Electron Injection-induced Effects In III-nitrides: Physics And Applications

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ELECTRON INJECTION-INDUCED EFFECTS IN III-NITRIDES:
PHYSICS AND APPLICATIONS

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Physics
in the College of Arts & Sciences
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ABSTRACT

This research investigated the effect of electron injection in III-Nitrides. The combination of electron beam induced current and cathodoluminescence measurements was used to understand the impact of electron injection on the minority carrier transport and optical properties. In addition, the application of the electron injection effect in optoelectronic devices was investigated.

The impact of electron injection on the minority carrier diffusion length, \( L_n \), was studied at various temperatures in Mg-doped p-GaN, p-Al\(_x\)Ga\(_{1-x}\)N, and p-Al\(_x\)Ga\(_{1-x}\)N/GaN superlattices. It was found that \( L_n \) experienced a multi-fold linear increase and that the rate of change of \( L_n \) decreased exponentially with increasing temperature. The effect was attributed to a temperature-activated release of the electrons, which were trapped by the Mg levels.

The activation energies, \( E_a \), for the electron injection effect in the Mg-doped (Al)GaN samples were found to range from 178 to 267 meV, which is close to the thermal ionization energy of the Mg acceptor. The \( E_a \) observed for Al\(_{0.15}\)Ga\(_{0.85}\)N and Al\(_{0.2}\)Ga\(_{0.8}\)N was consistent with the deepening of the Mg acceptor level due to the incorporation of Al into the GaN lattice. The \( E_a \) in the homogeneously doped Al\(_{0.2}\)Ga\(_{0.8}\)N / GaN superlattice indicates that the main contribution to the electron injection effect comes from the capture of injected electrons by the
The electron injection effect was successfully applied to GaN doped with an impurity (Mn) other than Mg. Electron injection into Mn-doped GaN resulted in a multi-fold increase of $L_n$ and a pronounced decrease in the band-to-band cathodoluminescence intensity. The $E_a$ due to the electron injection effect was estimated from temperature-dependent cathodoluminescence measurements to be 360 meV. The decrease in the band-to-band cathodoluminescence is consistent with an increase in $L_n$, and these results are attributed to an increase in the minority carrier lifetime due to the trapping of injected electrons by the Mn levels.

A forward bias was applied to inject electrons into commercially built p-i-n and Schottky barrier photodetectors. Up to an order of magnitude increase in the peak (360 nm) responsivity was observed. The enhanced photoresponse lasted for over four weeks and was attributed to an electron injection-induced increase of $L_n$ and the lifetime.
Dedicated to my father, Harrill Don Burdett, my son William Leonardo Alexander Burdett, my daughter Marie Isa-Lee Burdett, and my wife Lee Evans Burdett.

My father, who was also my first Physics teacher, is responsible for installing in me my love of science. To this day he is an avid reader of science fiction books and is always asking me questions about the ideas behind the science in the books he reads.

I would also like to thank my son and daughter for giving me the drive to get up in the morning, not only to take care of them, but also to get a better job so that I can provide a better life for them.

Finally, I would like to thank my wife for standing by me for all of these years.
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TABLE OF CONTENTS

ABSTRACT .......................................................................................................................... iii
ACKNOWLEDGMENTS ...................................................................................................... vi
TABLE OF CONTENTS .................................................................................................. vii
LIST OF FIGURES ......................................................................................................... x
LIST OF TABLES ............................................................................................................ xix
LIST OF ABBREVIATIONS .......................................................................................... xx
CHAPTER ONE: INTRODUCTION ................................................................................. 1
  Structure and Properties of III-Nitrides ........................................................................ 2
  Electrical and Optical Properties of III-Nitrides ......................................................... 8
  Background of Electron Injection ............................................................................... 11
  Introduction of the Electron Injection Effect Problem ............................................... 15
  Dissertation Outline ................................................................................................. 16
CHAPTER TWO: EXPERIMENTAL ................................................................................. 18
  Sample Preparation ..................................................................................................... 19
  Schottky Diode .......................................................................................................... 23
  p-n Junction .............................................................................................................. 26
  EBIC Setup .............................................................................................................. 29
Calculating Diffusion Length from EBIC Measurements .......................................................... 31
Calculation of the activation energy from the temperature-dependent EBIC measurements 38
Cathodoluminescence ........................................................................................................... 40
Calculation of the activation energy for temperature-dependent cathodoluminescence
measurements ....................................................................................................................... 42
Photoresponse ....................................................................................................................... 43

CHAPTER THREE: RESULTS ........................................................................................................ 46

III-Nitrides Doped with Mg .................................................................................................. 46
Minority carrier transport properties in GaN:Mg ............................................................... 47
Optical properties of GaN:Mg ............................................................................................. 50
Minority carrier transport properties in Al\textsubscript{x}Ga\textsubscript{1-x}N:Mg ................................ 55
Optical properties of Al\textsubscript{0.15}Ga\textsubscript{0.85}N:Mg .......................................................... 61
GaN Doped with Mn ............................................................................................................. 65
Minority carrier transport properties in GaN:Mn ............................................................... 65
Optical properties of GaN:Mn ............................................................................................. 67
Application of the Electron Injection Effect in Commercial Photodiodes ....................... 70
Schottky barrier photovoltaic detectors ............................................................................... 80

CHAPTER FOUR: DISCUSSION .................................................................................................. 82
Model of the Electron Injection Effect in Mg-doped (Al)GaN ............................................. 82
Model of the Electron Injection effect in Mn-doped GaN .................................................... 86
Kinetics of the Electron Injection Effect ............................................................................. 89
Grain Boundaries ................................................................................................................ 90
LIST OF FIGURES

Figure 1.1  The primitive cell of the wurtzite lattice contains four atoms, where $c$ is the height and $a$ is the base of the primitive cell. ................................................................. 3
Figure 1.2  The hexagonal bonds of GaN form mirror images of each other. Here, the Ga atoms are represented by the yellow spheres and N by the blue spheres. ......................... 4
Figure 1.3  Graph of the band gap energy versus hydrostatic pressure for room temperature GaN. 5
Figure 1.4  Graph of the band gap energy versus temperature for GaN. ......................... 6
Figure 1.5  Graph of the band gap energy versus percent of composition of Al in $\text{Al}_x\text{Ga}_{1-x}\text{N}$. 7
Figure 1.6  Cathodoluminescence intensity versus photon energy for MBE-grown $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ at room temperature................................................................. 11
Figure 2.1  The experimental workstation includes a Philips SEM that is integrated with a Gatan CL. This setup allows for the ability to perform electrical and optical measurements in situ. The column (2) is where the electron beam is generated and focused. The other parts of the workstation include, the secondary electron detector (1), the SEM vacuum chamber (3), Gatan MonoCL3 monochromator (4), and Hamamatsu photomultiplier tube (5). 19
**Figure 2.2** Optical image of an Au Schottky barrier, 1 mm in diameter, on an MOCVD-grown p-type GaN sample. .............................................................. 24

**Figure 2.3** Energy band diagram of a Schottky diode at thermal equilibrium. This Schottky diode consists of a metal contact and a p-type semiconductor. .................................................. 25

**Figure 2.4** Energy band diagram for the p-n junction at thermal equilibrium. .................. 27

**Figure 2.5** Illustration of the drift and diffusion currents in a p-n junction at thermal equilibrium; solid circles represent electrons and the hollow circles are holes. .................. 27

**Figure 2.6** Picture of the EBIC experimental set up. The parts of the setup used to record the EBIC signal are the EG&G lock-in amplifier (1), SRS function generator (2), Keithley voltmeter (3), and SEM (4). ......................................................... 30

**Figure 2.7** Diagram of the EBIC experimental setup. The function generator provides a reference signal to the lock-in amplifier and is used to modulate the SEM electron beam. The lock-in technique is employed to significantly enhance the signal-to-noise ratio. The signal is digitized using the voltmeter and is recorded by the PC. ......................... 30

**Figure 2.8** The planar configuration uses a Schottky diode to collect the minority carrier electrons in a p-type semiconductor. ................................................................. 32

**Figure 2.9** EBIC measurement for MBE-grown p-type Al0.2Ga0.8N at a magnification of 5,000 and a temperature of 70°C. ................................................................. 36

**Figure 2.10** $L_n$ is determined from the slope of the linear fit to the data, $L_n = -\frac{1}{Slope}$. This graph is for MBE-grown p-type Al0.2Ga0.8N ......................................................... 37
Figure 2.11  \( L_n \) dependence on the duration of electron injection for MBE-grown p-type \( \text{Al}_{0.2}\text{Ga}_{0.8}\text{N} \). It can be seen that \( L_n \) starts to saturate after \( \sim 700 \) s of electron injection. 39

Figure 2.12  Inside the SEM chamber. The stand (2) is not only used to position the samples but to heat and cool them. A parabolic mirror (1), which is integrated with a light guide, is used to collect the light from the sample. Liquid Nitrogen cooled gas is sent through the plastic hoses (4) to cool the sample, which is mounted on top of the stage. A computer controlled heater and a Platinum Resistance Thermometer (3) are connected to the stage. 41

Figure 2.13  Photoresponse experimental setup. The Jobin Yvon monochromator (6) selects the specific wavelength of light to be sent to the photodetector (5) from the light source, generated by the Xenon lamp (7). The Scitec optical chopper (1) is used to modulate light, by way of a mechanical interruption (4), and also sends a reference signal to the Perkin Elmer lock-in amplifier (3). The voltage output is digitized by the Keithley voltmeter (2) and then recorded by a PC, where the voltage is recorded versus wavelength. 44

Figure 2.14  Diagram of the photoresponse experimental setup. The monochromator takes the light generated by the Xenon lamp and outputs a specific wavelength to the photodetector. A standard lock-in technique using a 7225 Perkin Elmer lock-in amplifier was employed with a Scitec optical chopper to record the signal from the photodetector. 45

Figure 3.1  EBIC Measurements for MBE-grown p-type GaN, sample B, at a magnification of 2,000 and a temperature of 40 °C. Plot (1) corresponds to 0 s of electron injection, (2) to 720 s, and (3) to 1,440 s of electron injection; solid and dashed lines represent the linear fit. 47
Figure 3.2 Variable temperature dependence of $L_n$ versus the duration of electron injection for MOCVD-grown p-type GaN, sample A. Squares, circles, and triangles are experimentally obtained values of $L_n$ at 25, 75, and 130 °C, respectively; solid and dashed lines represent the linear fit. Saturation of $L_n$ is not shown in this graph.......................... 48

Figure 3.3 Arrhenius graph for sample A. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 178 meV.... 50

Figure 3.4 Cathodoluminescence measurements performed at 23 °C after different time intervals of electron injection. The maximum (379 nm) in spectrum 1 nearly corresponds to the pre-injection situation (less than 20 s time difference). The maximum in spectra 2,3,4, and 5 corresponds to 660, 1,200, 1,680, and 2,200 s of electron injection respectively. These measurements were made on MOCVD-grown p-type GaN, sample A. The peak intensity dropped ~66 % in 2,200 s. ........................................................................................................ 51

Figure 3.5 Peak CL intensity versus duration of electron injection for MOCVD-grown p-type GaN, sample A, at 23 °C. The circles represent the peak CL intensity at ~379 nm and the solid line is the quadratic fit.......................................................... 52

Figure 3.6 Square root of the inverse normalized peak CL intensity versus duration of electron injection for MOCVD-grown p-type GaN, Sample F. Squares, circles, and triangles are the experimentally obtained values at 26, 70, and 135 °C, respectively. Solid and dashed lines represent the linear fit to these values.................................................. 53

Figure 3.7 Arrhenius graph for sample F. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 207 meV.
**Figure 3.8** Dependence of the peak CL intensity (squares) on the duration of electron injection and the quadratic fit for sample A, at room temperature. Also shown: dependence of the $L_n$ (circles) on the duration of electron injection for sample A and the linear fit. Saturation of $L_n$ is not shown in this graph.

**Figure 3.9** EBIC Measurements for MBE-grown homogeneously doped p-type $Al_{0.2}Ga_{0.8}N/GaN$ superlattice, sample E, at a magnification of 12,000 and a temperature of 40°C. Plot 1 corresponds to the pre-injection situation. Plots 2 and 3 correspond to 480 and 720 s of electron injection respectively.

**Figure 3.10** Typical temperature dependence of minority carrier diffusion length on duration of electron injection for a modulation doped $Al_{0.2}Ga_{0.8}N/GaN$ superlattice, sample D. Circles, squares, and diamonds are experimentally obtained values at 34, 75, and 130 °C, respectively. Solid lines represent the linear fit. Saturation of $L_n$ is not shown in this graph.

**Figure 3.11** Arrhenius graph for sample E. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 189 meV.

**Figure 3.12** Temperature dependence for the rate of change of $L_n$ for bulk MBE p-GaN (circles), bulk MBE $p-Al_{0.2}Ga_{0.8}N$ (diamonds), and bulk MOCVD p-GaN (squares). Solid lines represent the best fit.

**Figure 3.13** Temperature dependence of the rate of change of $L_n$ for MBE-grown...
homogeneously doped p-Al_{0.2}Ga_{0.8}N/GaN superlattice (circles) and modulation doped p-Al_{0.2}Ga_{0.8}N/GaN superlattice (squares). Solid lines represent the best fit.

**Figure 3.14** Cathodoluminescence measurements performed at 25 °C after different time intervals of electron injection for MOCVD-grown p-Al_{0.15}Ga_{0.85}N, sample H. The maximum (371 nm) in spectrum 1 was taken after 130 s of electron injection. The maximum in spectra 2, 3, and 4 corresponds to 584, 1,026, and 1,902 s of electron injection, respectively.

**Figure 3.15** Square root of the inverse normalized peak CL intensity versus duration of electron injection for MOCVD-grown p-type Al_{0.15}Ga_{0.85}N, sample H. Squares, circles, and triangles are the experimentally obtained values at 25, 70, and 130 °C, respectively. Solid and dashed lines represent the linear fit.

**Figure 3.16** Arrhenius graph for sample H. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 220 meV.

**Figure 3.17** Room temperature EBIC Measurements for PAMBE-grown GaN:Mn, sample J. Plot 1 corresponds to the pre-injection situation. Plots 2 and 3 correspond to 60 and 210 s of electron injection respectively.

**Figure 3.18** Diffusion length versus duration of electron injection for GaN:Mn, sample J. $L_n$ increases over three-fold after 200s of electron injection. Saturation of $L_n$ is not shown in this graph.

**Figure 3.19** CL intensity as a function of wavelength after 22 s (1) and 2,070 s (6) of electron injection.
injection for sample J. ........................................................................................................... 67

**Figure 3.20** Cathodoluminescence measurements performed at 25 °C after different time
intervals of electron injection. The maximum in spectra 1, 2, 3, 4, 5, and 6 corresponds to
22, 417, 833, 1,257, 1,661, and 2,070 s of electron injection respectively. These
measurements were performed on PAMBE-grown GaN:Mn, sample J. ......................... 68

**Figure 3.21** Variable temperature dependence for the square root of inverse normalized peak
CL intensity versus the duration of electron injection for GaN:Mn, sample J. The rate at
every temperature is obtained from the slope of the linear fit. ............................................. 68

**Figure 3.22** Arrhenius graph for sample J. Circles are the experimentally obtained values and
the solid line represents the best fit. The activation energy was found to be 360 meV. ...... 69

**Figure 3.23** a) Mixed EBIC (dark vertical contrast) and secondary electron image of the p-n
junction, cleaved perpendicular to the growth plane. Inset: p-n junction forward I-V curve.
b) EBIC line-scan across the p-n junction [60]........................................................................ 71

**Figure 3.24** A graph of $n_L$ (squares) as a function of the duration of electron injection into the
p-region of a GaN p-n junction. A 6 Volt forward bias was applied to a 500 µm-diameter p-
n junction mesa, to create a current density of 12 A/cm². The same plot presents the
calculated $\tau_n$ (circles) dependence on the duration of electron injection, based on
experimentally obtained $L_n$ values. Saturation of $L_n$ for times larger than 1500 s is not
shown in this graph [38]. ......................................................................................................... 72

**Figure 3.25** p-side illuminated SVTA GaN photodetector with ultra-violet-enhanced window.
74
Figure 3.26  p-i-n photodetector architecture................................................................. 75

Figure 3.27  Zero bias spectral photoresponse of the p-i-n photodetector before (1) and after (2, 3, 4) injection of electrons by applying a forward bias. Spectra 2, 3, and 4 correspond to 18, 40, and 83 s of electron injection, respectively. Inset: Forward branch of the photodetector’s I-V curve. A 5 V forward bias was used for the injection of electrons. .... 76

Figure 3.28  Dependence of the photodetector’s peak responsivity at 360 nm versus the duration of electron injection. The solid lines represents the quadratic fit. Saturation occurs after ~83 s of electron injection. ......................................................................................... 76

Figure 3.29  Leakage current of the p-i-n photodetector before (squares) and after (circles) 83 s of electron injection. .................................................................................................................. 77

Figure 3.30  Photoresponse spectrum from one of the SVTA p-i-n photodetectors before (1) and after (2) several hundred seconds of applying a 5 V forward bias. The peak responsivity at ~360 nm showed a 4.5 times increase. Inset: Relaxation of zero bias peak responsivity at 360 nm after 30 minutes of 10 V reverse bias................................. 78

Figure 3.31  Dependence of the total photoresponse for a Schottky barrier on time of forward bias electron injection. A forward current of 1 mA was flown through a structure for ~650 s. The photoresponse is normalized with respect to the initial value measured immediately before an electron injection................................................................. 81

Figure 3.32  Dependence of the total normalized Schottky barrier detector response on post-injection time. Time 0 corresponds to the moment when the forward bias was turned off. The photoresponse is normalized relative to its pre-injection level. .......................... 81

Figure 4.1  Proposed model for the electron injection effect using the SEM electron beam. A
neutral Mg level traps an electron, which was injected by the SEM electron beam. These ionized Mg levels stop playing a role in the recombination process. As a result, the electrons in the conduction band, which normally recombine through these Mg levels, cannot do so. This means that the electrons stay in the conduction band longer and the lifetime of the conduction band electrons will increase. These Mg levels will become available to play a role in the recombination process after it has captured a hole. $E_c$ represents the bottom of the conduction band, $E_v$ is the top of the valence band, and Mg$^-$ represents the ionized Mg acceptors [61].

**Figure 4.2** Configuration coordinate model for Mg-doped (Al)GaN. A hole (open circle) in the valence band has to overcome the hole capture barrier, $E_c$, before the ionized Mg acceptor can capture the hole.

**Figure 4.3** Mechanism for the observed electron injection-induced effects in Mn-doped GaN [65]. (1) corresponds to the ionization of Mn$^{3+}$ to Mn$^{2+}$ due to an SEM beam excitation and a consequent electron (dashed arrow in 4.3a, left) transition to a vacant $t_{2g}$-orbital. (2) represents the band-to-impurity recombination through a vacant Mn$^{3+*}$ $e_{1g}$-orbital (4.3a, right). (3) represents the thermally activated hole emission (electron capture) from an $e_{1g}$-orbital of the Mn$^{3+*}$ state to the valence band. This leads to ionization of Mn$^{3+*}$ state to the Mn$^{2+}$ state and to a suppression of (2).
LIST OF TABLES

Table 1.1  Properties of GaN and AlN in the wurtzite crystal structure. ........................................ 9
Table 2.1  Electronic properties of the samples studied. ................................................................. 22
Table 3.1  Activation energies obtained from EBIC measurements................................................. 63
Table 3.2  Activation energies obtained from CL measurements...................................................... 64
Table 3.3  Activation energies obtained from CL measurements on GaN:Mn......................... 70
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AlN</td>
<td>Aluminum Nitride</td>
</tr>
<tr>
<td>AlGaN</td>
<td>Aluminum Gallium Nitride</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
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<td>Carbon</td>
</tr>
<tr>
<td>Cd</td>
<td>Cadmium</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
</tr>
<tr>
<td>EBIC</td>
<td>Electron Beam Induced Current</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FCC</td>
<td>Face-Centered Cubic</td>
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<td>Gallium Nitride</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
</tr>
<tr>
<td>Hg</td>
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xx
InN  Indium Nitride
K   Kelvin
\( k_B \)  Boltzmann’s constant
kbar Kilobar
keV  Kilo electron volt
LEEBI Low Energy Electron Beam Irradiation
LED Light Emitting Diode
Li  Lithium
\( L_n \)  Minority Carrier Diffusion Length
mA Milliamp
MBE Molecular Beam Epitaxy
Mg Magnesium
Mn Manganese
MOCVD Metal Organic Chemical Vapor Deposition
MOSFET Metal Oxide Semiconductor Field Effect Transistors
N Nitrogen
nA Nanoamp
\( NH_3 \)  Ammonia
PAMBE Plasma Assisted Molecular Beam Epitaxy
PC Personal Computer
PPC Persistent Photoconductivity
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PR</td>
<td>Photoresponse</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>RRR</td>
<td>Rate of Radiative Recombination</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon Carbide</td>
</tr>
<tr>
<td>TMG</td>
<td>Trimethylgallium</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
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<tr>
<td>UV</td>
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</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>$\tau_n$</td>
<td>Minority Carrier Lifetime</td>
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CHAPTER ONE: INTRODUCTION

III-Nitrides are attracting increased attention due to their importance in high power and high temperature electronics and optoelectronic devices. The list of devices that III-Nitrides can be applied to is quite extensive and includes Ultraviolet (UV) detectors, UV and visible Light Emitting Diodes (LEDs), laser diodes, ultrahigh power switches, and microwave applications [1-4]. GaN and AlN possess a wide band gap, which allows them to be used in high power and high temperature devices. GaN, AlN, and InN can be used separately or combined to form ternary & quaternary compounds with a band gap that ranges from 0.7 eV to 6.2 eV (1772 nm to 200 nm) [5, 6].

This chapter will start by reviewing the structural properties of III-Nitrides. This will be followed by a summary of the electrical and optical properties of III-Nitrides. Some background information on how electron injection has been used in these semiconductors will then be given. An introduction to the problem of how electron injection affects the transport properties of these p-type materials will be next. The introduction will conclude with a brief outline of the contents of this dissertation.
The crystal structure of a semiconductor has a direct impact on its electrical and optical properties, as well as the band gap energy. III-Nitrides can take on the form of three different crystal structures, hexagonal wurtzite (space group $C_{6v}^4 P6_3 mc$), cubic zincblende ( $T_d^2 - F4\bar{3}m$), and cubic rock salt ( $Fm\bar{3}m$) [5, 7]. The rock salt structure has not been used very much in research since it is only formed at very high pressures.

The zincblende lattice comprises two different sublattices, one lattice being made up of N atoms and the other consisting of either Ga or Al atoms. Each sublattice is Face-Centered Cubic (FCC), and the two sublattices are oriented in such a way so that they interpenetrate each other to form the zincblende structure. Since most of the high quality GaN crystals have been grown in the wurtzite form; Zincblende has not been the lattice of choice for GaN research. In addition, there exists a small energy difference in the calculated energy between the wurtzite and the zincblende lattice. The calculated values for the energy difference between the wurtzite and zincblende lattice structures are $\Delta E_{W-ZB} = -9.88 \text{ meV / atom}$ for GaN, $\Delta E_{W-ZB} = -18.41 \text{ meV / atom}$ for AlN [8]. Therefore, the wurtzite structure is energetically preferred over the zincblende structure for both GaN and AlN.

The wurtzite crystalline structure for GaN comprises two different sublattices. These sublattices are Hexagonal Close Packed (HCP) lattices and one lattice consists of N atoms while the other consists of either Ga or Al atoms. These two sublattices interpenetrate each other to form the wurtzite lattice. The hexagonal wurtzite lattice is 6-fold symmetric and for GaN has a
base $a = 3.189 \text{ Å}$ and a height $c = 5.186 \text{ Å}$ [9]. Since wurtzite is an HCP lattice the stacking order is ABAB. The primitive cell of the wurtzite HCP has four atoms per unit cell [10], as seen in Figure 1.1. In the case of GaN, each N atom is bound to four Ga atoms, and each Ga atom is bound to four N atoms. In Figure 1.2, it can be seen that the hexagonal bonds form mirror images of each other.

\[ \alpha = 189.3^\circ \]
\[ a = \text{base} \]
\[ c = \text{height} \]

**Figure 1.1** The primitive cell of the wurtzite lattice contains four atoms, where $c$ is the height and $a$ is the base of the primitive cell.

III-Nitrides do not normally occur in nature. As a result, there is no suitable substrate on which to grow III-Nitrides. The mismatch between the lattice structures of the substrates and III-Nitrides introduces a strain in the III-Nitride lattice. This strain can dramatically change the band gap energy, and it can be detrimental to the electrical and optical properties of the material. The equation for the dependence of the band gap energy on pressure [9] in III-Nitrides can be
written as

\[ E_g = E_g(0) + \alpha P + \beta P^2 \]  

(1.1)

where \( \alpha \) and \( \beta \) are pressure coefficients, and \( E_g(0) \) is the band gap energy of a stress free semiconductor. For GaN at room temperature \( E_g(0) = 3.39 \text{ eV}, \ \alpha = 4.2 \times 10^{-3} \frac{\text{eV}}{\text{kbar}}, \) and

\[ \beta = -1.8 \times 10^{-5} \frac{\text{eV}}{\text{kbar}^2} \].

A graph of \( E_g \) versus pressure is shown in Figure 1.3.

Figure 1.2 The hexagonal bonds of GaN form mirror images of each other. Here, the Ga atoms are represented by the yellow spheres and N by the blue spheres.

Sapphire, \( \text{Al}_2\text{O}_3 \), is the substrate of choice for growing III-Nitrides. This is because Sapphire substrates are fairly inexpensive to obtain and high quality crystals can be grown on them. The lattice mismatch between GaN and Sapphire is around 15%, which results in poor quality crystals when GaN is grown directly on Sapphire substrates. Most III-Nitride semiconductors have a layer of Sapphire as the foundation, then a buffer layer of either AlN or GaN, \( \sim 10 \text{ nm} \) thick. This buffer layer serves to alleviate some of the stress due to the lattice mismatch that may occur between the substrate and the III-Nitride material. Finally, the III-
Nitride material is laid on top of the buffer layer to create a high quality crystal. The quality of the GaN crystal is improved when AlN is used as the buffer layer because there is only a 2% mismatch between the AlN and GaN lattices.

![Graph of the band gap energy versus hydrostatic pressure for room temperature GaN.](image)

The energy band gap for III-Nitrides is temperature dependent [9]. This dependence can be expressed as

\[ E_g = E_g(0) + A \frac{T^2}{T + B} \]  

(1.2)

where A and B are constants and \( E_g(0) \) is the band gap energy at \( T=0 \) K. For GaN and AlN A is negative, and therefore, the band gap energy will decrease as the temperature increases. For wurtzite GaN \( E_g(0) = 3.47 \text{ eV}, \ A = -7.7 \times 10^{-4} \frac{\text{eV}}{K}, \) and \( B = 600 \text{ K}. \)
The band gap energy for ternary alloys of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be given to a first approximation by [11]

$E_g(\text{Al}_x\text{Ga}_{1-x}\text{N}) = (1-x)E_g(\text{Ga}_{1-x}\text{N}) + xE_g(\text{Al}_x\text{N}) - bx(1-x)$  \hspace{1cm} (1.3)

where $b$ is the bowing parameter and $x$ is the percent composition of Al in the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ lattice.

Vurgaftman and Meyer [11] suggest that a bowing parameter of 0.7 eV should be used for $\text{Al}_x\text{Ga}_{1-x}\text{N}$. In these ternary alloys Ga is replaced by Al in the lattice structure. This replacement of Ga with Al will introduce stress into the crystal structure.
One of the applications of being able to tailor the band gap energy by varying the percent of Al composition can be seen when building a photodetector. $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be used to build excellent p-n and p-i-n photodetectors. The percent of Al in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ can be varied so that the photodetector has a wavelength range of 200 to 364 nm (6.2 to 3.42 eV). The atmosphere of the Earth absorbs light with a wavelength of 240-285 nm (5.17 to 4.35 eV); hence this spectral region is called solar blind. Solar blind photodetectors can be fabricated using the ternary compound $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$, which will have a peak wavelength cutoff of 285 nm [12].
The III-Nitrides possess a mix of covalent and ionic bonding. 31% to 40% [13] of the III-Nitride bonds are ionic in character (excluding BN). One of the reasons why it has been so difficult to produce p-type material for III-Nitrides is because the III-Nitride bonds are a mix between covalent and ionic bonds. Since the bonds are partly ionic, none of the acceptor energy levels can be shallow enough to easily generate holes for p-type conduction at room temperature. There have been several elements that have been used as acceptors in GaN, these are Mg, Si, Zn, Hg, Cd, Be, Li, and C. Out of these dopants, Mg is most commonly used to make GaN p-type.

Mg can act as either an acceptor or a donor of electrons inside GaN. When Mg acts as an acceptor in p-type GaN the ionization energy levels range from 140 meV to 210 meV [9], as measured from the top of the valence band. Since the Mg acceptor energy values are in the 140 - 210 meV range, these energy levels are not easily ionized at room temperature. Because of the large Mg acceptor ionization energy levels, approximately 1% of the Mg dopant is ionized at room temperature for GaN [14]. One can see that the concentration of Mg will have to be quite high to produce enough holes to effectively overcome the native n-type characteristics of GaN and produce p-type GaN.

For $\text{Al}_x\text{Ga}_{1-x}\text{N}$ the Mg level will deepen as the percent of Al is increased [14] (remember that the band gap energy will also increase when Al is added to the GaN lattice). The activation energy for ionization of the Mg acceptors will increase 3.2 meV for every 1% of Al in the ternary compound. This means that for $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ the ionization energy of Mg will range
between 204 - 274 meV.

Electrical properties for wurtzite GaN and AlN [9] are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>GaN</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>6.15</td>
<td>3.23</td>
</tr>
<tr>
<td>Energy Gap (eV) at 300 K</td>
<td>3.39</td>
<td>6.2</td>
</tr>
<tr>
<td>Electron Mobility (cm²/Vs)</td>
<td>≤1,000</td>
<td>300</td>
</tr>
<tr>
<td>Hole Mobility (cm²/Vs)</td>
<td>≤200</td>
<td>14</td>
</tr>
<tr>
<td>Electron Diffusion Coefficient (cm²/s)</td>
<td>25</td>
<td>7</td>
</tr>
<tr>
<td>Hole Diffusion Coefficient (cm²/s)</td>
<td>5</td>
<td>0.3</td>
</tr>
<tr>
<td>Electron Thermal Velocity (m/s)</td>
<td>2.6×10⁵</td>
<td>1.85×10⁵</td>
</tr>
<tr>
<td>Hole Thermal Velocity (m/s)</td>
<td>9.4×10⁴</td>
<td>4.1×10⁴</td>
</tr>
<tr>
<td>( L_n ) (( \mu )m)</td>
<td>( \leq 3-4 )</td>
<td>N/A</td>
</tr>
<tr>
<td>( L_p ) (( \mu )m)</td>
<td>( \leq 3.4 )</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The minority carrier diffusion length depends on many different variables, crystalline quality, doping levels, and minority carrier injection to name a few. As a result, the values for the minority carrier diffusion length can possess a broad range of values for III-Nitrides. For n-type GaN, the minority carrier diffusion length, \( L_p \), ranged from 70 nm to 3.4 \( \mu \)m [15-19]. The minority carrier diffusion length, \( L_n \), for p-type GaN ranged from 80 nm to 3-4 \( \mu \)m [15, 17,20, 21]. For p-type Al₀.₁Ga₀.₉N, \( L_n \) was found to be 55 nm [15].

Mn-doped GaN exhibits ferromagnetic properties at room temperature. The Curie temperature has been found to exhibit a wide range from 10 K to 940 K [22]. Mn forms deep acceptor levels at 1.42 eV [23] and 1.8 eV [24] above the top of the valence band. Mn exists in
two different states inside GaN, the Mn$^{3+}$ and the Mn$^{2+}$ state [25]. The Mn$^{2+}$ state has five electrons in the 3d shell and two electrons in the 4s shell; the electronic configuration can be written as [Ar] 3d$^5$ 4s$^2$, where the five d electrons yield a spin of 5/2 [26].

GaN also exhibits a high luminescence efficiency [27]. The high luminescence efficiency is due in part to a low surface recombination velocity [28], which has a value ~500 m/s [29]. The high luminescence efficiency of GaN is what lends this material to be used in optoelectronic applications.

There are several luminescence peaks in (Al)GaN that are worth noting: the conduction band to valence band transition, the conduction band to Mg acceptor transition, and the broad yellow luminescence band. The conduction band to valence band transition occurs at 3.4 eV (365 nm) for GaN and 3.84 eV (323 nm) for Al$_{0.2}$Ga$_{0.8}$N at room temperature.

The conduction band to Mg acceptor transition occurs around 3.27 eV (379 nm) for GaN and 3.34 eV (371 nm) for Al$_{0.2}$Ga$_{0.8}$N, at room temperature. This transition plays a major role in the electron injection effect, which will be described below, in p-type Mg-doped (Al)GaN. The energy level of this transition will shift as the percent of Al is increased in the GaN lattice. Sometimes the conduction band to Mg acceptor spectrum is so large that it will dominate the conduction band to valence band transition.

The yellow luminescence band has a broad spectrum, which is centered at ~2.2 eV (564 nm). This yellow band is thought to be due to transitions from the conduction band to deep acceptor levels or transitions from shallow donors to deep acceptor levels [30]. The yellow band is generally not seen when the sample is lightly doped with Mg or when the quality of the sample
is high. This indicates that the yellow band is the result of defects in the material.

![Graph showing cathodoluminescence intensity versus photon energy for MBE-grown Al$_{0.2}$Ga$_{0.8}$N at room temperature.](image)

**Figure 1.6** Cathodoluminescence intensity versus photon energy for MBE-grown Al$_{0.2}$Ga$_{0.8}$N at room temperature.

Figure 1.6 shows a graph of the cathodoluminescence (CL) intensity versus wavelength for p-type Al$_{0.2}$Ga$_{0.8}$N at room temperature. One can see the two peaks, one for Al$_{0.2}$Ga$_{0.8}$N (~3.89 eV or 319 nm) and a broad yellow luminescence band (~2.45 eV or 506 nm).

**Background of Electron Injection**

Doping GaN and related compounds with Mg to obtain a high concentration of holes has been a difficult problem. For many years it was not possible to obtain p-type GaN material
because of residual n-type defects, which are thought to be from N vacancies and other unintentionally doped impurities that occurred during the growth process. This problem was also compounded by the fact that most of the acceptor dopants had high ionization energy levels. H was also found to form neutral complexes with the Mg acceptors [1]. The Mg-H complexes had the effect of increasing the resistivity, decreasing the carrier concentration, and increasing the mobility because there would be less scattering due to ionized impurities. To form p-type III-Nitrides a way had to be found to break the bonds of the Mg-H complexes.

Electron injection into GaN played an important role in the development of p-type material in III-Nitrides. In 1989 Amano et al. [31] found that highly resistive Mg-doped GaN could be made p-type by the application of Low Energy Electron Beam Irradiation (LEEBI). Amano found that the luminescence properties, in particular the UV emission, were increased; in addition to a change in the electrical properties after a LEEBI treatment was performed with a Scanning Electron Microscope (SEM). This p-type GaN was achieved after applying LEEBI near room temperature. The as-grown Mg-doped GaN had a resistivity of $10^8 \, \Omega \, \text{cm}$ where the LEEBI treated GaN was found to have a resistivity of $35 \, \Omega \, \text{cm}$.

Nakamura et al. [32] showed that simple thermal annealing, either in a vacuum or in a Nitrogen atmosphere, could be used to make GaN p-type. Temperatures above 700 °C were used to break the bonds of the Mg-H complexes. Once the Mg-H bonds have been broken, some of the H is removed from GaN by further heating of the material. Nakamura found that the resistivity of the GaN changed after thermal annealing. Before thermal annealing the resistivity was $1 \times 10^6 \, \Omega \, \text{cm}$ while after annealing the resistivity decreased by several orders of
magnitude to $2 \, \Omega \text{cm}$. Nakamura saw no change in the resistivity when the annealing temperature ranged from room temperature to $400 \, ^\circ\text{C}$.

Nakamura et al. [33] also showed that resistivity of p-type GaN would change if it was annealed in NH$_3$ and that it would not change if annealed in N$_2$. When p-type GaN was annealed in NH$_3$, the resistivity changed from $2 \, \Omega \text{cm}$ to $1 \times 10^6 \, \Omega \text{cm}$; a decrease in the blue emission was also observed after annealing in NH$_3$. The sample that was annealed in N$_2$ showed no increase in the resistivity. The sample that was annealed in NH$_3$ was annealed a second time in N$_2$, and the resistivity decreased from $1 \times 10^6 \, \Omega \text{cm}$ to the pre-annealed values 2 to 8 $\Omega \text{cm}$. This showed that H plays a role in the passivation of the Mg acceptors. When NH$_3$ is used to anneal the sample, H is available for indiffusion into GaN. When H forms neutral complexes with the Mg acceptors the resistivity of the material will increase.

$$\text{Mg}^- + \text{H}^+ \rightarrow (\text{Mg} - \text{H})^0 \quad (1.4)$$

More recent experiments by Miyachi et al. [34] and Pearton et al. [35] showed that the presence of minority carrier electrons in Mg-doped GaN facilitates the temperature activation process of the Mg dopants to form p-type GaN. Miyachi examined how the injection of electrons and annealing affected the activation of the Mg acceptors. One method was to anneal GaN under a forward bias on the p-n junction diode, and the other method was to anneal the sample in an open circuit. The experiment was carried out with a metal deposition on the surface so that H could not desorb out of the GaN. Miyachi noticed that the resistance started to decrease when a forward bias was applied for temperatures above $300 \, ^\circ\text{C}$, but there was no
change in the resistance in the open circuit for temperatures up to 600°C. Miyachi suggested that when a forward bias is applied to p-type GaN, the H is changed into a state that does not passivate the Mg acceptors.

Pearton found that the dissociation of the Mg-H complexes was enhanced during electron injection. Pearton observed that the acceptor concentration density would increase when electrons were injected, by applying a forward bias to a p-n junction, when the annealing temperature was 175°C. It was shown that the kinetics of the reactivation process of Mg in GaN could be described by a second order equation

$$\frac{d}{dt} N_i(t) = C N_i^2(t)$$

(1.5)

where $N_i$ is the inactive acceptor concentration, $t$ is the time of forward bias annealing, and $C$ is a constant.

Gelhausen et al. [30, 36] found that the CL intensity increased by a factor of 30 for the band-to-acceptor transition (~3.26 eV or 381 nm) when LEEBI was applied to a p-type GaN sample. After annealing the LEEBI sample, the CL spectrum returned to its pre-injection state. Gelhausen proposed this was because H does not leave the sample, but forms a complex with the N vacancies. A broad yellow luminescence band, centered at 2.2 eV (564 nm), also appeared after performing LEEBI on the p-type GaN. Gelhausen concluded that not only can LEEBI be used to dissociate the Mg-H complexes, but that it can also be used to dissociate H from other defect complexes.
Introduction of the Electron Injection Effect Problem

Transport properties of minority carriers are an important indicator of the quality of III-Nitride materials. A small minority carrier diffusion length, \( L \), is one of the main difficulties that must be overcome in III-Nitrides. Enhancement of \( L \) presents a serious technological challenge, since an improved \( L \) cannot simply be achieved by the growth of low defect materials. Limitations, especially in heteroepitaxy, arise from the lattice mismatch between the III-Nitride epitaxial layer and the underlying substrate, such as Sapphire, SiC, or Si.

It has been found that the injection of electrons into p-type Mg-doped GaN and AlGaN/GaN superlattices will increase the electron minority carrier diffusion length, \( L_n \) [37], and the electron minority carrier lifetime, \( \tau_n \) [38]. This injection of electrons can be achieved by either performing a forward bias in the solid-state device (p-n junction) or by using the SEM electron beam to inject the electrons.

To better understand how electron injection can be used to increase the minority carrier diffusion length in p-type III-Nitrides, it will be necessary to understand the pivotal role that Mg plays in this process. This dissertation addresses the question of how Mg interacts with the injected electrons and the impact that this interaction has on the transport properties, \( L_n \) and \( \tau_n \).

It has already been shown [39] that when the composition of Al in \( Al_x Ga_{1-x} N \) is increased the position of Mg acceptor energy levels in the forbidden gap will also increase. Therefore, it is necessary to understand the impact of Al composition in \( Al_x Ga_{1-x} N \) on the electron injection effect. This dissertation addresses this problem.
This dissertation also considers whether other dopants, beside Mg, can be used to increase the minority carrier diffusion length in III-Nitrides. The analysis will lead to a better understanding of the type of dopant that can be used for practical applications of the electron injection effect in III-Nitrides.

Understanding how the electron injection effect changes the transport properties in III-Nitrides will be helpful in improving III-Nitride devices. As a practical application, this dissertation will examine whether the electron injection effect can be applied to improve the performance of commercially built p-i-n or Schottky barrier photodetectors.

**Dissertation Outline**

This dissertation focuses on understanding how the transport properties of the minority carriers in p-type (Al)GaN are affected by electron injection; in particular how electron injection impacts $L_n$ and $\tau_n$ of GaN:Mg and Al$_x$Ga$_{1-x}$N :Mg. A model for the electron injection-induced effects will be proposed. It will be shown that Mg acceptors are responsible for trapping of the injected electrons, and that these ionized acceptors impact the minority carrier transport. Mn-doped GaN will be investigated to determine if the electron injection effect could be successfully applied to other dopants besides Mg.

The study of the electron injection effect to improve the transport properties of III-Nitrides is as follows. Chapter 2 describes the experimental techniques that were used to understand the impact of electron injection on the transport properties; these techniques are
Electron Beam Induced Current (EBIC), CL, and photoresponse (PR). This chapter will also describe the preparation of the samples and their electronic properties.

Chapter 3 will present the results of this dissertation, which will include EBIC, CL, and PR measurements. Chapter 4 will propose a model to describe the electron injection effects in Mg-doped (Al)GaN and Mn-doped GaN. Finally, Chapter 5 will provide some concluding remarks about this dissertation and suggest further areas of interest in the phenomenon of electron injection.
CHAPTER TWO: EXPERIMENTAL

To understand the electron injection effect on minority carrier transport properties, electrical and optical experiments were carried out on p-type (Al)GaN-based structures. These experiments were done to understand the role that Mg plays in the electron injection effect and what the impact of Al composition is in III-Nitrides.

Three major experimental techniques were used to investigate the electron injection effect. The EBIC technique was used to understand how the injection of electrons affected the electrical properties of these materials. CL measurements were performed to understand how the injection of electrons affected the optoelectric properties of the samples. Finally, photoresponse measurements were carried out to demonstrate that the electron injection effect could be applied to improve the performance of commercially built photodetectors.

A Gatan MonoCL3 cathodoluminescence system is integrated into a Philips XL 30 SEM. This experimental workstation allows for electrical and optical measurements to be performed in situ. The SEM allows for temperature-dependent measurements that range from -196 °C to 200 °C. The SEM also allows for a high degree of spatial resolution, which is ~ 2-3 nm at 30 keV acceleration voltage for highly conductive samples. The CL technique offers great advantages over its photoluminescence counterpart, because it combines high spatial and spectral (~1.2 nm for 0.5 mm slit width) resolution. This experimental setup is shown in Figure 2.1.
Figure 2.1 The experimental workstation includes a Philips SEM that is integrated with a Gatan CL. This setup allows for the ability to perform electrical and optical measurements in situ. The column (2) is where the electron beam is generated and focused. The other parts of the workstation include, the secondary electron detector (1), the SEM vacuum chamber (3), Gatan MonoCL3 monochromator (4), and Hamamatsu photomultiplier tube (5).

Sample Preparation

The samples were grown by three different methods, Metal Organic Chemical Vapor Deposition (MOCVD), Molecular Beam Epitaxy (MBE), and Plasma Assisted Molecular Beam Epitaxy (PAMBE). SVTA grew the MOCVD and MBE samples, while the PAMBE samples were grown by a group at the Walter Schottky Institute in Munich, Germany. All of the samples studied were grown on sapphire substrates. The majority carrier concentration and mobility for
the Mg-doped p-type samples were determined by room temperature Hall effect measurements by SVT Associates.

The MOCVD growth technique flows reactant gases over a substrate to grow the III-Nitride films. In the two-flow MOCVD method, the substrate is rotated to allow a uniform growth while the reactant gases flow parallel across the rotating substrate. A sub flow of $N_2$ and $H_2$ is used to bring the reactant gases into contact with the substrate by flowing perpendicularly to the substrate. The reactant gases used to grow GaN films generally consist of $H_2$, $NH_3$, and trimethylgallium (TMG) $Ga(CH_3)_3$. GaN films with the best electrical and optical properties are grown at $1050 \, ^\circ C$ [5].

The MBE growth technique employs an Ultrahigh Vacuum (UHV) evaporation system to grow III-Nitrides and lends itself very easily to the building of heterostructures because of the precise control of the chemical compositions. Directed thermal beams of atoms or molecules are created by heating elements inside furnaces. These beams of atoms or molecules are directed towards a substrate where they condense. Because of the strength of the bond between N atoms, temperatures above $950 \, ^\circ C$ [5] must be used to grow III-Nitrides. Solid or metalorganic sources can be used in the MBE growth techniques; Mg is generally evaporated from a solid source.

PAMBE uses a radio frequency plasma source to activate N to improve on the MBE technique. Using the radio frequency to generate the Nitrogen plasma allows the use of lower temperatures [40] in the growing of III-Nitrides. For our samples, the growth temperatures were $690 \, ^\circ C$ for GaN:Mn and $820 \, ^\circ C$ for GaN:Mn:Si.

Three of the p-type GaN samples were grown by MOCVD. The thickness of these
samples ranged from 2-3 \( \mu m \). The hole concentration, \( p \), for these samples was in the mid \( 10^{17} cm^{-3} \) and the hole mobility, \( \mu_p \), was found to be \( 7 cm^2/Vs \). In addition to GaN, a 1 \( \mu m \) thick p-type MOCVD-grown \( Al_{0.15}Ga_{0.85}N \) was investigated. The \( Al_{0.15}Ga_{0.85}N \) samples showed a majority carrier concentration of \( 2\times10^{16} cm^{-3} \) and a mobility comparable to that of the GaN samples.

Four of the samples studied were grown by the MBE technique; bulk GaN, bulk \( Al_{0.2}Ga_{0.8}N \), homogeneously doped \( Al_{0.2}Ga_{0.8}N/GaN \) superlattice, and a modulation doped \( Al_{0.2}Ga_{0.8}N/GaN \) superlattice. The bulk p-type GaN sample was \( \sim 2\mu m \) thick and demonstrated a hole concentration in the mid \( 10^{17} cm^{-3} \) and a mobility of \( \sim 3.5cm^2/Vs \).

Likewise bulk p-type \( Al_{0.2}Ga_{0.8}N \) was \( \sim 1.5\mu m \) thick and the \( p \) and \( \mu_p \) were the same as for the MBE-grown GaN.

The two \( Al_{0.2}Ga_{0.8}N/GaN \) superlattices consisted of 20 periods with a well and barrier thickness of 10 nm each, where \( Al_{0.2}Ga_{0.8}N \) represents the barrier in these superlattices. The homogeneous superlattice had both the barriers and wells doped with Mg, while for the modulation-doped superlattice only the barriers were doped with Mg.

For the modulation doped \( Al_{0.2}Ga_{0.8}N/GaN \) superlattice the effective measured parameters were \( p = 8\times10^{17} cm^{-3} \) and \( \mu_p = 31cm^2/Vs \), while for the homogeneously doped \( Al_{0.2}Ga_{0.8}N/GaN \) superlattice the majority carrier concentration and mobility were \( 2\times10^{18} cm^{-3} \) and \( 2cm^2/Vs \) respectively.
### Table 2.1  
Electronic properties of the samples studied.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Majority Carrier Concentration (cm^{-3})</th>
<th>Mobility (cm^2/Vs)</th>
<th>Resistivity (\Omega \cdot cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 (\mu m) thick.</td>
<td>(4 \times 10^{17})</td>
<td>7</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>MBE-grown p-GaN doped with Mg, 2 (\mu m) thick.</td>
<td>(4 - 6 \times 10^{17})</td>
<td>3.5</td>
<td>4.5-3.0</td>
</tr>
<tr>
<td>C</td>
<td>MBE-grown p- (Al_{0.2}Ga_{0.8})N doped with Mg, 1.5 (\mu m) thick.</td>
<td>(4 - 6 \times 10^{17})</td>
<td>3.5</td>
<td>4.5-3.0</td>
</tr>
<tr>
<td>D</td>
<td>MBE-grown p- (Al_{0.2}Ga_{0.8})N/GaN modulation doped with Mg, 0.4 (\mu m) thick.</td>
<td>(8 \times 10^{17})</td>
<td>31</td>
<td>0.25</td>
</tr>
<tr>
<td>E</td>
<td>MBE-grown p- (Al_{0.2}Ga_{0.8})N/GaN homogenously doped with Mg, 0.4 (\mu m) thick.</td>
<td>(2 \times 10^{17})</td>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>F</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 (\mu m) thick.</td>
<td>(4 - 6 \times 10^{17})</td>
<td>7</td>
<td>2.2-1.5</td>
</tr>
<tr>
<td>G</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 (\mu m) thick.</td>
<td>(4 - 6 \times 10^{17})</td>
<td>7</td>
<td>2.2-1.5</td>
</tr>
<tr>
<td>H</td>
<td>MOCVD-grown p- (Al_{0.15}Ga_{0.85})N doped with Mg, 1 (\mu m) thick.</td>
<td>(2 \times 10^{16})</td>
<td>7</td>
<td>45</td>
</tr>
<tr>
<td>I</td>
<td>MOCVD-grown p- (Al_{0.15}Ga_{0.85})N doped with Mg, 1 (\mu m) thick.</td>
<td>(2 \times 10^{16})</td>
<td>7</td>
<td>45</td>
</tr>
<tr>
<td>J</td>
<td>PAMBE-grown GaN doped with Mn, 1 (\mu m) thick.</td>
<td>N/A</td>
<td>N/A</td>
<td>&gt;1\times10^6</td>
</tr>
<tr>
<td>K</td>
<td>PAMBE-grown GaN doped with Mn &amp; Si, 1 (\mu m) thick.</td>
<td>N/A</td>
<td>N/A</td>
<td>&gt;1\times10^6</td>
</tr>
</tbody>
</table>

Doped and undoped GaN samples with Ga-face polarity and a thickness of 1 \(\mu m\) were grown by Plasma Assisted Molecular Beam Epitaxy (PAMBE) on c-plane sapphire substrates. Mn doping resulted in concentrations of up to \(1.2 \times 10^{20} cm^{-3}\), as determined by elastic recoil
detection measurements, and almost intrinsic films with a specific resistance of more than $10^4 \, \Omega \cdot \text{cm}$ [25].

Schottky diodes were used to measure the diffusion length of the minority carrier electrons. For the MBE and MOCVD-grown samples, Au was evaporated onto the samples to form the Schottky diodes. These Schottky diodes were ~500 $\mu$m in diameter and 150 nm thick. For the PAMBE-grown samples a 30 nm-thick Pt contact was evaporated on top of the sample’s surface.

It should be noted that the value of the hole mobility for these samples will decrease as the number of ionized Mg acceptors is increased [1]. This is because when the number of Mg acceptors increases there will be more ionized centers with which the holes can interact.

**Schottky Diode**

Schottky diodes are used to collect the Electron Beam Induced Current, which is generated by the SEM electron beam. The Schottky diodes for the MBE and MOCVD-grown samples were fabricated by evaporating gold onto the semiconductor surface. These diodes had a diameter of ~500 $\mu$m and are much larger than $L_n$, which ranges from 1 to 10 $\mu$m, for these samples. Since the Schottky diode is an essential component to performing EBIC measurements a brief discussion of its properties will follow.

A Schottky diode is a unipolar device and is created when a metal layer is evaporated on top of a semiconductor. A unipolar device predominately has only one type of carrier that
participates in the conduction process, where a bipolar device will have both electrons and holes participating in the conduction process. The transport process for the Schottky diode is due mainly to the majority carriers, for a metal/p-type semiconductor contact the majority carriers would be holes.

Figure 2.2 Optical image of an Au Schottky barrier, 1 mm in diameter, on an MOCVD-grown p-type GaN sample.

A space charge region is created in the semiconductor due to the built in potential difference, $V_{bi}$, between the Fermi levels of the metal contact and semiconductor. At thermal equilibrium, the Fermi energy levels, $E_f$, for the metal contact and the p-type semiconductor must be equal. For this to occur, the spatial gradient of the Fermi energy level must be zero; this is because the drift current and the diffusion current for each type of carrier have to be equal at thermal equilibrium.

For p-type material, the space charge region in the semiconductor will contain negatively charged ions. This means that the part of the metal layer that is in contact with the p-type semiconductor will be positively charged and the electric field will point away from the metal contact and towards the p-type semiconductor; this electric field points in the same direction as for a p-n junction, which will be described below. The electric field is used to separate the
electron hole pairs and draw in the minority carrier electrons into the Schottky diode.

Figure 2.3 shows an energy band diagram for the Schottky diode at thermal equilibrium. In this case it is a metal/p-type semiconductor structure. In Figure 2.3, $W$ represents the width of the space charge region, $\varepsilon$ is the electric field, $q\phi_m$ is the metal work function, $q\phi_s$ is the semiconductor work function, $q\chi$ is the electron affinity, $E_v$ is the top of the valence band, $E_c$ is the bottom of the conduction band, and $E_0$ is the free electron energy.

![Energy band diagram of a Schottky diode at thermal equilibrium. This Schottky diode consists of a metal contact and a p-type semiconductor.](image)

**Figure 2.3** Energy band diagram of a Schottky diode at thermal equilibrium. This Schottky diode consists of a metal contact and a p-type semiconductor.

A forward bias can be applied to the Schottky diode in Figure 2.3 by connecting the positive terminal to the p-type semiconductor and the negative to the metal contact; this will
decrease the space charge region. When a forward bias is applied to the Schottky diode the potential difference between the metal contact and the p-type semiconductor will decrease. Since the space charge region has become smaller the electric field will also decrease, which means that the drift current will become less. When a forward bias is applied, the drift current will become less than the diffusion current and there will be an injection of electrons into the p-type material from the metal contact.

**p-n Junction**

The p-n junction is a bipolar device, meaning both holes and electrons contribute to the conduction process. The most important characteristic of a p-n junction is its ability to allow current to flow easier in one direction than the other; it is a rectifier of current. p-n junctions are the building blocks for most other devices used in integrated circuits and are used in the construction of Metal Oxide Semiconductor Field Effect Transistors (MOSFETs), bipolar transistors, and thyristors. The p-n junction is divided into three different regions, the neutral p-type region, the neutral n-type region, and the depletion region.

When the p- and n-type semiconductors are first joined together a diffusion current is created which sweeps the holes from the p-side to the n-side and the electrons from the n-side to the p-side. This creates a charged region known as the depletion region. The p-side of the depletion region now contains negatively charged ions and extends out a distance $-x_p$ from the p-n interface, while the n-side contains positively charged ions and extends a distance $x_n$ from
the p-n interface.

![Energy band diagram for the p-n junction at thermal equilibrium.](image)

**Figure 2.4** Energy band diagram for the p-n junction at thermal equilibrium.

![Illustration of the drift and diffusion currents in a p-n junction at thermal equilibrium; solid circles represent electrons and the hollow circles are holes.](image)

**Figure 2.5** Illustration of the drift and diffusion currents in a p-n junction at thermal equilibrium; solid circles represent electrons and the hollow circles are holes.
The charged regions of the depletion region create an electric field, which cause the electrons and holes to move with a drift velocity. At thermal equilibrium, the drift current from the electric field and the diffusion current from the concentration gradient are equal to one another. A requirement for the existence of thermal equilibrium is that the Fermi levels, $E_f$, be constant and equal. When the Fermi levels for both the n- and p- type semiconductors are at the same level a built in potential, $V_{bi}$, is created.

To apply a forward bias to a p-n junction the positive terminal is connected to the p-side and the negative terminal is connected to the n-side of the p-n junction. When a forward bias is applied to a p-n junction the electron energy levels are lowered in the p region relative to the n-region [41] and the electric field in the depletion region will decrease. This allows for an increase in the flow of electrons from the n to p regions and an increase of holes from the p to n regions, so electrons are being injected into the p-region from the n-region when a p-n junction is forward biased.

The electron current density in the p-region is a function of the applied voltage, $V$, and the distance $x$ is given by the following equation

$$J_n = \frac{eD_n n_i^2}{L_n N_D} \left( \exp(eV / k_B T) - 1 \right) \exp((x + x_p) / L_n) \tag{2.1}$$

where $n_i$ is the intrinsic carrier density, $D_n$ is the electron diffusion coefficient, $L_n$ is the electron diffusion length, $k_B$ is Boltzmann’s constant, $T$ is the temperature, $e$ is the charge of the electron, and $N_D$ is the donor concentration.
EBIC Setup

In order to create the Electron Beam Induced Current, the electron beam of an SEM Philips XL 30 was used to irradiate the samples. Accelerating voltages between 20 to 30 keV were used. These voltages correspond to an electron range (penetration depth of the SEM electron beam) of 1.2 - 2.5 $\mu$m [42, 43]. A planar metal-semiconductor (Schottky) configuration was employed to perform the EBIC measurements for temperatures ranging from 25°C to 130°C.

Several instruments were used to record the EBIC signal. A standard lock-in technique using an EG&G 7220 lock-in amplifier was employed with the SRS DS335 function generator and the SEM. The function generator was used to modulate the electron beam of the SEM. The EBIC signal from the SEM was synchronously amplified by the lock-in amplifier to significantly enhance the signal-to-noise ratio. The lock-in amplifier sends the analog EBIC signal to the Keithley 2000 voltmeter, where it is digitized before a Personal Computer (PC) records it. The PC records the voltage versus the distance scanned by the SEM electron beam, starting at the edge of the Schottky diode and scanning away from it.

The sample is positioned so that the EBIC line scans will be perpendicular to the outer edge of the Schottky contact (see Figure 2.8); a typical EBIC line scan will take 12 s to complete. At a magnification of 25,000 the EBIC line scan will cover a distance of $\sim 4.4 \mu m$. An initial EBIC line scan is performed to get a pre-electron injection value for $L_n$; the electron beam is then allowed to continue scanning the same area of the sample.
**Figure 2.6** Picture of the EBIC experimental set up. The parts of the setup used to record the EBIC signal are the EG&G lock-in amplifier (1), SRS function generator (2), Keithley voltmeter (3), and SEM (4).

**Figure 2.7** Diagram of the EBIC experimental setup. The function generator provides a reference signal to the lock-in amplifier and is used to modulate the SEM electron beam. The lock-in technique is employed to significantly enhance the signal-to-noise ratio. The signal is digitized using the voltmeter and is recorded by the PC.
The total time of the multiple line scans was up to 3,000 s. Periodically during the electron injection, EBIC line scans would be performed to obtain additional values of $L_n$. In this way a set of values for $L_n$ were obtained while continually injecting electrons into the material. The amount of current absorbed by the material is $\sim 2$ nA when a 30 keV beam is used. For each temperature-dependent measurement a new location was chosen. This was done to ensure that the new site was not affected by the injection of electrons from the previous site.

**Calculating Diffusion Length from EBIC Measurements**

Diffusion occurs when there is a spatial variation of the carrier concentration. When this spatial variation exists inside a semiconductor the carriers will move from an area of high concentration to an area of low concentration; this is also known as the diffusion current. The electron diffusion current density is proportional to the gradient of the electron density by the following equation

$$J_n = eD_n \frac{dn}{dx}$$

(2.2)

where $n$ is the electron concentration, $e$ is the charge of the electron, and $D_n$ is the electron diffusion coefficient.

For a p-type semiconductor the diffusion length for the minority carrier electron is defined as

$$L_n = \sqrt{D_n \tau_n}$$

(2.3)
where $L_n$ represents the mean distance that an electron will travel before it recombines with a hole and $\tau_n$ represents the lifetime of the minority carrier electron.

At thermal equilibrium, the diffusion coefficient is defined by the Einstein relation

$$D_n = \frac{k_B T}{e \mu_n} \tag{2.4}$$

where $\mu_n$ is the mobility of the minority carrier electrons, $k_B$ is Boltzmann’s constant, and T is the temperature. The Einstein relation relates the diffusivity to the mobility of the minority carrier electron.

The EBIC technique has been used very successfully to determine the diffusion length of semiconductor materials. Since 1980, the planar configuration has been used to determine the minority carrier diffusion length. The planar configuration uses a Schottky diode, a metal contact evaporated onto a semiconductor, to collect the minority carriers.

Figure 2.8 The planar configuration uses a Schottky diode to collect the minority carrier electrons in a p-type semiconductor.
An SEM is used with the planar configuration to determine the minority carrier diffusion length. In the planar configuration, the SEM electron beam irradiates the sample perpendicularly as it moves away from the Schottky diode, as seen in Figure 2.8. When the electron beam irradiates the sample, it will generate electron-hole pairs. These electron-hole pairs are separated by the electric field of the space charge region, which exists in the semiconductor underneath the Schottky diode. For p-type materials, the electron minority carriers are then collected by the Schottky diode to create the Electron Beam Induced Current.

Ioannou et al. [44, 45] used the method of images to solve the planar configuration model; Dimitriadis later solved the special case problem of a thin semiconductor layer [46]. Ioannou used several assumptions to solve this problem. The sample dimensions were considered to be much larger than the diffusion length; actually Ioannou took the sample to be semi-infinite for his calculation. The scan should be performed far away from the ends of the semiconductor material and the thickness should be quite large compared to $L$. This is generally true if the thickness of the sample and the distance from the edge is greater than $2L$.

The dimensions of the Schottky diode were considered to be semi-infinite, and the EBIC line scan is to be performed perpendicularly to the outer edge of the Schottky diode. This assumption implies that the physical dimensions of the Schottky diode should be much larger than $L$. This is generally not a problem since the diameter of the Schottky diodes used in this research is on the order of a millimeter.

Ioannou assumed the surface recombination velocity, $\nu_s$, to be infinite for this problem. This assumption is valid when the surface recombination velocity is much greater than the
recombination velocity in the bulk. This relation can be written as

\[ \nu_s \gg D_n / h \]  \hspace{1cm} (2.5)

where \( h \) represents the penetration depth and is the distance from the surface to where the electron-hole pairs are generated.

There were some other assumptions that Ioannou used to solve the Schottky diode planar configuration problem. The distance from the Schottky diode to the electron beam had to be larger than the diffusion length, \( x > L \). Ioannou found that good results could be obtained when \( x > 2L \) was used. One other assumption is that the penetration depth of the electron beam should be smaller than the distance from the Schottky diode to the electron beam, \( h << x \).

The final expression that was derived using these assumptions for the planar configuration shows that EBIC decays exponentially when the electron beam moves away from the Schottky diode and can be written as

\[ I = A x^{-3/2} \exp(-x/L) \]  \hspace{1cm} (2.6)

where \( A \) is a constant. Equation (2.6) is taken to be valid when \( x > 2L \) and \( \nu_s = \infty \).

Donolato [47] used Green’s functions to solve the planar configuration problem. He derived two asymptotic expressions, one for \( \nu_s = \infty \) and another for \( \nu_s = 0 \). The expression that Donolato obtained, for when the surface velocity is equal to infinity, is the same as what Ioannou obtained in reference [44]. The expression for \( \nu_s = 0 \) was found to be

\[ I = A x^{-1/2} \exp(-x/L) \]  \hspace{1cm} (2.7)

By comparing equations (2.6) and (2.7) it can be seen that EBIC will decrease more slowly when \( \nu_s = 0 \) than when \( \nu_s = \infty \). This implies that more current will be collected when \( \nu_s = 0 \) than
when $\nu_s = \infty$.

Chan [48] proposed that equations (2.6) and (2.7) could be used to extract the diffusion length from an EBIC measurement for any value of $\nu_s$. The two asymptotic expressions for EBIC can be combined and written as

$$I = Ax^{-\alpha} \exp(-x/L) \quad (2.8)$$

where $\alpha = \frac{1}{2}$ for $\nu_s = 0$ and $\alpha = \frac{3}{2}$ for $\nu_s = \infty$.

The natural logarithm can be taken of equation (2.8) to give

$$\ln(Ix^\alpha) = -\frac{x}{L} + \ln(A) \quad (2.9)$$

When $\ln(Ix^\alpha)$ is plotted versus $x$, a straight line is obtained for a correctly chosen value of $\alpha$. The slope of this line will give the value for $L$, slope $= \frac{1}{L}$.

Kuiken [49] compared the asymptotic expression for $\nu_s = \infty$ to a more rigorous calculation of $L$. Kuiken used the results from Ioannou [50] as a comparison to the more exact results. In reference [50] EBIC measurements were made on p-type Si, doped with B. Ioannou used equation (2.6) to fit straight lines to the experimental EBIC data. Kuiken found that the asymptotic expression overestimated $L$ by 25% for this example. Kuiken compared other examples to his calculation of $L$ and found the overestimation to be around 13%. So the asymptotic expressions that were derived for the planar configuration yield a reasonable value.
for $L$, but the asymptotic expression for $\nu_s = \infty$ overestimates the actual value of $L$.

For this research, the voltage was measured as a function of distance from the Schottky diode. $L_n$ can be extracted from EBIC graphs similar to the one in Figure 2.9.

![EBIC measurement for MBE-grown p-type Al$_{0.2}$Ga$_{0.8}$N at a magnification of 5,000 and a temperature of 70 °C.](image)

**Figure 2.9** EBIC measurement for MBE-grown p-type Al$_{0.2}$Ga$_{0.8}$N at a magnification of 5,000 and a temperature of 70 °C.

Since $I=V/R$, equation (2.9) can be written as

$$\ln(V x^{1/2} ) = -\frac{x}{L_n} + \ln(A \cdot R) \quad (2.10)$$

where $\alpha$ has been chosen to be $\frac{1}{2}$ since GaN exhibits a high luminescence efficiency.

Equation (2.10) is accurate for $x > 2 L_n$, so when equation (2.10) is plotted, a straight line can be
expected in this region. Figure 2.10 shows the graph of equation (2.10) for the data taken from Figure 2.9.

One can see that a straight line is obtained for $4.6 \mu m < x < 8.5 \mu m$. The slope of this line is found to be $-0.8575 \mu m^{-1}$, which will yield a value of $L_n = 1.17 \mu m$ (remember that $L_n = -\frac{1}{\text{Slope}}$). So indeed, the minority carrier diffusion length can be obtained from the slope of a straight line of the plot of equation (2.10) for values of $x$ greater than $2L_n$.

![Graph of equation (2.10)](image)

**Figure 2.10** $L_n$ is determined from the slope of the linear fit to the data, $L_n = -\frac{1}{\text{Slope}}$. This graph is for MBE-grown p-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$. 

37
Calculation of the activation energy from the temperature-dependent EBIC measurements

For III-Nitrides the diffusion coefficient depends on temperature by the following equation [51]

\[ D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \]  \hspace{1cm} (2.11)

where \( E_a \) is the activation energy for the process.

From equations (2.3) and (2.11) it can be seen that the diffusion length is also temperature-dependent [52] and can be described by

\[ L_n = L_0 \exp\left(-\frac{E_{a1}}{2k_B T}\right) \]  \hspace{1cm} (2.12)

For the temperature-dependent measurements of the diffusion length the rate \( R = dL_n / dt \) was used to calculate the activation energy. \( R \) is a measure of the change of \( L_n \) with the duration of electron injection, \( t \).

The diffusion length, \( L_n \), will increase as the duration of electron injection increases. The growth of \( L_n \) will saturate at some point during electron injection and the growth of \( L_n \) will level off. The rate of growth of \( L_n \) is used to calculate the activation energy for the temperature dependent EBIC measurements. As a result, only the linear portion of the growth of \( L_n \) is used in the calculation of the rate, \( R \). Figure 2.11 shows the growth and saturation of \( L_n \) for MBE grown p-type \( \text{Al}_{0.2}\text{Ga}_{0.8}\text{N} \), only the first four points were used in the calculation of \( R \).
Differentiating equation (2.12) with respect to $t$ yields

$$ R = \frac{dL_n}{dt} = \exp(-E_{a1} / 2k_B T) \frac{dL_0}{dt} \quad (2.13) $$

Now, the $L_0$ dependence on the duration of electron injection is given by

$$ \frac{dL_0}{dt} = R_0 \exp(E_{a2} / k_B T) \quad (2.14) $$

There are two different activation energies used in equations (2.12) and (2.14). In equation (2.12) $E_{a1}$ is due to temperature dependence. In equation (2.14) $E_{a2}$ is due to the duration of electron injection. It is assumed that $E_{a1}$ and $E_{a2}$ are close to one another and that they describe the same process. Therefore, $E_{a1}$ and $E_{a2}$ are set equal to one another and the rate
becomes

$$ R = R_0 \exp \left( \frac{E_a}{2k_B T} \right) \quad (2.15) $$

The rates are calculated for each sample. Equation (2.15) is then used to fit the linear part of the data to obtain a value for the activation energy of the process. Equation (2.15) can be rearranged to yield an Arrhenius graph, $\ln \left( \frac{R}{R_0} \right) = \frac{E_a}{2k_B T}$. The activation energy can be found from the slope of the straight line from the Arrhenius graph.

### Cathodoluminescence

Cathodoluminescence measurements were carried out *in situ* inside the Philips XL30 SEM. The sample temperatures in the SEM varied from –50 to 135°C. The emitted radiation was analyzed using a single grating (1200 lines/mm, blazed at 500nm) and a Hamamatsu photomultiplier tube, which is sensitive in the 185-850 nm range. Accelerating voltages between 10 – 30 keV were used to cause the sample to luminesce. These voltages correspond to an electron range of 0.37–2.5 μm [42, 43]. The excitation was combined with periodic acquisition of cathodoluminescence spectra, taken under an SEM magnification of 4,000 – 30,000.

Figure 2.1 shows how the CL experimental setup is integrated with the SEM. The monochromator (4) is on the right side of the SEM and houses the mirrors and the diffraction grating system. To the right of the monochromator is the Hamamatsu photomultiplier tube (5). A PC is used to record the intensity of light (number of counts) for each specific wavelength.
Figure 2.12  Inside the SEM chamber. The stand (2) is not only used to position the samples but to heat and cool them. A parabolic mirror (1), which is integrated with a light guide, is used to collect the light from the sample. Liquid Nitrogen cooled gas is sent through the plastic hoses (4) to cool the sample, which is mounted on top of the stage. A computer controlled heater and a Platinum Resistance Thermometer (3) are connected to the stage.

Figure 2.12 shows the inside of the SEM chamber. The samples are mounted on top of the brass cylinder stage (2) that is in the bottom of the picture. Inside the stage a computer-controlled heater is inserted. A Platinum Resistance Thermometer is inserted inside the stage on the opposite side of the heater. Liquid Nitrogen cooled gas is used to cool the brass stage and the samples (4). The parabolic mirror (1) is located at the top of Figure 2.12 and collects the emitted
light from the samples. A hole is cut in the middle of the mirror so that the SEM electron beam can irradiate the sample when the mirror extends out over the sample; the mirror is positioned ~1 mm above the sample. The parabolic mirror collimates the light and sends it down the wave-guide to the monochromator.

The electron beam of the SEM was used in the spot and scan mode to generate the cathodoluminescence spectrum. An initial CL measurement was taken at the beginning of electron injection; periodic CL measurements were performed thereafter. The samples were continuously excited for up to 2,200 s. A new site was chosen for each set of temperature measurements so as to not be affected by the injection of electrons from the previous site.

**Calculation of the activation energy for temperature-dependent cathodoluminescence measurements**

The CL intensity of the band to Mg acceptor transition for a p-type III-Nitride sample will decrease as the duration of electron injection increases. This occurs because the lifetime of the electron in the conduction band increases as the electrons from the SEM electron beam are injected into the material. It is known that the intensity of luminescence is proportional to the Rate of Radiative Recombination (RRR) and that the rate of radiative recombination is inversely proportional to the lifetime \( RRR \propto \frac{n}{\tau_n} \) where \( n \) is the number of carriers [53]. Now equation (2.3) states that \( I_n \) is proportional to the square root of the lifetime; it will be shown in Chapter 3 that \( I_n \) is also proportional to the duration of electron injection. This means that the CL
intensity should be proportional to the inverse square of the duration of electron injection.

\[ I \sim \frac{1}{RRR} \sim \frac{1}{\tau_n} \sim \frac{1}{L_n^2} \sim \frac{1}{t^2} \]  \hspace{1cm} (2.16)

Equation (2.16) can be rearranged to show that

\[ \frac{1}{\sqrt{I}} \sim t \]  \hspace{1cm} (2.17)

It will be shown in Chapter 3 that a straight line is obtained when the square root of the inverse normalized peak CL intensity is plotted versus the duration of electron injection.

The rate of change of \( I^{-1/2} \) can be found for every temperature measurement. For temperature-dependent CL measurements the rate, \( R_{CL} \), is given by

\[ R_{CL} = \frac{\Delta[I^{-1/2}]}{\Delta t} \]  \hspace{1cm} (2.18)

where \( I \) represents the normalized CL peak intensity and \( t \) is the duration of electron injection.

Once the rates have been found equation (2.15) can be used to fit the data to obtain the activation energy for the process.

**Photoresponse**

The commercially built p-i-n photodetectors used to study the electron injection effect were purchased from SVT Associates. These detectors have a peak responsivity of 0.1 A/W at 360 nm. Figure 2.13 shows the experimental setup used to measure the photoresponse of these detectors and Figure 2.14 is a block diagram showing how the various instruments are connected.
Figure 2.13  Photoresponse experimental setup. The Jobin Yvon monochromator (6) selects the specific wavelength of light to be sent to the photodetector (5) from the light source, generated by the Xenon lamp (7). The Scitec optical chopper (1) is used to modulate light, by way of a mechanical interruption (4), and also sends a reference signal to the Perkin Elmer lock-in amplifier (3). The voltage output is digitized by the Keithley voltmeter (2) and then recorded by a PC, where the voltage is recorded versus wavelength.

An HP-4145A semiconductor parameter analyzer was used to perform current and voltage measurements on the photodetectors. These I-V measurements were performed to monitor the leakage current of the detectors. The grating (2400 line/mm and blazed at 250 nm) of the Jobin Yvon monochromator is used to select a specific wavelength of light from the Xenon lamp. A standard lock-in technique using a 7225 Perkin Elmer lock-in amplifier was employed with a Scitec optical chopper to record the signal from the photodetector to the voltmeter.

An initial spectral response was performed before electron injection. After this initial characterization, a bias of 5 V was applied to the photodetector for up to 300 s. After each time interval of forward bias was completed, another measurement of the spectral response was performed. After the forward bias experiment, a reverse bias was used to see if it would change
the spectral response. For this purpose a reverse bias of 10 V was applied for 30 minutes to the previously forward biased photodetector.

**Figure 2.14** Diagram of the photoresponse experimental setup. The monochromator takes the light generated by the Xenon lamp and outputs a specific wavelength to the photodetector. A standard lock-in technique using a 7225 Perkin Elmer lock-in amplifier was employed with a Scitec optical chopper to record the signal from the photodetector.
CHAPTER THREE: RESULTS

The samples in Table 2.1 were chosen to provide systematic studies of the electron injection effect in III-Nitrides. EBIC measurements were performed on samples A, B, C, D, E, J, and K to determine how the transport properties of the III-Nitrides are affected by electron injection. CL measurements were performed on samples A, F, G, H, I, J, and K to understand how the optical properties of the III-Nitrides are affected by electron injection.

III-Nitrides Doped with Mg

EBIC measurements were performed on samples A, B, C, D, and E. These samples were chosen to provide systematic studies of the electron injection effect in p-type (Al)GaN as a function of the sample’s temperature, Al concentration, structure (bulk or alternating layers of AlGaN and GaN in the superlattices), and doping (distribution of Mg in the superlattices). These experiments demonstrated a multi-fold increase in $L_n$.

CL measurements were performed on samples A, F, G, H, and I. These samples were chosen to provide systematic studies of the electron injection effect in p-type (Al)GaN as a function of the sample’s temperature and Al concentration. These measurements show how
Minority carrier transport properties in GaN:Mg

Two different p-type GaN samples were studied using the EBIC technique, these were samples A and B from Table 2.1. Sample A is MOCVD-grown bulk GaN:Mg and sample B is MBE-grown GaN:Mg. These two samples were chosen to investigate if the different growth techniques had a major impact on the electron injection effect.

Figure 3.1 EBIC Measurements for MBE-grown p-type GaN, sample B, at a magnification of 2,000 and a temperature of 40 °C. Plot (1) corresponds to 0 s of electron injection, (2) to 720 s, and (3) to 1,440 s of electron injection; solid and dashed lines represent the linear fit.

Figure 3.1 shows the EBIC measurements for MBE-grown GaN:Mg at a temperature of 40 °C. It can be seen that the slope of the lines changes as the duration of electron injection...
increases. Since \( L_n = -\frac{1}{\text{slope}} \), Figure 3.1 shows that \( L_n \) increases as electrons are injected into the material by the SEM electron beam.

![Graph showing the relationship between diffusion length and duration of electron injection for different temperatures.](image)

**Figure 3.2** Variable temperature dependence of \( L_n \) versus the duration of electron injection for MOCVD-grown p-type GaN, sample A. Squares, circles, and triangles are experimentally obtained values of \( L_n \) at 25, 75, and 130 °C, respectively; solid and dashed lines represent the linear fit. Saturation of \( L_n \) is not shown in this graph.

Figure 3.2 shows the \( L_n \) values which were extracted from the EBIC measurements of MOCVD-grown GaN:Mg. This graph shows the dependence of \( L_n \) on the duration of electron injection for three different temperatures. It can be seen from Figure 3.2 that there is a multi-fold linear increase of \( L_n \) with respect to the duration of electron injection for each temperature measurement. \( L_n \) becomes saturated for times of electron injection greater than 2,100 s. The
total charge injected into the sample by the SEM electron beam is \( \sim 1.4 \ \mu C \) for an injection time of 2,100s. Notice that it takes less time for \( L_n \) to saturate when the sample temperature is lower, 1,500 s for 25°C and 2,100 s for 130°C. Once \( L_n \) has been increased by electron injection it will persist for several days [37,54].

The rate, \( R = dL_n / dt \), is obtained from the slopes of the linear fit of the data in Figure 3.2. It can be seen that \( R \) decreases as the temperature increases. These rates are used to obtain an Arrhenius graph of \( \ln(\text{Rate of change of } L_n) \) versus the thermal energy \( 1/2k_B T \) in Figure 3.3.

Equation (2.15) is used to fit this data to obtain the activation energy for the process. The best fit for MOCVD- and MBE-grown GaN:Mg was obtained for an activation energy of 178 and 190 meV respectively. The difference of 12 meV between the activation energies of the two differently grown GaN samples is within the acceptable range of thermal ionization energy variance for Mg-doped GaN [55].

The activation energy for a hole captured by an ionized Mg acceptor in GaN is generally lower than the thermal ionization energy of the same Mg acceptor. However, the measurements of persistent photoconductivity (PPC) in p-type GaN [56, 57] imply that these two activation energies may be quite close to one another, with the difference not exceeding 30 meV. This assumption is used in the interpretation of these experimental results.

Because the activation energy for the electron injection effect is close to the Mg acceptor thermal ionization energy [55, 56, 58, 59] the process for the activation energy obtained from the electron injection effect is ascribed to charging of Mg acceptor in GaN. Therefore, the activation energy represents the energy needed for an ionized Mg acceptor to capture a hole.
Both MOCVD- and MBE-grown GaN were studied to determine if H played a major role in the electron injection effect. MOCVD-grown GaN is grown in a H rich environment while MBE-grown GaN does not incorporate as much H in the growth process as GaN grown by the MOCVD technique [56]. The fact that the electron injection effect is observed in both MOCVD- and MBE-grown GaN implies that H does not play a significant role here.

**Optical properties of GaN:Mg**

Three different MOCVD-grown GaN samples (samples A, F, and G) were used to study how the injection of electrons affects the CL intensity of the conduction band to Mg acceptor
level transition. For sample A, temperature-dependent CL measurements were correlated with the electron injection-induced enhancement of $L_n$ seen in the EBIC experiments.

![Graph showing CL intensity vs. wavelength for different durations of electron injection](image)

**Figure 3.4** Cathodoluminescence measurements performed at 23 °C after different time intervals of electron injection. The maximum (379 nm) in spectrum 1 nearly corresponds to the pre-injection situation (less than 20 s time difference). The maximum in spectra 2, 3, 4, and 5 corresponds to 660, 1,200, 1,680, and 2,200 s of electron injection respectively. These measurements were made on MOCVD-grown p-type GaN, sample A. The peak intensity dropped ~66% in 2,200 s.

Figure 3.4 shows the CL spectra as a function of wavelength and duration of electron injection for sample A at a temperature of 23 °C. This spectra features a relatively broad luminescence band with a ~ 365 nm shoulder, which corresponds to the band-to-band transition of GaN. The peak CL intensity occurs at ~ 379 nm and corresponds to an excited electron transition, by the SEM electron beam, from the conduction band to the Mg acceptor level [36]. Figure 3.4 shows the continuous decay of the CL intensity as the duration of electron injection
increases. The electron injection-induced decrease in luminescence intensity persists for several
days at room temperature [60].

![Figure 3.5](image)

Figure 3.5 Peak CL intensity versus duration of electron injection for MOCVD-grown p-type
GaN, sample A, at 23 °C. The circles represent the peak CL intensity at ~379 nm and the solid
line is the quadratic fit.

The decrease in CL intensity is attributed to an increase in the lifetime of the minority
carrier electrons in the conduction band. The increase of $\tau_n$ is due to charging of the neutral Mg
acceptors in p-type GaN. Trapping of the injected electrons by the Mg acceptors prevents
recombination of the conduction band electrons through the ionized Mg$^-$ acceptors. This leads
to an increase of $\tau_n$ in the conduction band. Since the CL intensity is proportional to the rate of
radiative recombination and the rate decreases with increasing $\tau_n$, the CL intensity should decay
as $\tau_n$ increases, as is seen in Figure 3.4. A ~ 2 nm blue shift of the CL peak intensity is observed
as a function of the duration of electron injection in Figure 3.4. This shift is most likely attributed to the continuous charging of additional Mg levels in the forbidden gap by electron injection. It can be seen that the decrease in CL intensity starts to saturate at around 2,200 s.

Figure 3.5 shows a plot of the peak CL intensities versus the duration of electron injection for sample A. It is clear from Figure 3.5 that the peak CL intensity does not exhibit a linear relationship with the duration of electron injection and starts to saturate after 2,200 s.

![Figure 3.5](image_url)

**Figure 3.5** Shows a plot of the peak CL intensities versus the duration of electron injection for sample A.

The square root of the inverse normalized peak CL intensity as a function of duration of electron injection and temperature is shown in Figure 3.6. The rates, $R_{CL}$, are obtained from the slopes of the linear fits for each temperature. It can be seen from Figure 3.6 that, the different
rates decrease as the temperature of the sample increases. The $R_{cl}$ are used in Figure 3.7 to obtain an Arrhenius graph. Equation (2.15) was used to obtain the activation energies for samples A, F, and G; these energies were 190, 207, and 179 meV respectively. These activation energies are consistent with the ones found from the EBIC measurements and with the Mg acceptor thermal ionization energy [55, 56, 58, 59].

![Arrhenius graph for sample F. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 207 meV.](image)

**Figure 3.7** Arrhenius graph for sample F. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 207 meV.

Figure 3.8 shows the linear dependence of $L_n$ (circles) on the duration of electron injection for sample A from the EBIC measurements. Sample A was used in both the EBIC and CL measurements so that the different activation energies obtained by each method could be compared. The increase in $L_n$ is consistent with the decrease in the peak CL intensity, which is also shown in Figure 3.8 (squares), since $L_n \sim t \sim I^{-1/2}$. The activation energies obtained from
the EBIC and CL measurements of sample A were found to be 179 and 190 meV respectively. This implies that these two experimental techniques provide complimentary views of the electron injection effect.

![Graph showing the dependence of peak CL intensity and diffusion length on electron injection duration.]

Figure 3.8  Dependence of the peak CL intensity (squares) on the duration of electron injection and the quadratic fit for sample A, at room temperature. Also shown: dependence of the $L_n$ (circles) on the duration of electron injection for sample A and the linear fit. Saturation of $L_n$ is not shown in this graph.

Minority carrier transport properties in Al$_{x}$Ga$_{1-x}$N:Mg

Three different MBE-grown p-type Al$_{0.2}$Ga$_{0.8}$N samples were investigated by performing EBIC measurements. These samples were C, D, and E from Table 2.1. Sample C is bulk Al$_{0.2}$Ga$_{0.8}$N. Sample D is a modulation doped superlattice where only Al$_{0.2}$Ga$_{0.8}$N is doped.
with Mg in the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice. Sample E is homogenously doped with Mg in both the GaN and $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ parts of the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice.

![Graph](image)

**Figure 3.9** EBIC Measurements for MBE-grown homogeneously doped p-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice, sample E, at a magnification of 12,000 and a temperature of 40°C. Plot 1 corresponds to the pre-injection situation. Plots 2 and 3 correspond to 480 and 720 s of electron injection respectively.

Figure 3.9 shows EBIC measurements performed on sample E at a temperature of 40°C. This graph shows $L_n$ increasing as the duration of electron injection increases. Figure 3.10 graphs the extracted $L_n$ values, which were obtained from the EBIC measurements, as a function of duration of electron injection for three different temperatures. The general trend observed for all samples was for $L_n$ to exhibit a multi-fold linear increase.

The rate, $R = dL_n / dt$, is found from the slopes of the linear fit to the data in Figure 3.10;
this graph also shows how $R$ decreases as the temperature increases. This implies the existence of a thermally-activated process, which compensates for the electron injection effect. At $34^\circ C$, $L_n$ increased ten times before becoming saturated at $\sim 1100$ s.

![Figure 3.10](image)

**Figure 3.10** Typical temperature dependence of minority carrier diffusion length on duration of electron injection for a modulation doped Al$_{0.2}$Ga$_{0.8}$N/GaN superlattice, sample D. Circles, squares, and diamonds are experimentally obtained values at 34, 75, and 130 °C, respectively. Solid lines represent the linear fit. Saturation of $L_n$ is not shown in this graph.

The rates are then used to obtain the Arrhenius graph of Figure 3.11. $E_a$ is obtained by fitting the data using equation (2.15). The activation energies for bulk Al$_{0.2}$Ga$_{0.8}$N, modulation doped Al$_{0.2}$Ga$_{0.8}$N/GaN superlattice, and homogenously doped Al$_{0.2}$Ga$_{0.8}$N/GaN superlattice were found to be 252, 267, and 189 meV respectively [21, 61, 62].

The activation energy obtained for the bulk Al$_{0.2}$Ga$_{0.8}$N sample provides additional
evidence that Mg plays a role in the electron injection effect. The activation energy obtained for bulk $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ is close to the Mg acceptor thermal ionization energy [63]. The assumption is, that since the activation energy obtained for bulk $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ is close to the thermal ionization energy of the Mg acceptor in $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ (270 meV [63]) the electron injection effect is due to charging of these Mg levels. This is in good agreement with the activation energy (252 meV) obtained from the electron injection effect.

![Arrhenius graph for sample E](image)

**Figure 3.11** Arrhenius graph for sample E. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 189 meV.

According to Lambert et al. [14] every atomic percentage of Al in the p-GaN lattice results in a deepening of the Mg acceptor energy level by 3.2 meV. Therefore, incorporating 20% Al into the p-type GaN lattice would deepen the Mg level by 64 meV. Taking the value for the activation energy obtained from MBE-grown GaN (190 meV) and adding 64 meV to it yields
The activation energy obtained for the homogeneously doped $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N} / \text{GaN}$ superlattice was found to be 189 meV (Figure 3.11). This compares to the value of 190 meV obtained for MBE-grown GaN. The value of the activation energy for the homogeneously doped $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N} / \text{GaN}$ superlattice suggests that the main contribution to the electron injection effect is due to trapping of electrons by the GaN wells, not by the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ barriers. Apparently the trapping of electrons by barriers is minor when compared to the wells because of the higher Mg-
level position of the barriers.

![Graph showing temperature dependence of rate change of L_s](image)

**Figure 3.13** Temperature dependence of the rate of change of $L_s$ for MBE-grown homogeneously doped p-$\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice (circles) and modulation doped p-$\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice (squares). Solid lines represent the best fit.

The activation energy for the modulation doped $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}/\text{GaN}$ superlattice was found to be 267 meV, see Figure 3.13. This value is in good agreement with the thermal ionization energy of the Mg level for $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ found in reference [63] and with the value for the $E_a$ found for $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ in this work, 252 meV (Figure 3.12). This is to be expected since this superlattice only has the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ part doped with Mg. When only the barriers are doped with Mg in the modulation doped superlattice the only place that electrons can be captured is by
the Mg in the barriers.

It should be noted that the rate of change of $L_n$ for the superlattices is higher than the rate of change of $L_n$ in bulk GaN and Al$_{0.2}$Ga$_{0.8}$N (cf Figure 3.12 and 3.13). This agrees with previous experiments performed on other homogeneously doped superlattices [37]. A steeper increase for the rate of change of $L_n$ could be due to a higher internal electric field caused by spontaneous and piezoelectric polarization [37]. Polarization effects increase the minority carrier lifetime and diffusion length in the superlattices by an order of magnitude as compared to bulk material.

**Optical properties of Al$_{0.15}$Ga$_{0.85}$N:Mg**

Variable temperature-dependent CL measurements were performed on an MOCVD-grown Al$_{0.15}$Ga$_{0.85}$N :Mg sample as a function of duration of electron injection to better understand the impact of electron injection on its optical properties. The CL measurements performed on this sample were taken from two different regions of the sample, samples H and I. The final activation energy obtained from these measurements is an average of the two regions.

The spectra in Figure 3.14 were smoothed because of a noisy raw signal. The CL peak intensity for Al$_{0.15}$Ga$_{0.85}$N :Mg occurs at ~ 371 nm. This wavelength corresponds to the transition of an electron from the conduction band to a neutral Mg level. The decay of the CL intensity is evident from Figure 3.14, and the decay saturates at around 1,900 s.
Figure 3.14  Cathodoluminescence measurements performed at 25 °C after different time intervals of electron injection for MOCVD-grown p-Al_{0.15}Ga_{0.85}N, sample H. The maximum (371 nm) in spectrum 1 was taken after 130 s of electron injection. The maximum in spectra 2, 3, and 4 corresponds to 584, 1,026, and 1,902 s of electron injection, respectively.

The rates, $R_{CL}$, are found from the slopes of the linear fit to the data in Figure 3.15. These rates are then plotted against the thermal energy to yield the Arrhenius graph of Figure 3.16. Equation (2.15) is used to fit the data and obtain $E_a$. The activation energies for the two different regions of the Al_{0.15}Ga_{0.85}N sample were found to be 220 and 243 meV [64]; the average of these two regions is 232 meV. Remember that for every percentage of Al in the GaN lattice the Mg level deepens by 3.2 meV. Therefore, 15% of Al in the GaN lattice should result in a deepening of the Mg level by 48 meV. A value of 240 meV is obtained when 48 meV is added to the average activation energy, 192 meV, obtained from samples A, F, and G. This is in good agreement with the experimentally obtained average of $E_a$ (232 meV) obtained
for Al$_{0.15}$Ga$_{0.85}$N:Mg and is another indication of the involvement of Mg in the electron injection effect.

Figure 3.15  Square root of the inverse normalized peak CL intensity versus duration of electron injection for MOCVD-grown p-type Al$_{0.15}$Ga$_{0.85}$N, sample H. Squares, circles, and triangles are the experimentally obtained values at 25, 70, and 130 °C, respectively. Solid and dashed lines represent the linear fit.

Table 3.1  Activation energies obtained from EBIC measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Activation Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 µm thick.</td>
<td>178 ± 19</td>
</tr>
<tr>
<td>B</td>
<td>MBE-grown p-GaN doped with Mg, 2 µm thick.</td>
<td>190 ± 19</td>
</tr>
<tr>
<td>C</td>
<td>MBE-grown p-Al$<em>{0.2}$Ga$</em>{0.8}$N doped with Mg, 1.5 µm thick.</td>
<td>252 ± 69</td>
</tr>
<tr>
<td>D</td>
<td>MBE-grown p-Al$<em>{0.2}$Ga$</em>{0.8}$N / GaN modulation doped with Mg, 0.4 µm thick.</td>
<td>267 ± 32</td>
</tr>
<tr>
<td>E</td>
<td>MBE-grown p-Al$<em>{0.2}$Ga$</em>{0.8}$N / GaN homogenously doped with Mg, 0.4 µm thick.</td>
<td>189 ± 13</td>
</tr>
</tbody>
</table>
Figure 3.16  Arrhenius graph for sample H. Circles are the experimentally obtained values and the solid line represents the linear fit. The activation energy was found to be 220 meV.

Table 3.2  Activation energies obtained from CL measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Activation Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 ( \mu )m thick.</td>
<td>190 ± 36</td>
</tr>
<tr>
<td>F</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 ( \mu )m thick.</td>
<td>207 ± 55</td>
</tr>
<tr>
<td>G</td>
<td>MOCVD-grown p-GaN doped with Mg, 2-3 ( \mu )m thick.</td>
<td>179 ± 34</td>
</tr>
<tr>
<td>H</td>
<td>MOCVD-grown p- Al(<em>{0.15}) Ga(</em>{0.85}) N doped with Mg, 1 ( \mu )m thick.</td>
<td>220 ± 20</td>
</tr>
<tr>
<td>I</td>
<td>MOCVD-grown p- Al(<em>{0.15}) Ga(</em>{0.85}) N doped with Mg, 1 ( \mu )m thick.</td>
<td>243 ± 53</td>
</tr>
</tbody>
</table>
Mn-doped GaN was studied to see if the electron injection effect could be applied to other highly doped GaN samples. EBIC measurements were carried out and showed that the injection of electrons into GaN:Mn did increase $L_n$. After the increase of $L_n$ was verified, CL measurements, similar to the ones performed on Mg-doped III-Nitrides, were performed to investigate how the optical properties are affected by electron injection.

Sample J was investigated to determine the effects of electron injection on Mn-doped GaN. In addition, a GaN sample codoped with Mn and Si, sample K, was studied.

**Minority carrier transport properties in GaN:Mn**

EBIC measurements on Mn-doped GaN, sample J, were investigated to understand the impact of electron injection on this sample. A single EBIC line-scan took 12 s to complete and the excitation of the sample by the electron beam continued for ~200 s, with near-simultaneous EBIC measurements after several time intervals. Figure 3.17 shows $L_n$ increasing, $L_n = -1 / \text{slope}$, as the duration of electron injection increases. Figure 3.18 shows a three-fold linear increase of $L_n$ was obtained after ~200 s of electron injection.

These results show that the electrical properties of GaN:Mn are changed by electron injection. The linear increase in $L_n$ allows for the assumption that the same procedures that were used to study Mg-doped (Al)GaN can be applied to Mn-doped GaN.
Figure 3.17  Room temperature EBIC Measurements for PAMBE-grown GaN:Mn, sample J. Plot 1 corresponds to the pre-injection situation. Plots 2 and 3 correspond to 60 and 210 s of electron injection respectively.

Figure 3.18  Diffusion length versus duration of electron injection for GaN:Mn, sample J. $L_n$ increases over three-fold after 200s of electron injection. Saturation of $L_n$ is not shown in this graph.
Optical properties of GaN:Mn

Figure 3.19 shows the full range CL spectrum of the Mn-doped GaN, sample J, after 22 s and 2,070 s of electron injection at room temperature. This spectrum exhibits a broad luminescence band, 400 to 700 nm, which remains unaffected by the injection of electrons. This band is attributed to radiative transitions from shallow donors to deep acceptor levels. The peak at ~730 nm is a 2nd order effect of the grating system, the 730 nm wavelength is approximately twice that of peak 1.

Figure 3.19  CL intensity as a function of wavelength after 22 s (1) and 2,070 s (6) of electron injection for sample J.

Figure 3.20 shows a magnified view of the decay of the narrow band-to-band transition, 350 to 385 nm, from Figure 3.19. A small blue shift of the peak CL spectrum is observed as the duration of electron injection increases.
Figure 3.20  Cathodoluminescence measurements performed at 25 °C after different time intervals of electron injection. The maximum in spectra 1, 2, 3, 4, 5, and 6 corresponds to 22, 417, 833, 1,257, 1,661, and 2,070 s of electron injection respectively. These measurements were performed on PAMBE-grown GaN:Mn, sample J.

Figure 3.21  Variable temperature dependence for the square root of inverse normalized peak CL intensity versus the duration of electron injection for GaN:Mn, sample J. The rate at every temperature is obtained from the slope of the linear fit.
This shift is possibly attributed to continuous charging of Mn levels in the forbidden gap.

Since Figure 3.18 shows a linear relationship between $L_n$ and the duration of electron injection, equation (2.15) can be used to study the CL decay in GaN:Mn. Temperature-dependent CL measurements, -50 to 80 °C, were carried out to understand the impact of electron injection on $\tau_n$ in Mn doped GaN.

Figure 3.21 shows the dependence of the square root of the inverse normalized peak CL intensity versus the duration of electron injection. The rates are obtained from the slope of the linear fits and are used in equation (2.15) to obtain $E_a$. The increase in temperature results in a decrease in the rate, $R_{c2}$. This suggests the existence of a thermally-activated process, which compensates for the electron injection effect.

Figure 3.22 Arrhenius graph for sample J. Circles are the experimentally obtained values and the solid line represents the best fit. The activation energy was found to be 360 meV.
The Arrhenius graph of equation (2.15) is shown in Figure 3.22. An activation energy of 360 meV [65] was calculated for this process and might represent the hole capture barrier between the excited Mn$^{3+*}$ state and the ground Mn$^{3+}$ state. It has recently been shown that Mn forms a deep neutral acceptor level (Mn$^{3+}$) in Mn-doped GaN, where only a very small number of acceptors become ionized (Mn$^{2+}$) [25]. Si doping results in a shift of the Fermi energy level towards the conduction band and to almost complete ionization of the Mn acceptors in GaN:Mn:Si. There was no dependence on the duration of electron injection observed in the CL band-to-band transition or for $L_n$ in GaN:Mn:Si, sample K. Therefore, it can be concluded that the activation energy of the observed effects in GaN:Mn is due to the presence of neutral Mn acceptors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Activation Energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>PAMBE-grown GaN doped with Mn, 1 $\mu$m thick.</td>
<td>360 ± 3</td>
</tr>
</tbody>
</table>

**Application of the Electron Injection Effect in Commercial Photodiodes**

A significant increase of $L_n$ was observed in p-type (Al)GaN after an electric current had been injected into the solid-state devices. $L_n$ was measured using the EBIC technique *in-situ* in the SEM.
Figure 3.23  a) Mixed EBIC (dark vertical contrast) and secondary electron image of the p-n junction, cleaved perpendicular to the growth plane. Inset: p-n junction forward I-V curve. b) EBIC line-scan across the p-n junction [60].
The electrons were injected from the n-region into the p-region of a GaN p-n junction by applying a forward bias [38]. While there was an increase of $L_n$ on the p-side of the p-n junction, there was no increase of $L_p$ on the n-side (Figure 3.23 and 3.24). This was the first indication that Mg is involved in the electron injection effect, because Mg was used to make GaN p-type.

![Figure 3.24](image.png)

**Figure 3.24** A graph of $L_n$ (squares) as a function of the duration of electron injection into the p-region of a GaN p-n junction. A 6 Volt forward bias was applied to a 500 µm-diameter p-n junction mesa, to create a current density of 12 A/cm². The same plot presents the calculated $\tau_n$ (circles) dependence on the duration of electron injection, based on experimentally obtained $L_n$ values. Saturation of $L_n$ for times larger than 1500 s is not shown in this graph [38].

Figure 3.23a shows a mixed secondary electron and EBIC (dark vertical contrast) image of the GaN-on-sapphire wafer, cleaved through one of the p-n junctions. Figure 3.23b presents
one of the EBIC line-scans. The maximum of the EBIC signal corresponds to the interface between the p- and n-layers. The inset of Figure 3.23a shows a p-n junction forward I-V curve. Initially, an EBIC line scan measurement was performed before forward bias was applied [38, 60]. The EBIC measurements revealed a more than two-fold increase of the electron diffusion length, Figure 3.24, in the p-type region of the p-n junction. Saturation of $L_n$ was observed for times of injection larger than 1500 seconds. Figure 3.24 also presents the calculated values of $\tau_n$.

This early work on electron injection into a p-n junction provided the impetus for the following research in photodetectors. The questions of how electron injection could be applied to photodetectors and to what extent it would improve them are one of the goals of this dissertation.

Spectral response of GaN photodetectors is limited by a large absorption coefficient at high energies and a small $L_n$. Several design changes have been used to overcome these limitations. These changes to GaN photodetectors include the use of a p-i-n junction instead of a p-n one [14,66-68], using Al$_x$Ga$_{1-x}$N instead of GaN for the windows [14,66,67], the use of semitransparent windows [67], and using a back-illuminated detector [14]. The photoresponse experiments carried out in this work were designed to see if electron injection could be used to improve p-i-n photodetectors much like the design changes mentioned in references [14, 66-68].

When UV photons are absorbed on the p-side of a p-i-n photodetector, the quantum
efficiency, $\eta$, is defined by [69]:
\[
\eta = (1 - R)(1 - \frac{e^{-\alpha W}}{1 + \alpha L_n})
\] (3.1)

where $R$ and $\alpha$ are the reflection and absorption coefficients, respectively and $W$ is the width of the depletion layer in the p-i-n junction. The quantum efficiency represents the number of electron-hole pairs generated per photon. It can be seen from equation (3.1) that the quantum efficiency of the photodetector will improve when $L_n$ increases.

Figure 3.25 shows a GaN p-i-n photodetector manufactured by SVT Associates and Figure 3.26 shows the p-i-n detector architecture. Prior to injection of electrons, a spectral response of the photodetector was measured using the experimental setup described in chapter 2.

Figure 3.25  p-side illuminated SVTA GaN photodetector with ultra-violet -enhanced window.
Current-Voltage measurements were carried out on the photodetector as part of the initial characterization. Upon characterization completion, a constant forward bias of 5 Volts (corresponding to a current of ~ 42 mA; cf. inset of Figure 3.27) was applied to the photodetector during several time intervals, to inject electrons into its p-region. The spectral photoresponse was measured after each time interval of electron injection. The obtained spectra (2-4) are also shown in Figure 3.27.

A 3.5 times increase of the peak responsivity (360nm), relative to the pre-injection value, was observed after applying a forward bias for 83 seconds. A comparable increase in the photoresponse is also observed for the shoulder in the 255-330 nm range and for a peak of ~ 235 nm in Figure 3.27. It should be noted that a significant enhancement in the commercial photodetector responsivity occurs within an order of magnitude shorter time frame as compared to the laboratory p-n junction structure (up to 1200 seconds) [70]. This may be explained by a higher concentration of Mg (higher doping level, which is ~ 10^{18} cm^{-3}) in the p-region of a
Figure 3.27  Zero bias spectral photoresponse of the p-i-n photodetector before (1) and after (2, 3, 4) injection of electrons by applying a forward bias. Spectra 2, 3, and 4 correspond to 18, 40, and 83 s of electron injection, respectively. **Inset:** Forward branch of the photodetector’s I-V curve. A 5 V forward bias was used for the injection of electrons.

Figure 3.28  Dependence of the photodetector’s peak responsivity at 360 nm versus the duration of electron injection. The solid lines represents the quadratic fit. Saturation occurs after ~83 s of electron injection.
The increase of responsivity due to electron injection is attributed to an increase of $L_n$, due to charging of the Mg-related levels [70], in the p-type region of the p-i-n photodetector. Figure 3.28 shows the dependence of the photodetector’s peak responsivity at 360 nm (cf. Figure 3.27) on the duration of electron injection. It can be seen that the photoresponse is close to its saturation after 83 seconds of electron injection.

Figure 3.29 Leakage current of the p-i-n photodetector before (squares) and after (circles) 83 s of electron injection.

The leakage current of the p-i-n photodetector was monitored before and after electron injection, to see if there was any significant change in this parameter. Figure 3.29 shows the reverse branches of the detector’s current-voltage (I-V) curves before electron injection and after 83 seconds of injection. It can be seen that although a low voltage (up to –2 Volts) leakage current for the device after injection is at most 20% higher than before injection, the difference in reverse currents at higher voltage (-5 Volts) does not exceed 5%. This is an encouraging result.
as in some cases the photodetectors are used under reverse bias, to increase their quantum efficiency. On the other hand, the results of Figure 3.27 suggest that a reverse bias mode may be unnecessary, if periodic electron injection is used to boost responsivity.

![Figure 3.30](image)

**Figure 3.30** Photoresponse spectrum from one of the SVTA p-i-n photodetectors before (1) and after (2) several hundred seconds of applying a 5 V forward bias. The peak responsivity at \(\sim 360\) nm showed a 4.5 times increase. **Inset:** Relaxation of zero bias peak responsivity at 360 nm after 30 minutes of 10 V reverse bias.

One of the SVTA p-i-n photodetectors was forward biased at 5 Volts (without illumination) for several hundred seconds. This resulted in a \(\sim 4.5\)-fold increase of the peak photoresponse from the initial value of 0.7 Volts at 360 nm. The enhanced photoresponse spectrum is shown in Figure 3.30. After achieving a significant response enhancement, the kinetics of its relaxation back to the pre-injection level under zero-bias at the wavelength of 360 nm (peak responsivity) was monitored. It was found that the peak photoresponse remained unchanged (within the 10% range) for a post-injection time of at least four weeks. This result
clearly indicates that forward biasing by electron injection can induce significant and lasting improvements of a photodetector’s quantum efficiency.

The next step was to see if application of a reverse bias to a photodetector, that already possessed an enhanced response, could affect it. For this purpose, the same detector as in Figure 3.27 was used and a reverse bias of 10 Volts for 30 minutes was applied. As before, the photoresponse after reverse bias was monitored under zero-bias at 360 nm. The result is shown in the inset of Figure 3.30. A decrease in the photoresponse immediately after turning off the reverse bias is observed (it is still more than twice as large when compared to before forward current injection). However, a full response recovery was observed under 360 nm illumination within ~ 2 minutes. The obtained results indicate that:

1. A partial discharging of the levels, which trapped the injected electrons by forward bias, is possible when a sufficiently large reverse bias is applied.

2. Photodetector illumination (with a light energy comparable to GaN band gap) after reverse bias fully recovers the photoresponse. This is due to a generation of photoelectrons, which get trapped by the level(s) involved in the phenomenon of interest.

3. Illumination of a p-\textit{i}-n photodetector with no prior forward bias does not enhance a photoresponse. This indicates that a forward bias application is needed to activate the traps.
Schottky barrier photovoltaic detectors

The experiments were carried out on Au/p-GaN Schottky barriers of 500 µm-diameter. It has to be noted that a sufficient forward bias application to a Schottky barrier is needed to create electron injection conditions similar to that in p-n junctions, with a sufficient amount of electrons injected in the conduction band of p-type GaN [53]. In contrast to the experiments in which a monochromatic light was used, here a multi-spectral light from a halogen lamp was employed for monitoring the total response (cf. Figure 3.31). One can see from Figure 3.31 that in Schottky barriers, an electron injection with a relatively low current leads to a pronounced change in the photoresponse. This is likely related to a large amount of Mg traps, which play a role in the effect.

In a separate experiment, however, a forward current of 3 mA applied for 600 seconds to another Schottky diode, caused a 17 times enhancement of the total photoresponse. The decay of this response to a pre-injection level is shown in Figure 3.32. Note that it takes over 3 days for a photoresponse to totally relax. This result, although not as impressive as the p-i-n detectors (over 4 weeks of device stability), indicate that the effect of electron injection has, indeed, a practical application and can be used in commercial products.
Figure 3.31  Dependence of the total photoresponse for a Schottky barrier on time of forward bias electron injection. A forward current of 1 mA was flown through a structure for ~650 s. The photoresponse is normalized with respect to the initial value measured immediately before an electron injection.

Figure 3.32  Dependence of the total normalized Schottky barrier detector response on post-injection time. Time 0 corresponds to the moment when the forward bias was turned off. The photoresponse is normalized relative to its pre-injection level.
CHAPTER FOUR: DISCUSSION

This chapter will present the models that are used to describe the electron injection effect in Mg-doped (Al)GaN and Mn-doped GaN. Both the Mg- and Mn-doped samples were heavily doped, $\sim 10^{20} \text{ cm}^{-3}$. This implies that it might be possible to apply the electron injection effect to other heavily doped materials that have impurities which form deep levels and can trap electrons.

**Model of the Electron Injection Effect in Mg-doped (Al)GaN**

Figure 4.1 shows the proposed model used to describe the electron injection effect in Mg-doped (Al)GaN. One of the key points of this model is that less than 1% of the total number of Mg impurities ($\sim 10^{20} \text{ cm}^{-3}$) are ionized at room temperature and the nonionized Mg impurities act as traps for the injected electrons.

A neutral Mg level traps an electron, which has been injected into the sample by the SEM electron beam. The concentration of ionized Mg acceptors increase as the duration of electron injection increases. Note that the concentration of neutral Mg acceptors in p-type (Al)GaN is quite significant (up to $10^{20} \text{ cm}^{-3}$) because of the large values (130-208 meV [55,56,59]) of the thermal ionization energy of the Mg acceptors. A high concentration of Mg is needed to
generate enough holes to compensate for the n-type defects in GaN and the high thermal ionization energy of the Mg acceptors.

Figure 4.1 Proposed model for the electron injection effect using the SEM electron beam. A neutral Mg level traps an electron, which was injected by the SEM electron beam. These ionized Mg levels stop playing a role in the recombination process. As a result, the electrons in the conduction band, which normally recombine through these Mg levels, cannot do so. This means that the electrons stay in the conduction band longer and the lifetime of the conduction band electrons will increase. These Mg levels will become available to play a role in the recombination process after it has captured a hole. $E_c$ represents the bottom of the conduction band, $E_v$ is the top of the valence band, and $Mg^-$ represents the ionized Mg acceptors [61].

As the number of ionized Mg acceptors increase, the electrons in the conduction band, which would normally recombine through the Mg levels, are forced to stay there until a neutral Mg acceptor becomes available for transition. Trapping of an injected electron by the Mg acceptor prevents recombination of the conduction band electrons through this level. This leads to an increase in the lifetime of the minority carrier electron in the conduction band. An
increasing $\tau_n$ leads to a decrease in the rate of radiative recombination, which is observed in the decrease of CL intensity, and to an increase of the minority carrier diffusion length,

$$L_n = \sqrt{D_n \tau_n}.$$ Nakamura et al. [71] performed some experiments that indicated the hole mobility remained unchanged before and after electron injection. This result is used to make the assumption that $D_n$ will remain unchanged before and after electron injection.

The ionized Mg acceptor which has trapped an injected electron will become available for recombination of the conduction band electrons after it has captured a hole. In other words, capturing a hole means that the trapped electron makes a transition to the valence band. As the temperature of the sample increases, the probability for the trapped electron to escape the charged Mg level also increases [69]. This is seen in Figure 4.2 because the hole must overcome the hole capture barrier before the ionized Mg acceptor can capture the hole.

PPC measurements in p-type GaN [56, 57] imply that the thermal ionization energy and the energy for a hole capture are quite close to one another, with the difference not exceeding 30 meV. This dissertation showed that the activation energy, $E_a$, would increase as the percent of Al increased in the GaN lattice. The increase of $E_a$ agreed very well with the deepening of the Mg acceptors. These results were used to ascribe the activation energy, which includes both a temperature dependence and a dependence on the duration of electron injection, for the electron injection effect to the energy needed for a ionized Mg acceptor to capture a hole.
Figure 4.2 Configuration coordinate model for Mg-doped (Al)GaN. A hole (open circle) in the valence band has to overcome the hole capture barrier, $E_c$, before the ionized Mg acceptor can capture the hole.

The configuration coordinate diagram [72] in Figure 4.2 is used to describe the process of an ionized Mg acceptor capturing a hole. A hole in the valence band must overcome the hole capture barrier, $E_c$, before it can be captured by the ionized Mg acceptor. As the temperature of the sample is increased there is an increased probability that the hole will overcome $E_c$ and be captured by the Mg$^-$ acceptor. The average activation energy for GaN found in this dissertation, $E_a = 189\text{meV}$, represents the hole capture barrier in Figure 4.2. The thermal ionization energy and the optical ionization energy are represented by $E_{\text{th}}$ and $E_{\text{opt}}$ respectively.
in Figure 4.2. It was shown [56] that Mg acts as an AX center inside p-type GaN and $E_{th}$ was found to be $\sim 130$ meV [57] while $E_{opt} \sim 300$ meV [73].

As the rate of hole capture on the Mg level increases, the conduction band electrons have more chance to recombine through this level. This results in a shorter $\tau_n$ and a slower rate of increase in $L_n$ at higher temperatures. There is a competing process of additional Mg acceptor activation with an increase of temperature due to the transition of valence band electrons to the Mg levels, but this process is secondary to the electron injection effect.

**Model of the Electron Injection effect in Mn-doped GaN**

Figure 4.3 shows the model that is used to describe the electron injection effect in Mn-doped GaN, the defect molecule picture for Mn$^{3+}$ in GaN from reference [74] is used in the explanation of this effect. Graf et al. [25] found that Mn forms a deep neutral acceptor level (Mn$^{3+}$) in GaN where only a small number of the acceptors become ionized (Mn$^{2+}$). Graf also discovered that one path of the photoionization process consists of a neutral acceptor state (Mn$^{3+}$) and an excited state (Mn$^{3+*}$).

Initially, Mn impurities are present in the neutral acceptor state Mn$^{3+}$, characterized by two filled $e_\uparrow$-orbitals and three $t_{2\uparrow}$-orbitals (left side of Figure 4.3a). While electrons occupy two of the latter orbitals, the third one is empty. Recombination of non-equilibrium electron-hole pairs created by the SEM electron beam causes the band-to-band cathodoluminescence spectra.
In addition, electron beam injection can lead either to an electron transfer from $e_{\uparrow}$ to an empty $t_{2\uparrow}$-orbital or, competitively, to direct ionization of the Mn$^{3+}$ state to the Mn$^{2+}$ state (process (1) in Figure 4.3a).

![Diagram](image)

**Figure 4.3** Mechanism for the observed electron injection-induced effects in Mn-doped GaN [65]. (1) corresponds to the ionization of Mn$^{3+}$ to Mn$^{2+}$ due to an SEM beam excitation and a consequent electron (dashed arrow in 4.3a, left) transition to a vacant $t_{2\uparrow}$-orbital. (2) represents the band-to-impurity recombination through a vacant Mn$^{3+*}$ $e_{\uparrow}$-orbital (4.3a, right). (3) represents the thermally activated hole emission (electron capture) from an $e_{\uparrow}$-orbital of the Mn$^{3+*}$ state to the valence band. This leads to ionization of Mn$^{3+*}$ state to the Mn$^{2+}$ state and to a suppression of (2).

In the first case, electron transfer causes generation of the energetically higher Mn$^{3+*}$ state (one electron in the $e_{\uparrow}$-orbital and three electrons in the $t_{2\uparrow}$-orbitals), shown on the right side of Figure 4.3a. This leads to activation of a non-radiative recombination channel (2) via the vacant $e_{\uparrow}$-orbital and therefore to a decrease in the intensity of the band-to-band cathodoluminescence, as seen in Figure 3.20. The assumption is made that the transition (2) in Figure 4.3a dominates over the band-to-band transition after the electron irradiation is started, while a recombination
through the $t_{2g}$-orbitals of the Mn$^{3+}$ ground state (cf. Fig. 4.3a, left) is not allowed. Although the exact reason for this is unclear at the moment, the experimental evidence exists because this transition is not observed in the CL spectra. Note that the process of Mn$^{3+}$ ionization to Mn$^{2+}$ creates a hole in the valence band and would not lead to the observed increase of the minority carrier diffusion length. This is because the non-equilibrium electrons of the conduction band, induced by electron beam irradiation, would then recombine with the non-equilibrium holes, available in the valence band, leading to a decrease of the non-equilibrium carrier $\tau_n$ and $L_n$ in agreement with the equation (2.3).

Because the Fermi level in the GaN:Mn samples is close to the middle of the band-gap, the carrier diffusion length determined from EBIC measurements most likely represents the effective diffusion length for non-equilibrium electron-hole pairs. It has already been shown (Figure 3.18) that $L_n$ increases as the duration of electron injection increases. Equation (2.3) shows that when $L_n$ increases, $\tau_n$ will also increase. If $\tau_n$ increases then the number of recombination events will decrease, including those through the band-to-band transition. As the number of recombination events decrease, the CL band-to-band intensity will also decrease. Therefore, the band-to-band CL intensity will decrease as the duration of electron injection increases, until a saturation level is reached.

Two different mechanisms can cause a re-activation of the band-to-band channel when the temperature is increased. A thermally activated charge neutral transition of a metastable Mn$^{3+\ast}$ state to a Mn$^{3+}$ state (Figure 4.3b) establishes the initial situation and quenches the electron irradiation effects. Up to now, such a transition has not been reported in the literature.
It has to be noted that a thermally activated hole emission from an $e_t$-orbital of the Mn$^{3+}\ast$ state to the valence band is also likely to occur (process (3) in Figure 4.3a, right). According to reference [25], this process exhibits an activation energy of 300 meV. At the same time, the temperature dependent decrease in the rate of change of the CL intensity observed in this work shows the activation energy to be 360 meV.

Although it is presently impossible to clearly identify which of the two processes is responsible for the temperature dependence of the electron injection effect, the relatively large difference between the above activation energies indicate that a charge neutral thermally activated transition from Mn$^{3+}\ast$ to Mn$^{3+}$ might occur.

It should be noted that it is not possible to completely exclude the role of electron beam-induced defects in the decrease of CL intensity (due to creation of non-radiative centers); it is believed that their concentration is insufficient for a significant impact [75]. This is due to the observed increase of $L_s$ upon electron irradiation. In addition, the role of Mn in the phenomenon of interest is further supported by the fact that no CL decrease was observed in the nominally undoped GaN grown under the same conditions as the Mn-doped GaN samples studied here.

**Kinetics of the Electron Injection Effect**

This research has shown that the electron injection effect will persist from several days to four weeks. Injecting electrons into the solid-state of the optoelectronic devices for only several hundred seconds produces this long lasting effect. Several experiments were performed to
monitor the relaxation of the electron injection effect in photodetectors.

The Mg acceptor thermal ionization energy levels in GaN range from 130-208 meV. Because of these large values less than 1% of the Mg acceptors become ionized at room temperature. These results indicate on the metastability of Mg levels: once a Mg acceptor has become ionized it will stay ionized for a long period of time. This is in part due to the high thermal ionization energy for Mg levels and the hole capture barrier that must be overcome by a hole before it is captured by an ionized Mg acceptor.

When the temperature is increased the rate of increase for \( L_n \) becomes slower. This implies that the number of ionized Mg acceptors becomes less as the temperature increases and is due to the increased probability of the Mg\(^-\) acceptor capturing a hole.

**Grain Boundaries**

It is not possible to completely exclude charging of the grain boundaries in p-type (Al)GaN as a possible mechanism of the electron injection effect, since there is growing evidence of the impact of these boundaries on carrier transport in p-type GaN [76]. In such a case, the grain boundaries may trap electrons in the potential wells, with the holes either going over the potential barrier or tunneling through it to recombine with these electrons. Under the SEM electron beam excitation, the electron pockets in the potential profile might be metastably filled so that recombination would occur via ordinary recombination centers (after long times of electron injection, \( L_n \) is much higher than the expected dimensions of the GaN domains). The
competing process is the electron emission from the grain boundary potential well. The latter process becomes more pronounced as the temperature of the sample increases. This may explain the decreased rate of increase for $L_n$ with an increase in temperature. However, additional experiments are needed to make a decisive conclusion.

**Electron Beam Induced Defects**

Although the role of electron beam-induced defects cannot be completely excluded in the decrease of CL intensity due to nonradiative centers; it is believed that the concentration of these defects is insufficient to have a significant impact. The influence of defect density on minority carrier diffusion length in thick hydride vapor-phase epitaxy grown GaN films has already been studied [77]. It was found that the minority carrier diffusion length in these films showed a several-fold decrease when the defect density increases from $10^8$ to $10^9 cm^2$. Therefore, if a significant amount of defects was induced by an electron beam it would be expected that $L_n$ would decrease and not increase as is reported in this dissertation.
CHAPTER FIVE: CONCLUSION

In conclusion, the electron injection effect can be used to improve the minority carrier transport properties of p-type III-Nitrides doped with Mg. The improvement in $L_n$ and $\tau_n$ is due to charging of the neutral Mg levels through the injection of electrons. Electrons can be injected into the solid state by either performing a forward bias or by using the electron beam of an SEM. The electron injection effect also can be employed to improve the performance of commercially built photodetectors.

Variable temperature EBIC and CL experiments were used to find the activation energy for the effect of electron injection. Several experimental findings indicate that Mg is involved in the enhancement of $L_n$ and $\tau_n$ in (Al)GaN.

The first observation that Mg is the impurity responsible for the improvement of $L_n$ and $\tau_n$ is that $L_n$ was observed to increase on the p-side of a GaN p-n junction, but no increase of $L_p$ was observed on the n-side of the p-n junction, as shown in Figure 3.24.

The second observation showed that there was a decrease in the rate of increase of $L_n$ as the temperature increased. This suggests that there is a thermally-activated process, which compensates for the electron injection effect. Therefore the activation energy of the process is attributed to the energy needed for an ionized Mg acceptor to capture a hole. PPC
measurements [56, 57] imply that the hole capture energy is very close to the thermal ionization energy of a Mg acceptor in GaN. Because of the close proximity of these two energy levels it is assumed that the activation energy of the process is due to Mg acceptors. The average value of the activation energy for GaN was found to be 189 meV.

The third observation showed that the activation energy level would increase with an increase of Al in the p-type GaN lattice. \( \text{Al}_{0.15}\text{Ga}_{0.85}\text{N} \) and \( \text{Al}_{0.2}\text{Ga}_{0.8}\text{N} \) were studied to observe how the activation energy level would change with differing amounts of Al concentration. The Mg levels will deepen by 3.2 meV for every percentage increase of Al in the GaN lattice. It was found that the activation energy for the electron injection effect did increase by \( \sim 48 \) and \( \sim 64 \) meV for 15% and 20% Al concentration.

The electron injection effect was used in Mn-doped GaN, which is highly resistive and almost intrinsic, to see if the electron injection effect could be applied to other highly doped III-Nitrides to improve their transport properties. It was found that \( L_n \) increased and the CL intensity decreased, implying an increase in \( \tau_n \) after electron injection. This enhancement of the transport properties is attributed to trapping of the injected SEM electrons by the Mn levels. The activation energy was found to be 360 meV and represents the energy difference between the two different Mn energy levels.

The electron injection effect was used successfully to improve the peak responsivity (360 nm) as well as a comparable increase for the 255-330 nm shoulder of photodetectors. It was found that the peak photoresponse remained unchanged, within the 10% range of its value, for a post-injection time of at least 4 weeks.
There are several areas of research that could be explored within the phenomenon of electron injection. The areas that warrant further investigation of the electron injection effect are in $\text{In}_x\text{Ga}_{1-x}\text{N}$, developing a mathematical model to describe the electron injection effect in III-Nitrides, and studies of the effect in other wide band gap semiconductors, for example ZnO.

The incorporation of In into the GaN lattice will decrease $E_g$ and should make the Mg energy levels shallower. This means that the activation energy obtained from the temperature-dependent measurements on $\text{In}_x\text{Ga}_{1-x}\text{N}$ should be less than the activation energy obtained for GaN.

A mathematical model that describes how $L_n$ and $\tau_n$ are improved after electron injection into (Al)GaN would help further the understanding of this process and give insight into what other materials electron injection could be effectively applied to.

How electron injection affects other wide band gap semiconductors needs to be explored. p-ZnO is a material whose transport properties could be improved by electron injection.
Articles


APPENDIX B: PHYSICAL CONSTANTS
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LIST OF REFERENCES


106


