $E_V + 3.28$ eV state, which is often attributed to the $+/0$ transition of $V_N$ (the Frenkel pair counterpart of N$_I$), [34] increases in concentration at a similar rate, as seen in Table 9.1. Finally, regarding the other detected levels at $E_V + 1.50$ eV and $E_V + 3.00$ eV, they have not been previously reported or associated with any specific physical origins.

9.6 Summary

In summary, the combined application of DLOS and DLTS measurements performed on specially designed test structures have been able to reveal the energy positions and concentrations of deep levels throughout the entire p-GaN bandgap before and after proton irradiation. Multiple defect states were observed in the as-grown material, with all but one showing strong dependence on high-energy proton irradiation, and a state has been identified that only forms after proton irradiation for p-type GaN. The differential behaviors observed suggest different physical sources and comparison with prior theoretical calculations and device transport results suggest that nitrogen vacancy, nitrogen
interstitial and gallium vacancy related defects are culprits, consistent with their formation energies and displacement energies in the proton irradiation environment.
9.7 Reference


Chapter 10

Proton Irradiation Induced Threshold Voltage Shift in AlGaN/GaN HEMT devices and Heterostructures

10.1 Introduction

With the proton irradiation-induced trap states in GaN being fully characterized in prior chapters, we can now use such information in a systematic study of the proton irradiation-induced device degradations in AlGaN/GaN HEMTs, and explore the possible correlations between specific device degradation with the creation of defects at a materials level. As mentioned earlier, though the excellent transport properties coupled with relatively high radiation tolerance have made AlGaN/GaN HEMTs competitive candidates for high power high frequency electronics for space communication systems, [1-3] these devices still degrade after exposure to large doses of high energy particle irradiation. [4-13] For example, recent studies have shown that GaN-based HEMTs subjected to 1.8 MeV proton irradiation at fluences in the range of $10^{13}$~$10^{15}$ cm$^{-2}$ exhibit positive shifts in threshold voltage ($V_T$), reductions in saturation current ($I_{D,sat}$), and increases in contact resistance, along with degradation of other parameters. [6, 9, 10] Particularly, the positive $V_T$ shift has been widely observed, and is particularly insidious for device applications,
since it not only directly causes $I_{D,sat}$ reduction, but uncontrolled $V_T$ values will introduce instability and reliability issues at the circuit level. Although such irradiation induced $V_T$ instabilities have been extensively investigated over the last decade, and several models have been proposed to explain the phenomenon, [4-13] to date there has not been a firm consensus on the source and the exact degradation mechanism remains unclear. This is in part due to the difficulty in measuring and quantifying trap properties during radiation (i.e., energy levels, introduction rate and charge states) across the wide energy bandgap profile of AlGaN/GaN heterostructures, which is essential for precise modeling of trap-induced device degradation as a function of radiation exposure. Fortunately, thanks to the DLOS/DLTS characterizations, such information becomes available now, allowing for the re-investigation of the proton irradiation-induced $V_T$ instability.

In this chapter, we first characterize a commercial GaN-HEMT device exposed to high-energy proton irradiation to verify that the $V_T$ shift is the primary irradiation-induced degradation. Next, we use Schottky diodes on the heterostructures to investigate the $V_T$ evolution as a function of proton fluence, so as to explore the detailed degradation mechanism. With the combination of DLTS and DLOS to track trap state introduction, $C-V$ measurements to monitor changes in $V_T$, and TCAD (Technology Computer-Aided-Design) simulations to model the device behavior with the experimentally determined parameters as inputs, we are able to specify the location (i.e. buffer or barrier) and energy positions for the trap states that are responsible for the observed $V_T$ degradation. Finally, based on the revealed degradation model, possible approaches for mitigating $V_T$ instability through materials and device designs are proposed for the next generation radiation-hard GaN-HEMTs.
10.2 Proton Irradiation Induced Degradations in HEMT Device

A set of commercial AlGaN/GaN HEMTs were fully characterized before and after proton irradiation to reveal the major irradiation-induced degradation. [14] The HEMTs were mounted and measured on a 64-pin ceramic pin grid array package. After pre-rad characterizations, the devices were sent out for irradiation with all pins grounded. The proton irradiation was performed using a Pelletron accelerator that generates 1.8 MeV protons up to a total fluence of $1 \times 10^{14}$ cm$^{-2}$. The devices were kept at room temperature under vacuum throughout the radiation process.

![Graph](image1.png)

![Graph](image2.png)

Figure 10.1 (a) Output $I-V$ characteristics for AlGaN/GaN HEMT before and after 1.8 MeV proton irradiation at a fluence of $1 \times 10^{14}$ cm$^{-2}$. A significant drop in saturation current ($I_{DS,\text{max}}$) in irradiated device is clearly revealed. (b) Triode region of the output $I-V$ curves. Accounting for the $+0.59$ V threshold voltage shift, the on-resistance degradation is less than 0.05 $\Omega$-mm.
Figure 10.2 (a) Transfer $I$-$V$ curves for AlGaN/GaN HEMT before and after proton irradiation. Proton irradiation clearly induced a positive threshold voltage ($V_T$) shift. (b) Transconductance ($g_m$) vs. voltage for AlGaN/GaN HEMT before and after proton irradiation. Proton irradiation had little impact on transconductance peak values.

Figure 10.1 (a) shows a comparison of the output $I$-$V$ characteristics, where a substantial drop (~ 30%) in saturation current ($I_{DS, max}$) at $V_{GS} = 0$ V is clearly observed. While there also seems to be an increase in the on-resistance after proton irradiation, as shown in Fig. 10.1 (b), by comparing the output $I$-$V$ with the same saturation current (effectively, accounting for a $+0.59$ V threshold voltage shift), the on-resistance degradation is revealed to be less than 0.05 Ω-mm (<2%), and thus is a much smaller effect as compared with the $I_{DS, max}$ reduction. Figure 10.2 (a-b) presents the transfer characteristics of these devices before and after the proton irradiation, where a ~ 0.59 V positive $V_T$ shift is unambiguously revealed. The transconductance peak value reduces by ~ 5%, corresponding to a slight increase in total series resistance. Overall, the $I_{DS, max}$ reduction and the positive $V_T$ shift are the most prominent degradations at this proton
irradiation dose. Since the $I_{DS, \text{max}}$ reduction is just a consequence of the positive $V_T$ shift as shown in Fig. 10.1 (b), the $V_T$ degradation is indeed the primary degradation in proton irradiated GaN-HEMTs. In fact, such a degradation mode in proton-irradiated HEMT devices is substantially different from those induced by electrical stressors. While both RF and high voltage stress have been shown to introduce defects in the gate-drain access region and manifest as on-resistance increase and knee-walkout, [15, 16] high-energy particle irradiation seems to primarily influence the electrostatics under the gate.

10.3 Proton Irradiation Induced Threshold Voltage Shift in AlGaN/GaN Heterostructures

![Figure 10.3 Schematic diagram of the AlGaN/GaN test sample structure.](image)

To further investigate this effect, large area AlGaN/GaN Schottky diodes were employed. The use of these devices effectively eliminates possible impacts from device geometry, gate dielectrics, and parasitic effects in a real HEMT; thus the intrinsic $V_T$ behavior in AlGaN/GaN heterostructure can be revealed. The AlGaN/GaN heterostructure
was grown by NH$_3$MBE on a GaN template having a dislocation density in the mid 10$^8$ cm$^{-2}$ range. As shown in Fig. 10.3, the epitaxial structure consists of, from top to bottom, a 25 nm-thick un-intentionally doped (UID) Al$_{0.2}$Ga$_{0.8}$N barrier, an 800 nm-thick UID GaN buffer, and a 300 nm-thick highly doped n-GaN layer (Si~1×10$^{18}$ cm$^{-3}$). The highly doped n-GaN layer enables high quality epitaxy of the test structure and also screens any irradiation effects we expect to observe in the UID AlGaN/GaN heterostructure from the template. [17] Multiple 300 µm × 300 µm Schottky diodes were fabricated by depositing a 500 nm-thick Ti/Al/Ni/Au metal stack on AlGaN surface, which was annealed at 850 °C in N$_2$ for 30 seconds to form an Ohmic contact, and depositing an 8 nm-thick Ni layer on the AlGaN to serve as a semitransparent Schottky contact, which facilitated optical measurements. Details of the Schottky diode fabrication process can be found in earlier work. [18, 19]

Prior to irradiation, the sample was first characterized by 1 MHz capacitance-voltage ($C$-$V$) measurements at room temperature. The doping profile revealed a background n-type carrier density of 2×10$^{15}$ cm$^{-3}$ in the as-grown UID GaN buffer. By analyzing the integral of the $C$-$V$ curve, the $V_T$ values associated with the formation of 2DEG at AlGaN/GaN interface were determined for each diode. [20] To yield statistically valid results, multiple diodes were measured over the whole wafer, all revealing similar pre-radiation $V_T$ values with a small diode-to-diode variation of ±0.03 V. Additionally, internal photoemission (IPE) measurements were performed to directly measure the Ni/AlGaN Schottky barrier height in the samples. Details of the IPE procedure and analysis can be found in Reference 21.
After the initial, pre-radiation screening, the sample was diced into multiple pieces, and each piece was separately exposed to 1.8 MeV protons at a specific fluence of $5 \times 10^{12}$, $1 \times 10^{13}$, $3 \times 10^{13}$, $5 \times 10^{13}$, $6 \times 10^{13}$, $8 \times 10^{13}$ or $1 \times 10^{14}$ cm$^{-2}$. The irradiation conditions were identical to the ones used in prior chapters as well as in the HEMT device study. [14] C-$V$ and IPE measurements were then performed for each radiation condition on the same diode as measured before irradiation, thus the changes in $V_T$ and $\phi_B$ can be revealed and compared as a function of proton fluence.

Figure 10.4 Room temperature 1 MHz C-$V$ results for AlGaN/GaN Schottky diodes before and after irradiation. The inset reveals the shift of measured $V_T$ as a function of proton fluence.
Figure 10.4 shows the $C-V$ measurement results for AlGaN/GaN Schottky diodes before and after all radiation exposures. As seen, the $C-V$ curves shift toward a more positive voltage as irradiation fluence increases. The inset illustrates this effect more clearly by plotting $V_T$ as a function of proton fluence, where a monotonic but non-linear increase of $V_T$ is revealed. The maximum shift of $+0.63$ V occurs for the sample exposed to a fluence of $1 \times 10^{14}$ cm$^{-2}$ protons, as $V_T$ increases from $-2.98$ V before irradiation to $-2.35$ V after irradiation. In fact, such a large shift in $V_T$ is similar to the one detected in GaN HEMTs that were irradiated at identical conditions, [14] suggesting that the $V_T$ shift in the AlGaN/GaN heterostructure Schottky diodes observed here is indeed a major component of the total $V_T$ degradation in actual HEMT devices.

10.4 Factors That May Impact Threshold Voltage in AlGaN/GaN Heterostructure

Figure 10.5 Schematic band diagram of Ni/AlGaN/GaN Schottky diode.
To understand the dependence of the threshold voltage on proton fluence, it is important to first identify all the parameters that can influence $V_T$. Figure 10.5 shows a schematic band diagram of Ni/AlGaN/GaN Schottky diode. According to Poisson equation, the threshold voltage can be given by: [22]

$$V_T = \frac{\phi_B}{q} - \frac{\Delta E_C}{q} - \frac{d \cdot \sigma}{\varepsilon_{AlGaN}} - \frac{E_{fo}}{2\varepsilon_{AlGaN}} - \frac{d \cdot Q_{it}}{\varepsilon_{AlGaN}} - \frac{Q_{GaN}}{C_{effective}(Q_{GaN})}$$  \hspace{1cm} (10.1)

Here, $\phi_B$, $\Delta E_C$ and $\sigma$ are the Ni/AlGaN Schottky barrier height, AlGaN/GaN conduction band offset and net polarization charge at the AlGaN/GaN interface, respectively. The terms $\varepsilon_{AlGaN}$ and $d$ represent the AlGaN dielectric constant and thickness. $E_{fo}$ is the 2DEG Fermi level position with regard to the GaN conduction band edge at the AlGaN/GaN interface. Three terms $Q_{AlGaN}$, $Q_{it}$ and $Q_{GaN}$ represent the trapped charges in the AlGaN barrier, at the AlGaN/GaN interface, and in the GaN buffer, respectively. Finally, $C_{effective}(Q_{GaN})$ is the effective capacitance for the charges in GaN. Each of these terms has been individually considered or measured to determine whether it is responsible for a change in $V_T$. 

199
Figure 10.6 Internal Photoemission (IPE) measurement results for AlGaN/GaN Schottky diodes before and after $5 \times 10^{13}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$ 1.8 MeV proton irradiation. The solid lines are linear fittings for obtaining the onset energies (Ni/AlGaN Schottky barrier).

First, Fig. 10.6 shows that the Ni/AlGaN Schottky barrier height $\phi_B$ measured by IPE was unchanged at 1.4 eV ($\pm0.1$ eV) before and after proton irradiation, indicating the first term of Equation (10.1) is not responsible. Secondly, the fundamental material parameters $\Delta E_C$ and $\sigma$ are very unlikely to exhibit a significant change because the maximum dose of proton irradiation used here ($1 \times 10^{14}$ cm$^{-2}$) is well below the amorphization threshold of $\sim10^{16}$ cm$^{-2}$ for GaN. [23] Similarly, the dielectric constant $\varepsilon_{AlGaN}$ and thickness $d$ of the AlGaN barrier do not change in this proton fluence range, which is indeed consistent with the $C-V$ results as the accumulation capacitance shows minimal change after irradiation indicating $d/\varepsilon_{AlGaN}$ is constant. Additionally, $E_{fo}$ itself is of
a very small value (< 100 mV), thus there should be very little change for this term before and after irradiation, which is certainly not enough to produce the large changes (~ +0.63±0.05 V) in $V_T$. Hence, with the first four terms in Equation (10.1) all being excluded, the only possible causes left for the sizable positive $V_T$ shift are negatively charged irradiation induced defect states within the AlGaN/GaN structure.

10.5 Impact of Proton Irradiation Induced Defects on Threshold Voltage

To further discriminate the impact from traps at different locations on $V_T$, TCAD Silvaco Altas simulations were conducted. In order to yield the most accurate simulation possible with minimal fitting parameters, experimentally determined values for AlGaN composition, doping concentration, barrier thicknesses and Schottky barrier height were used. With the baseline case (pre-radiation) set, additional simulations were carried out by separately placing traps at different physical locations, i.e., in the AlGaN barrier, at the AlGaN/GaN interface and in the GaN layers, respectively. Hence, by comparing the simulated $V_T$ dependencies with the measured data, specific defect states responsible for changes in $V_T$ can be identified.
Figure 10.7 Carrier removal effect as a function of 1.8 MeV proton fluence in a separate n-type GaN sample. The dashed line is for fitting the carrier removal rate. Inset shows the n-type doping profiles extracted from C-V measurements.

The effect of irradiation induced defects within the GaN layer was considered first. In prior studies, we have directly correlated the introduction of negatively charged defect states at $E_C - 1.25$ eV and $E_C - 3.25$ eV with the carrier removal effect in n-type GaN. [24, 25] For the purpose of this study, we verify this effect in a separate NH$_3$MBE-grown n-type GaN sample that experienced identical proton irradiation as these AlGaN/GaN heterostructures. As clearly seen in Fig. 10.7, the n-type carrier density linearly reduces as a function of proton fluence at a reduction rate of 500 cm$^{-1}$, which in fact represents the total introduction rate (i.e., the number of defects created by one proton per cm) for all negatively charged states in proton irradiated n-GaN. As our previous DLOS studies
revealed the $E_C - 3.25$ eV trap to be most dominant in concentration, [24] for simplicity here, we assume the presence of only an $E_C - 3.25$ eV trap in GaN layer with an introduction rate around $500 \text{ cm}^{-1}$. In addition, since the penetration depth of $1.8$ MeV protons in the test structure is $\sim 20 \mu\text{m}$, estimated by Transport of Ions in Matter (TRIM) simulations, we assume a uniform distribution of this trap in both $800 \text{ nm UID}$ buffer layer and $300 \text{ nm n}^+\text{-GaN}$ layer.

![Figure 10.8 TCAD simulation of $\Delta V_T$ as a function of proton fluence. The compensating trap at $E_C - 3.25$ eV is assumed to be present only in the GaN buffer. Simulation results using introduction rates of 400, 500 and 600 $\text{cm}^{-1}$ are shown, as well as experimentally obtained values.](image)
Figure 10.9 The band diagrams at equilibrium conditions for AlGaN/GaN Schottky diodes before and after $4 \times 10^{13}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$ proton irradiation, assuming irradiation induced traps at $E_C - 3.25$ eV were only present in GaN layers, with an introduction rate of 400 cm$^{-1}$.

The simulation results are shown in Fig. 10.8. As seen, the simulated $V_T$ behavior matches the measured result reasonably well throughout the entire range of proton fluence values without additional fitting parameters. This provides very strong support to a model where it is the irradiation-induced traps within the GaN buffer that causes large positive
shift in $V_T$. It is noted that the $V_T$-fluence relationship is sub-linear, which can be understood from the band diagram shown in Fig. 10.9: from pre-irradiation to lower proton fluence of $4 \times 10^{13}$ cm$^{-2}$, the irradiation induced acceptors mainly compensate the background n-type donors in the buffer and drastically lower the Fermi level toward valence band; whereas at the higher proton fluences between $4 \times 10^{13}$ cm$^{-2}$ to $1 \times 10^{14}$ cm$^{-2}$, as the Fermi level is pinned to the defect state, only the acceptors close to interface will further compensate the carriers in the 2DEG channel, leading to a more gradual shift in $V_T$.

Next, we consider a possible scenario in which the traps created within the AlGaN barrier are influencing $V_T$. M. Hayes et al. reported similar carrier removal rates (thus, introduction rates for compensating defects) of 300–500 cm$^{-1}$ for both GaN and Al$_{0.12}$Ga$_{0.88}$N under 2 MeV proton irradiation, [26] which one might indeed expect considering the physical nature of the displacement damage and similar bonding energies for GaN and low Al content AlGaN, which is typically used for HEMT barrier layers. To simulate the AlGaN compensation effect, a trap at $E_C$ - 3.7 eV that has been previously observed in bulk AlGaN is introduced in the barrier layer, [27] since a defect state at this position in the bandgap would likely be an efficient electron compensation center. However, a 500 cm$^{-1}$ introduction rate for this state results in very small $V_T$ shifts (~ +0.03 V at a fluence of $1 \times 10^{14}$ cm$^{-2}$) and the $V_T$ shifts are linear with proton fluence, both inconsistent with experimental results. In fact, in order to produce the $V_T$ shifts observed, an introduction rate between 10,000–15,000 cm$^{-1}$ would be required for AlGaN traps, which is more than 20× higher than the experimentally measured value and clearly not physically reasonable. A similar argument can be made to rule out AlGaN/GaN interface traps simply on the basis of it requiring an even more non-physical introduction rate (approximately
250,000–375,000 cm$^{-1}$ assuming they distribute within 0.5 nm width at interface) to create the massive amount of localized defects needed to explain the $V_T$ shift. Therefore, these simulations indicate that trapping in the AlGaN or AlGaN/GaN interface is not responsible for the observed $V_T$ shift, confirming that GaN traps are likely the source for such degradation.

Figure 10.10 The growth structures for AlGaN/GaN heterostructures with unintentionally doped (UID) buffer and Si-doped buffer.
This buffer compensation driven mechanism for $V_T$ shift can be experimentally verified by comparing the $V_T$ evolutions as a function of proton fluence for devices with different buffer designs. To this end, a new sample is introduced, which has almost identical structure as the earlier AlGaN/GaN sample except for that the 800 nm GaN buffer is now intentionally Si-doped to a concentration of $3.5 \times 10^{16}$ cm$^{-3}$ instead of the UID buffer for which the n-type background is measured to be $\sim 2 \times 10^{15}$ cm$^{-3}$, as shown in Fig. 10.10. The doping density was confirmed by $C-V$ measurement before irradiation. The hypothesis was that if the traps responsible for the $V_T$ shifts were in the GaN, these traps would first have to compensate the n-type doping in buffer before moving the Fermi level and inducing
$V_T$ shifts. Therefore, the unintentionally doped sample would show $V_T$ shifts immediately with proton irradiation while the doped sample would have no $V_T$ shift until a significant fluence was reached that compensated all the donors in the GaN buffer. However, if the trapping were in the AlGaN or AlGaN/GaN interface the change in GaN doping would have little effect on the measured threshold voltage. The results of this experiment are shown in Fig. 10.11. It is clearly revealed that the sample with undoped buffer immediately shows a shift even at the lowest fluence of $5 \times 10^{12}$ cm$^{-2}$, whereas for the sample with doped buffer, the onset of significant $V_T$ shift is delayed until $\sim 4 \times 10^{13}$ cm$^{-2}$. This is generally consistent with the simple model and demonstrates the role and mechanism of irradiation induced GaN buffer traps in impacting $V_T$ degradation.

10.6 Modeling the Buffer Trap Impact on Threshold Voltage

With the $V_T$ degradation mechanism being confirmed, we now explore possible approaches to mitigate this effect through materials and design optimizations. To this end, developing an analytic model is imperative, because unlike TCAD simulation, analytic modelling directly reveals the major impacting factors, thus guiding the systematic explorations of optimization pathways.
Figure 10.12 Schematic diagrams of back-gating effect in n-channel Si MOSFET. By applying a negative back-gate voltage $V_{\text{SB}}$, threshold voltage shifts toward more positive values. [28]

In fact, it is noted that the evolution of band diagrams in proton irradiated AlGaN/GaN structure is similar to the one associated with the back-gating effect in Si MOSFET as shown in Fig. 10.12, [28] thus we can build up from that well-understood model. Despite the similarities, there are two major differences between these phenomena: first, the Fermi-level in the proton irradiated GaN buffer is determined by the total distribution of pre-existing and proton irradiation induced defects, whereas in the Si MOSFET, the quasi Fermi-level in the buffer is determined by the back-gate bias; second, the density of the compensating center in the proton irradiated GaN buffer increases as a function of proton fluence, whereas the doping in MOSFET remains a constant value for different bias conditions. Taking these effects into account, we can develop the following
simple model to depict the proton irradiation induced $V_T$ shift of AlGaN/GaN heterostructure:

$$\Delta V_T = \frac{d}{\sqrt{\varepsilon}} \sqrt{(\varphi \times I.R. ) \phi_{GaN, final} - \sqrt{N_{A,initial} \phi_{GaN, initial}}}$$  \hspace{1cm} (10.2)

Here, $d$ and $\varepsilon$ are the thickness and dielectric constant for barrier layer, $\varphi$ is proton fluence, I.R. stands for the linear introduction rate of total compensating centers (i.e., carrier removal rate) in GaN, $N_{A,initial}$ is pre-existing net compensating density in buffer, $\phi_{GaN, final}$ and $\phi_{GaN, initial}$ represent the total band bending in the buffer layer before and after irradiation, respectively.

Figure 10.13 Comparison of the irradiation induced threshold voltage shifts that are obtained from experiment, TCAD simulation and analytic modeling (Equation (10.2)). Also listed are the parameters used in analytic modeling.
To further verify this model, ΔVT predicted by Equation (10.2) is plotted as a function of proton fluence, and compared with experimental data and TCAD simulation results. As shown in Fig. 10.13, reasonable consistency has been achieved throughout the whole fluence range (< 1×10^{14} \text{ cm}^{-2}), confirming that this simple model at least provides a good first order prediction in these irradiation conditions. Hence, based on Equation (10.2), the major impacting factors of proton irradiation induced ΔVT shift have been narrowed down to compensation center introduction rate, pre-existing compensation center density, band bending in GaN buffer layer, and AlGaN barrier thickness.
10.7 Possible Approaches to Mitigate Irradiation Induced Threshold Voltage Instability

10.7.1 Irradiation Induced Defect Density

Figure 10.14 TCAD simulations of buffer trap introduction rate influencing threshold voltage shift. The plots assume a 25 nm AlGaN barrier, pre-existing background n-type doping $2 \times 10^{15}$ cm$^{-3}$, no pre-existing acceptors and compensating center at $E_C - 3.25$ eV.

Now, we examine these factors one by one, and explore the corresponding approaches for further reducing $V_T$ instability. First, we consider the term of introduction rate for irradiation induced compensating centers. As shown in Fig. 10.14, the introduction rate clearly plays a major role in determining the radiation damage, and as expected smaller
introduction rate is more favorable as it leads to less $V_T$ shift at a fixed proton dose. Although one may further anticipate all GaN semiconductors have an identical defect introduction (carrier removal) rate, there is in fact evidence showing that the defect introduction rates in real samples may be growth dependent, as described below.

Figure 10.15 Structures for n-type GaN samples grown by NH3MBE and PAMBE.

Figure 10.16 (a-b) C-V results and n-type doping profiles in both samples before and after proton irradiation.

213
The defect generation in simultaneously irradiated n-type GaN grown by NH₃MBE and PAMBE have been comparatively studied. Figure 10.15 shows the structures and doping for the two samples grown by different techniques. Fig. 10.16 (a) and (b) present the C-V characteristics of the same diodes before and after proton irradiation on each sample. While the carrier removal effects are clearly observed in both cases, the amounts of the removed n-type carriers are indeed different. At a 1.8 MeV proton fluence of $1 \times 10^{13}$ cm$^{-2}$, NH₃MBE grown GaN reveals a carrier reduction of $6.0 \times 10^{15}$ cm$^{-3}$ while the n-type carriers reduced by $4.0 \times 10^{15}$ cm$^{-3}$ in the PAMBE grown sample, suggestive of an increased concentration of compensation centers in the irradiated NH₃-MBE grown GaN films.

Figure 10.17 Summary of proton irradiation induced traps in GaN samples grown by two different techniques.
DLTS and DLOS were applied on the same diodes before and after irradiation to characterize all proton irradiation induced defects in both samples, and the results are summarized in Fig. 10.17. As seen, though the identical proton irradiation induces the same traps (at the same energy positions) in both cases, the total proton-induced trap concentration in the NH$_3$-MBE grown GaN ($2.5 \times 10^{16}$ cm$^{-3}$) is $\sim 2 \times$ higher than that in the PAMBE grown GaN ($1.5 \times 10^{16}$ cm$^{-3}$). This is much greater than the measurement uncertainty (typically $\pm 10\%$), indicating there may indeed be a growth-mode dependence. In addition, the irradiation-induced trap at $E_C - 3.25$ eV, which has been previously revealed to be responsible for the carrier removal effect, does show a smaller concentration in the sample grown by PAMBE, consistent with the less carrier removal detected in that sample. The exact reason for such a difference is still unclear, and we speculate this may be related to the hydrogenation and dehydrogenation effect: [29] as compared with PAMBE grown samples, NH$_3$MBE grown films are expected to contain more hydrogen species sourced by NH$_3$, [30] causing a more evident hydrogenation and/or dehydrogenation effect after proton irradiation. While further investigation is needed to confirm that hypothesis, these results do suggest that proper materials engineering may be possible to reduce the introduction rate and mitigate radiation induced $V_T$ degradation.
Another way to reduce $V_T$ degradation through the introduction rate concept is thermal annealing. As has been demonstrated in Chapter 8, low temperature thermal annealing (at ~ 400 °C) can substantially reduce the concentrations of proton irradiation induced compensating centers. This results in a smaller “effective introduction rate”, and thus may lead to a significant recovery of $V_T$ degradation. Currently, detailed study of annealing effects on $V_T$ shift in AlGaN/GaN heterostructures is still ongoing. However, this effect has already been reported in AlGaN/GaN HEMT devices. [31] As can be seen in Fig. 10.18, $V_T$ first positively shifts after proton irradiation, then recovers back towards pre-rad condition after thermal annealing, all consistent with our predictions. Noting that the proton energy used in that study is much smaller than the one we applied on our samples, thus greater displacement damages were induced and larger $V_T$ degradation was observed there. [32]
10.7.2 Buffer Design

Figure 10.19 TCAD simulations of pre-existing acceptor-like states in GaN buffer affecting proton irradiation induced threshold voltage shift. The plots assume a 25 nm AlGaN barrier, pre-existing background n-type doping $2 \times 10^{15}$ cm$^{-3}$, the major compensate center at $E_C - 3.25$ eV trap and the total introduction rate 500 cm$^{-1}$.

Next, we consider the pre-existing acceptor concentration and band bending in GaN buffer layer. In fact, these two terms are correlated with each other in most conditions, because the later term is ultimately determined by the Fermi level position in the buffer, thus strongly depends on the bandgap state distribution, including pre-existing acceptor states. Here, the concentrations of pre-existing donor and acceptor states are two major parameters that can be controlled during growth. Although, in the earlier section, adding
n-type donors in the buffer has proven effective in delaying $V_T$ evolution, in real HEMT devices, a doped buffer is usually undesirable. Therefore, we now explore how to manipulate pre-existing acceptor concentrations ($N_A$) for reducing $V_T$ degradation. Figure 10.19 presents the TCAD simulations of $V_T$ evolution as a function of proton fluence with different initial $N_A$. As seen, the higher the pre-existing defect density, the less $\Delta V_T$ at almost all fluences. In fact, this effect can be understood by analyzing the sub-linearity of $\Delta V_T$ vs. fluence curve with $N_{A,\text{initial}} = 0$: the beginning of this curve has a larger slope, as Fermi level is drastically moving towards VB, whereas at larger fluences, $V_T$ shift tends to slow down, due to Fermi level pinning at the acceptor state. Therefore, when pre-existing acceptor density is large, it is equivalent to a point on the curve at a relatively large fluence, thus, by avoiding the initial rapid $V_T$ change, the same amount of additional proton irradiation will lead to less $V_T$ degradation as compared with $N_{A,\text{initial}} = 0$ case. Since very well controlled acceptor doping without sacrificing device performance is the key for this approach, [33] implementing it in a real device could be challenging.
10. 7. 3 Barrier Thickness

Figure 10.20 Schematic diagram of AlGaN/GaN heterostructures with different barrier thickness.

Figure 10.21 (a-d) Room temperature 1 MHz $C-V$ measurement results for AlGaN/GaN Schottky diodes with different barrier thicknesses before and after proton irradiation.
Figure 10.22 TCAD simulation and experimentally obtained threshold voltage shifts ($\Delta V_T$) as a function of AlGaN barrier thickness at proton irradiation fluences of $4 \times 10^{13}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$. The dashed lines are linear fits to the simulation results.

We notice that in Equation (10.2), the $V_T$ shift depends linearly on the barrier thickness; thus, we investigate the dependence of irradiation-induced $\Delta V_T$ as a function of AlGaN barrier thickness. Four samples were grown, with identical structures (as shown in Fig. 10.20) to the AlGaN/GaN sample with UID buffer as described earlier, except for now their AlGaN thicknesses are 20, 23, 27 and 31 nm, respectively. The same diodes were characterized prior and after proton irradiation at fluences of $4 \times 10^{13}$ cm$^{-2}$ and $1 \times 10^{14}$ cm$^{-2}$, and the resultant $C-V$ curves and $\Delta V_T$s are plotted in Fig. 10.21 and Fig. 10.22, respectively. As seen, the experimental results match very well with the simulations that assume only the presence of an $E_C - 3.25$ eV trap in the GaN buffer with an introduction rate of 500 cm$^{-1}$. This result again verifies the buffer trapping model. More importantly, it reveals that
barrier thickness scaling can be an effective way to reduce the irradiation induced \( V_T \) degradation. Particularly, lattice-matched AlInN barrier, which is capable of providing decent 2DEG density at much smaller thicknesses, is ideal for improving HEMT \( V_T \) stability under proton irradiation. [34, 35]

10. 8 Summary

In summary, proton irradiation induced \( V_T \) shift in AlGaN/GaN HEMT devices and heterostructures is systematically investigated, and has been correlated to the generation of compensating centers in the GaN buffer. Not only can the monotonic, non-linear evolution of \( V_T \) as a function of proton fluence be very well explained by the model accounting for GaN buffer traps without any fitting data, but also the change in buffer design substantially impacts the \( V_T \) evolution, clearly demonstrating that the buffer traps play an important role in causing the \( V_T \) instability in irradiated HEMT devices. Modeling of the buffer traps’ impact on \( V_T \) shift reveals that proper material and structural optimization may mitigate such an effect, and reducing the barrier thickness would be one of the most effective approaches for future irradiation-hard GaN technology.
10.9 Reference


Chapter 11

Conclusions and Future Directions

11.1 Conclusions

Expansion of GaN-based semiconductor technology for new functionalities will primarily depend on the capability of growing high quality novel materials and improving device reliability. Essential to both is a comprehensive understanding of the electrically active deep states in the materials. Defect presence and properties, as well as how they respond in intended device applications, will be critical, but unfortunately, this has only been sparsely reported. Therefore, the goal of this work has been to conduct an in-depth study of defect states in a wide range of state-of-the-art III-nitride materials, and explore their role in device level degradation, in particular, under high-energy proton irradiation for space communication applications.

To enable these objectives, a set of capacitance-based measurements, including DLTS, DLOS, $C-f$, $LCV$, which facilitated the quantitative characterization of deep states throughout the 3.4 eV GaN bandgap, has been performed on a variety of materials, such as non-polar m-plane GaN, NH$_3$MBE grown p-type GaN, proton irradiated n-type and p-type GaN. Systematically varied growth, irradiation and annealing conditions allowed for
methodical investigation of defect behaviors and properties, shedding light on the defect physical sources and atomic configurations. This information is important for suppressing defect formation through growth optimizations. Moreover, the impacts of these defects on materials electrical and optical properties, and ultimately the device performance, were also carefully examined where possible. Particularly, the proton irradiation-induced defect states at the materials level have been correlated with the primary degradation mode at device level (i.e., threshold voltage instability). With the detailed mechanism being unambiguously revealed and modeled, approaches for mitigating such degradation have been proposed and experimentally demonstrated. The following sections summarize the major research achievements and highlights for these two major thrusts of this dissertation.

11.1.1 The Presence and Properties of Defect States in III-Nitride materials

Chapter 4 and 5 report the first comprehensive deep level study of m-plane GaN. By comparing simultaneously grown c-plane and m-plane GaN, substantial impacts of growth surface on the defect formations were revealed. Both external and native defects were observed with much higher concentrations in m-plane GaN than c-plane GaN. Traps at $E_C - 0.14$ eV, $E_C - 0.20$ eV and $E_C - 0.66$ eV that were absent in c-plane GaN, were detected in m-plane samples. Among all these traps, $E_C - 0.14$ eV and $E_C - 0.66$ eV states were found to correlate linearly with V/III ratio (and/or oxygen content), indicative of their V/III ratio influenced (or oxygen related) origins.

In Chapter 7 and 8, the distribution and thermal stability of high-energy proton irradiation induced defects in the entire GaN bandgap was revealed for the first time. Proton
irradiation not only created new traps, but also brought monotonic concentration increases for all the pre-existing traps. Systematically controlled thermal annealing led to first order reductions in concentration for traps at $E_C - 0.13$ eV, $E_C - 0.16$ eV, and $E_C - 2.50$ eV; whereas more gradual reductions were observed for traps at $E_C - 0.72$ eV, $E_C - 1.25$ eV and $E_C - 3.28$ eV. Conversely, traps at $E_C - 0.20$ eV and $E_C - 0.25$ eV increased in concentration during annealing. These differential responses were due to different introduction/reduction mechanisms linked to individual defect origins.

![Graph showing concentration changes](image)

Figure 11.1 Summary of as-grown deep states in c-plane and m-plane n-type GaN, and proton irradiation induced deep states in n-type GaN.
In fact, comparing the novel materials grown along unconventional orientations and state-of-the-art materials exposed to high-energy proton irradiation, completely different sets of “new” traps were observed by DLTS (shown in Fig. 11.1). This is suggestive of defect origins and/or configurations specifically correlated to either m-plane growth surface configuration/dynamics or atomic displacement, therefore different solutions are needed to suppress their formations.

In Chapter 6, a p+/p/n+ diode structure was specially devised and enabled the capacitance-based, high frequency, high accuracy, defect characterization of p-GaN for the first time, where significant impact of growth method on deep level formation was clearly revealed. The emerging NH₃MBE, though far less mature than MOCVD, yields a less total trap concentration, suggesting the possibility of further improving performance for p-GaN containing devices through NH₃MBE technology. In Chapter 9, proton irradiation effects on deep states in p-GaN were investigated. By comparing with prior theoretical calculations and experimental results in n-type GaN, the nitrogen vacancy, nitrogen interstitial and gallium vacancy related defects have been ascribed as the origins for major traps detected in p-GaN.

11.1.2 The Impact of Proton Irradiation Induced Defects on AlGaN/GaN HEMT Device Performance

Chapter 10 dealt with the reliability of AlGaN/GaN HEMT devices exposed to high-energy proton irradiation for space communication applications. Comprehensive device level characterization revealed that positive shift of $V_T$ is the primary proton
irradiation induced degradation in HEMT devices. Systematic investigations of AlGaN/GaN heterostructures, including both carefully designed experiments and TCAD simulations, have correlated this effect to the generation of compensating centers in the GaN buffer. Specifically, the sub-linear evolution of $V_T$ as a function of proton fluence can be well modeled using experimentally measured GaN buffer trap energy and introduction rate. Further, changing buffer designs substantially altered the $V_T$ evolution, clearly demonstrating that the buffer traps play a major role in causing the $V_T$ instability. By analogizing to the Si-MOSFET back-gating phenomenon, an analytic model was developed to describe this irradiation-induced effect. The model suggests particular material and structural optimization path to mitigate such degradation, and scaling down the barrier thickness has been demonstrated as one of the most effective approaches for improving the radiation hardness of Ga-polar AlGaN/GaN HEMT.

11.2 Future Directions

With the electronic and optoelectronic applications of GaN-based semiconductors continuing to grow in scale and complexity, the knowledge regarding the crystal defects and their impact on device reliability will surely play more significant roles, and possibly even guide the future breakthroughs of III-Nitrides. Fortunately, the complete set of well-developed defect characterization techniques has been demonstrated to be powerful for exploring defect distributions throughout the bandgap and monitoring defect evolution as a function of systematically controlled parameters. These techniques can be readily applied to almost all the emerging novel materials and integrated with device level investigations.
to help solve “mysteries” in real applications. The following sections list some research topics that are either already on-going or, from the perspective of this dissertation, interesting to pursue in the near future.

In the realm of developing novel materials, characterizing defects in AlInN is most imperative. With a large spontaneous polarization field coupled with lattice-matching (LM) to GaN buffer, 17~18% Al\textsubscript{1-x}In\textsubscript{x}N barrier provides a higher 2DEG density and better structural stability as compared with the AlGaN barrier. [1-4] There have already been many AlInN/GaN devices demonstrating promising performance, although the material growth of AlInN is still far from well optimized. [2-4] In fact, the defect incorporation in LM AlInN is known to be an important issue, as studies has shown that carbon and oxygen impurities were incorporated with very high concentrations (on order of $1 \times 10^{18}$ cm\textsuperscript{-3}). [5] Based on our m-plane GaN study, these impurities likely create a high density of trap states inside the AlInN material. Hence, systematic investigations of deep levels in AlInN are expected to reveal the role of these high-density impurities. Furthermore, such AlInN studies will expand understanding of the material, optical and electrical properties, ultimately bringing further improvements to material quality and device performances.

Similarly, exploring defects incorporated in GaN-based materials and devices grown along N-face orientations is also of great practical importance. As mentioned before, due to the unique device structure and polarization field, N-polar HEMTs are of great interests for applications in the next generation electronics for high frequency applications. [6-8] However, despite the already demonstrated device advantages, still very little is known about point defects and their impact on physical properties and device characteristics to date. [9] In fact, the presence and properties of the trap states in those
materials are expected to be unique as has been revealed by the c-plane vs. m-plane comparison in this dissertation. Thus, defect studies of N-polar device structures and component layers would not only further guide the material optimization, leading to further enhanced device performance, but also is of fundamental interest for understanding the correlations between crystal orientation and defect incorporation in GaN.

In addition to GaN-based semiconductors, recently, other wide bandgap semiconductors are also generating extensive research interests, among which the beta-phase of gallium oxide (β-Ga$_2$O$_3$) has been considered as an attractive candidate for future power electronic device applications. This is being driven by its advantageous materials properties for high voltage electronics applications, e.g. a 4.8 eV bandgap, a breakdown field of 8 MV/cm and a Baliga’s figure of merit (FOM) that is more than 4 times larger than those for GaN and SiC. [10-12] Furthermore, unlike GaN, β-Ga$_2$O$_3$ single-crystal bulk substrates that can support homoepitaxial growth of device heterostructures are already available, thus providing a potential path for future low cost production. Moreover, the recent demonstrations of promising Ga$_2$O$_3$-based transistors using native substrates have ignited even greater interest for a future β-Ga$_2$O$_3$ device technology. [10-11] However, due to the relative immaturity of β-Ga$_2$O$_3$, experimental information regarding the electrically active defects is fairly limited. To this end, just like at the initial stage of GaN technology twenty years ago, comprehensive studies of the defect formation in this material, including the impact of such as growth techniques, orientations, dopants, etc., will be crucial for its rapid development.

With regard to the irradiation effects, future research directions may mainly extend in two thrusts: a) irradiation effect of novel device structures such as AlInN/GaN and N-
face devices; b) irradiation effect in operational HEMT devices. For the first thrust, knowledge from this dissertation has pointed out that the buffer trapping in GaN for Ga-polar AlGaN/GaN is the major reason for $V_T$ degradation, and scaling down the barrier thickness would be the most effective approach to suppress the irradiation impact. Here, the LM AlInN barrier, due to the large spontaneous polarization field, provides an opportunity to drastically reduce the barrier thickness from 20~30 nm in conventional AlGaN/GaN device to ~ 10 nm, and thus may lead to a significant mitigation of $V_T$ instability. [4] This hypothesis, however, has not yet been investigated. On the other hand, N-polar HEMTs employ a totally different GaN/AlGaN/GaN device structure, and thus may be associated with a unique degradation mechanism that has yet to be explored. Finally, all the device-level irradiation studies in this dissertation were done with all terminals grounded, but this does not reflect “real” operational conditions. Indeed, a recent preliminary study has shown evidence suggesting that high energy particle irradiation induced degradations seem to be more severe in devices at “semi-on” conditions, which is indeed more close to the real operating condition for devices deployed in space systems. Therefore, further investigations of that phenomenon, building on the knowledge obtained in this study, would be essential for fully understanding the irradiation effect in GaN-based devices.
11.3 Reference

Bibliography


