Title
Electron Emission Spectroscopy of III-Nitride Semiconductor Devices

Permalink
https://escholarship.org/uc/item/4497952q

Author
Myers, Daniel Joseph

Publication Date
2019

Peer reviewed|Thesis/dissertation
Electron Emission Spectroscopy of III-Nitride Semiconductor Devices

A dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy
in
Materials

by

Daniel Joseph Myers

Committee in charge:
Professor James S. Speck, Chair
Professor Claude Weisbuch
Professor Christopher Palmstrom
Professor Jacques Peretti, École Polytechnique

September 2019
The Dissertation of Daniel Joseph Myers is approved.

Professor Claude Weisbuch

Professor Christopher Palmstrom

Professor Jacques Peretti, École Polytechnique

Professor James S. Speck, Committee Chair

July 2019
Electron Emission Spectroscopy of
III-Nitride Semiconductor Devices

Copyright © 2019

by

Daniel Joseph Myers
To Laysa,

For always believing in me
even when I did not.
Acknowledgements

I would like to start off by saying that I was once a failed student. I dropped out of community college in the fall of 2004, carrying with me some truly abysmal transcripts. I was working part time as a martial arts instructor and eventually moved on to a tech support position at a small company. Progress was very slow in these jobs and I felt like I would never be able to improve my situation. I would often tell people during this time that I wanted to go back to school one day and pursue a bachelors degree in engineering; but this was mostly a hollow promise. I don’t think I ever truly believed I would go back. It was a story I told to make peace with a situation that I was unhappy with. A hope of something better.

To find myself now on the brink of earning a Ph.D. is one of the most surreal situations I have ever experienced. Not long ago I believed that completing an undergraduate degree was something that I would never be able to. The prospect of earning a doctorate was a notion that far exceeded a goal I already felt was unattainable. But here I am. And I am so thankful for everyone who helped me along the way.

There are a myriad of people who I would like to acknowledge for their support and contribution. First and foremost, I would like to thank my committee for their guidance and advice throughout my time as a PhD student at UCSB. In particular, Professor Jim Speck for taking the chance on me as an undergraduate intern from the physics department. He passed on my email to his group members and started a chain of events that would lead me where I am today. On top of that he agreed to take me on as a PhD student in his group upon my completion of my undergraduate studies. I also need to thank Professor Claude Weisbuch for being my co-advisor and always providing insightful conversation and analysis. His vast accumulation of physics knowledge was an invaluable resource, without which I do not think I could have been as successful in
my graduate work. I would also like to thank my other committee members Professors Jacques Peretti and Christopher Palmstrom for their time, contributions, and thought provoking questions; all of which made me a better researcher and motivated my own ambition to keep learning.

I would be remiss if I did not acknowledge a few very special people for their invaluable contributions over the past 5 years. First and foremost I need to thank Leah Kuritzky. Leah agreed to take me on as her undergraduate intern and spent many hours teaching me skills necessary to become a successful researcher. She was always willing to let me tag along as she went about her day and gave me first hand experience of the trails and tribulations I could expect in graduate school. Another person who’s contributions to my academic success need to be acknowledged is Justin Iveland. Justin served as my mentor once I began my studies as a Ph.D. student. He blazed a trail for me to follow and built the electron emission spectroscopy (EES) tool here at UCSB. A tool that would become the basis of all of my research.

I would also like to thank Ben Yonkee for being a fantastic friend and colleague. After moving offices Ben and I became close friends, something I had struggled to find before meeting him. Ben was a well known fountain of knowledge and everyone in the nitrides group (and several from outside) would stop by our office to have a chat with him and seek his advise. Sharing an office space with him allowed me extended access to him for all of my random questions and gave me the opportunity to absorb much of the advice he would give to others as well.

My experiments would not have been possible without John English and Kurt Olsson, the MBE lab managers. John psuedo-retired shortly after I began my graduate studies but I am thankful he was still accessible on campus a few days a week to answer my questions. Kurt had some very large shoes to fill when he took John’s place as the MBE lab manager but has done a great job since day one. I am very thankful for everything...
he has done to improve the lab space where the electron emission spectroscopy tool is located and his help moving heavy UHV parts when necessary because for several years I was working on the system alone.

It is also important that I acknowledge the UCSB Materials department staff for all of their hard work keeping things moving forward and providing help with the bureaucratic side of graduate school. Specifically, I would like to thank Yukina Warner, Fukiko Miyazaki, Jocelyn Guzman, and Tal Margalith.

A large portion of my research efforts were in the UCSB nanofabrication facility. This amazing resource could not function without the help of the talented staff who maintain all of the tools which are a necessity for semiconductor device processing. The staff members who often helped me personally and were always quick to issues include: Don Freeborn, Tony Bosch, and Tom Reynolds. I would also like to thank Brian Thibeault for taking the time to help me develop a new lithography process.

Another important group of people who helped me through my non-traditional path through college were my undergraduate physics study group: Chaitanya Gadre, Erenis Lemus, Gary Centers, Tina Hang, Jp Dodson, Shayan Lameh, Ted Robinson, Frank Gao, Dillon Allen, Luke Spooner, and Ryan Hoffman. Without this dedicated bunch of physicists I’m not sure I would have been able to make it through the tremendous workload required for a B.S. in physics from UCSB. Their companionship and collaboration was an essential component of my preparation for graduate school.

There are a few people from my past who I also need to thank for their key contributions to my education. First, Mr. Earl, my math 7th grade math teacher. He was a hilarious and amazing teacher and managed to accomplish this year after year with a particularly difficult age group. His single year of teaching somehow developed nearly every skill I would need in my future studies in mathematics. Also, my high school chemistry teacher, Mr. Cunningham. I always got the impression that he truly liked
teaching chemistry and it showed. I didn’t know it at the time but looking back he was a truly remarkable example of how passion carries weight and can be felt by the people you interact with.

I would also like to mention my calculus teacher from Orange Coast College, Marta Hidden. The amount of work she put into teaching was inspiring. Her class provided an amazing foundation to so many of the subsequent courses I would need to take. She also was kind enough to write me a letter of recommendation for my undergraduate internship in Jim’s group. Possibly one of the most pivotal moments in my higher education.

I also need to thank my family for making me the person I am today. I cannot claim I am proud of who I am today without acknowledging that I am proud of my family and where I came from. Everything I accomplish in this life is a direct result of their efforts, sacrifices, and choices.

I need give a very special thanks to my wife Laysa for all of her amazing support, kindness, and understanding throughout this process. She believed in me well before I did, and helped realize a dream of something bigger and better than I ever thought possible for myself. She was the first person to call me out when I told my story about going back to school one day. She simply asked me “Okay, well when are you signing up?”. She had called my bluff and I didn’t know what to say next. It seemed like the only choice I had was to simply do what I had been saying for years and go back to school. Without her this could not have happened. From the beginning she was the one telling me it was possible when I felt it wasn’t. Thank you from the bottom of my heart for helping me achieve what I have and making our future together look as bright as it does.

Isaac Newton once remarked, “If I have seen further it is by standing on the shoulders of Giants”. These people I have mentioned are my giants and without them I could not have accomplished this monumental task.
Lastly, a huge thank you to my little furry friend Lola. I believe that the animals with whom people share their lives are an essential component of human health. The final appendix of this dissertation is a tribute to her and her contributions to my mental and physical well being over the last 11 years.
Curriculum Vitæ
Daniel Joseph Myers

Education
Doctor of Philosophy, Materials
UC Santa Barbara
*July 22, 2019*
(Expected)

Bachelor of Science, Physics
UC Santa Barbara
*Sept 13, 2014*

Associate in Science, Engineering
Orange Coast College
*May 27, 2012*

Experience
Graduate Student Researcher
Materials Department, UC Santa Barbara
*Nov 1, 2014 - Present*

- Sole graduate student researcher for US Department of Energy (SSL) funded project. Achieved all project goals on time or ahead of schedule.
- Developed data analysis and interpretation techniques for electron emission spectroscopy experiments.
- Iteratively improved electron emission device design and measurement process spanning: Photolithography mask design, process flow optimization, data acquisition via LabView, sample cleaning and cathode activation.
- Design, construction, and modification of UHV electron energy analysis system.

Intern
Center for Energy Efficient Materials (CEEM)
*Jan 3, 2013 - Oct 10, 2013*

- MOCVD growth and characterization of m-plane GaN LEDs and laser diodes.
- Analyzed layer-by-layer morphology dynamics via growth interrupt studies using AFM to improve device performance and material properties.
- Luminescence characterization (PL, EL, CL).
- Clean room microfabrication tools and photolithography both contact and stepper, for LEDs and edge emitting laser diodes.

Awards
Best Paper
International Workshop on Nitride Semiconductors
*Nov, 16 2018*
• “Measurement of the effects of AlGaN electron blocking layers in GaN based LEDs by electron emission spectroscopy”

Publications


Patents


Conference Proceedings


Abstract

Electron Emission Spectroscopy of III-Nitride Semiconductor Devices

by

Daniel Joseph Myers

Gallium nitride (GaN) has proven to be a semiconductor material system that is ideal for the development of lasers and light-emitting diodes (LEDs) with emission wavelengths spanning the visible spectrum. In particular, the prevalence of white LEDs has been made possible by pairing GaN-based optoelectronic devices emitting at 450 nm (blue) with phosphors for down-conversion. The efficiency of these devices, although better than alternatives, is limited at high current densities (efficiency droop), elevated temperatures (thermal droop) and is markedly worse at longer wavelengths. Understanding the physical origins of these efficiency problems can provide a pathway for engineering solutions to these long-standing issues. Despite extensive efforts to improve and understand these limitations, the unambiguous identification of these efficiency loss mechanisms has remained an open topic of research.

Most studies of the efficiency loss mechanisms in GaN LEDs rely on an indirect measurement of carrier dynamics by analysis of the emitted light. The inadequacy of these indirect measurements has motivated the development of an electron spectroscopy technique, capable of directly probing several electron transport and recombination mechanisms in GaN-based optoelectronic devices. In 2013, electron emission spectroscopy (EES) was used for the first time to measure high energy electrons generated via Auger recombination in the active region of an LED. This result brought an end to the long-standing controversy over the causes for efficiency droop at high carrier densities.
Our analysis of the kinetic energy of vacuum emitted electrons from GaN-based LEDs has unambiguously identified carrier overshoot as the dominant mechanism responsible for thermal droop. Control experiments from p-n diodes show evidence for a previously unknown hot carrier generating process, likely trap-assisted Auger recombination (TAAR) occurring in AlGaN/GaN barrier heterostructures. We also discuss the possibility of TAAR occurring in InGaN quantum wells through examination of low-efficiency LEDs grown by molecular beam epitaxy. Finally, we discuss preliminary EES results regarding long wavelength GaN LEDs as well as the first EES measurements from semipolar (20\overline{2}1) GaN LEDs and p-n diodes.
Contents

**Curriculum Vitae** x

**Abstract** xiii

1 **Introduction** 1
   1.1 Light-Emitting Diodes 3
   1.2 Negative Electron Affinity 12
   1.3 Band Structure 14
   1.4 Electron Emission Spectroscopy 19

2 **Photoemission** 22
   2.1 3-Step Model of Photoemission 22
   2.2 Photoemission Spectroscopy Experiments 25
   2.3 Cesiation Experiments 28
   2.4 Origins of Low Energy Peaks 34
   2.5 In-Situ monitoring of Light Output Power 40
   2.6 Photoemission from n-type GaN 42

3 **EES of p-n Junctions** 46
   3.1 Diffusion Length 49

4 **Thermal Droop Mechanism** 55
   4.1 AlGaN Electron Blocking Layers 57
   4.2 LED Experiments 60

5 **Trap-Assisted Auger Recombination in InGaN QWs** 64

6 **Current & Future Work** 72
   6.1 Long Wavelength LEDs 72
   6.2 Semipolar LEDs and p-n Junctions 75
   6.3 EES from Tunnel Junction Devices 77
A UCSB Electron Energy Analysis System
  A.1 Sample Design .............................................. 81
  A.2 Ultra-High Vacuum ........................................... 82
  A.3 EES System Standard Operating Procedures .............. 83
  A.4 EES Process Flow ............................................ 92
  A.5 Analyzer Details, Calibration, and Problems ............ 97
  A.6 Possible Problems .......................................... 100

B Photolithography .............................................. 106
  B.1 Mask Design .................................................. 107
  B.2 Tutorial on SUSS MJB-3 Contact Aligners ............... 111

C Lock-In Amplifiers: Theory and Operation .................. 114

References ....................................................... 117
Chapter 1

Introduction

In the latter part of the 19th century we began to formally understand the nature of light and elections. One of the first major advancements involved the work of Scottish physicist James Clerk Maxwell and his “Dynamical Theory of the Electromagnetic Field”, published in 1864 [1]. This comprehensive theory included his (now eponymous) General Equations of the Electromagnetic Field, that to this day form the foundation of our understanding of light, optics, electricity and magnetism. Contemporary experiments had convinced most of the physics community that light was a periodic transverse wave. Conventional wisdom suggested that these waves of light required a medium to propagate within. Many experiments were done to understand the composition of this medium and all resulted in similar conclusions; that light could freely travel through vacuum where there was a negligible amount of matter for such a wave to propagate in. This led Maxwell and many of his peers to assume that there is some medium that remained immeasurable, and assumed this ethereal medium must fill all space and has the capability of being set in oscillatory motion to facilitate the propagation of light waves.

Over 20 years later, Heinrich Hertz published the first experimental evidence of what would be later known as the photoelectric effect [2]. His observations showed that the
sensitivity of a simple radio transmitter-receiver would increase when it was illuminated with visible or ultraviolet light. A complete understanding of the underlying physics of this effect could not be formally understood at the time and this would remain the case until Joseph J. Thomson and Albert Einstein’s incredible insights into the phenomenon.

Thomson measured the charge to mass ratio of particles that make up cathode rays, thus discovering the existence of the first sub-atomic particle, the electron [3]. Later, Einstein explained that the usual conception, that the energy of light is continuously distributed over the space through which it propagates, encounters very serious difficulties when one attempts to explain the photoelectric phenomena. He then explains the photoelectric effect by the transfer of energy from a quanta of light energy (now known as a photon) to an electron in a material [4]. These papers would eventually earn each of them the Nobel prize in physics.

Einsteins work in particular allowed for the field of photoemission spectroscopy (PES) to develop. Because he was able to show that the kinetic energy of a photoemitted electron is closely related to the energy of the incident photon it was then possible to study photoemission to develop experiments with the capability to probe information about both the electronic and structural properties of materials.

In this dissertation I explain the details of electron emission spectroscopy (EES), a relatively new electron spectroscopy technique that directly measures electrons emitted from the surface of semiconductor devices while they are being operated under electrical injection. This is in contrast to typical electron spectroscopy measurements that often rely on photoexcitation to impart sufficient energy for the emission of electrons from the surface of a material.

While Photoemission spectroscopy measurements are powerful tools for measuring the electronic structure of materials very near the surface they offer little insight into the inner workings of semiconductor devices. It is in this domain that EES has proven essen-
tial in broadening our understanding of III-N optoelectronic devices by providing a new way to measure and understand electron transport and efficiency loss mechanisms occurring in semiconductor devices that have until recently only been inferred from indirect measurements.

1.1 Light-Emitting Diodes

The first written report of a light-emitting diode (LED) was written in 1907 by Henry Joseph Round’s “A Note on Carborundum”. In this two paragraph publication, Round describes a yellowish light being emitted from a piece of single crystal silicon carbide. He had been trying find a cheaper replacement for vacuum diodes, and accidentally created the first known LED and is likely the first observation of the phenomenon of electroluminescence (EL) from a semiconductor.

The phenomenon of EL would pass mostly unnoticed and forgotten until it was rediscovered in 1923 by Oleg Vladimirovich Lossev. He not only published a more extensive study of the phenomenon he also provided the first photograph of EL. However, a correct explanation of EL would not be published until 1951 when Kurt Lehovec explained that the phenomenon was due to minority carrier injection through a forward biased p-n junction.

The ideal material system for visible spectrum (400-700 nm) LEDs would have a band gap spanning this energy regime (3.1 - 1.77 eV). Gallium nitride (GaN) when alloyed with indium and aluminum (figure 1.1) has a band gap that spans nearly this entire range (6.026 - 1.97 eV) making it an attractive material system to become the basis for both ultraviolet and visible spectrum LEDs. Although this material system is very attractive for this application, synthesis of GaN is remarkably difficult and it is not a naturally occurring material on earth. The first report of single-crystalline, colorless,
GaN was produced by a vapor-phase growth technique that had been used previously to synthesize GaAs, GaP, and GaSb using sapphire (0001) as a growth substrate [6]. Just two years after this first demonstration researchers measured EL in Zn-doped GaN with an emission wavelength of $\approx 475 \text{ nm}$ [7]. The first marked improvements in the quality of GaN growth was published in 1986 using metalorganic vapor phase epitaxy (MOVPE) growth on sapphire (0001) substrates using an AlN buffer layer [8].

As mentioned earlier from the work of Kurt Lehovec, efficient EL requires the formation of a p-n junction. This remained an issue due to the lack of an effective p-type dopant. The first demonstration of a p-n junction in this materials system utilized Mg-doped GaN that was subsequently treated with low-energy electron beam irradiation (LEEBI) [9]. The difficulties in p-type doping of GaN would persist until 1992 when Shuji Nakamura published a paper detailing the thermal annealing effects on p-type Mg-
doped GaN [10][11]. This paper showed a dramatic improvements in the resistivity, hole carrier concentration, and hole mobility of Mg-doped p-GaN after a thermal annealing process at temperatures above 700 °C. It would later be explained in a patent that the poor electrical characteristics of Mg-doped p-GaN were due to atomic hydrogen binding to, and passivating the Mg, p-type impurity. The thermal annealing procedure removes the hydrogen from the material after growth, activating the Mg dopants [12]. Finally, 1992 the first blue LED was demonstrated by utilizing a very large InGaN/GaN double heterostructure (DH). This DH structure would later be optimized and will eventually be replaced by quantum wells forming the basis for modern high efficiency solid state lighting [13].

The efficiency of LEDs can be broken into several components. The radiative efficiency, defined as the following,

$$\eta_{rad} = \frac{\text{# of photons emitted from active region per second}}{\text{# of electrons injected into active region per second}}$$

and describes the efficiency of the active region of the device.

The injection efficiency,

$$\eta_{inj} = \frac{\text{# of electrons injected into active region per second}}{\text{# of electrons injected into device per second}}$$

and describes the efficiency of electron transport from the electrical connections of the device to the active region.

The radiative and injection efficiency quantities can be combined to define a new efficiency, the internal quantum efficiency ($\eta_{IQE}$), and is formally defined as the product
of the radiative and injection efficiencies \([14]\).

\[
\eta_{IQE} = \eta_{rad} \times \eta_{inj} = \frac{\text{# of photons emitted from active region per second}}{\text{# of electrons injected into device per second}}
\]

Another more subtle efficiency that needs to be considered when talking about LEDs is the extraction efficiency \((\eta_{ext})\). Because photons are being created within the semiconductor material, for them to be of any use they need to be emitted from the surface of the device. Perhaps surprisingly this is not a trivial problem. Because of the high index of refraction contrast between GaN \((n \approx 2.49)\) and air \((n = 1)\), the critical angle for total internal reflection is only \(23.68^\circ\). Meaning that much of the light produced in a GaN LED can be trapped inside and never escape. That being said, extraction efficiency is entirely a problem of LED geometry and surface treatments and does not depend on the electrical performance of the device. We can write an expression for the extraction efficiency as well,

\[
\eta_{ext} = \frac{\text{# of photons emitted from device per second}}{\text{# of photons emitted from active region per second}}
\]

All of these aforementioned efficiencies are often lumped together into one quantity, the external quantum efficiency \((\eta_{EQE})\), that can be defined as the product of the radiative, injection, and extraction efficiencies.

\[
\eta_{EQE} = \eta_{rad} \times \eta_{inj} \times \eta_{ext} = \frac{\text{# of photons emitted from device per second}}{\text{# of electrons injected into device per second}}
\]

One of the largest obstacles preventing solid state lighting from widespread adoption for all lighting applications has been efficiency droop \([15, 16]\). Efficiency droop is the decrease in \(\eta_{IQE}\) as carrier density increases (figure 1.2). First observed by Krames et al. and Mukai et al., efficiency droop prevents the efficient conversion of electrical energy
into light by LEDs when operating at high current densities \cite{17, 18}. Many state of the art LEDs produced today have a peak efficiency of around 70-80\%, that occurs at a current density of 2-4 A/cm$^2$. At higher current densities the efficiency of these devices continues to decrease from this point.

![Efficiency Loss at High Current Density](image)

**Figure 1.2**: Efficiency droop is the decrease of electroluminescence efficiency at increasing current densities.

The cause of efficiency droop was widely researched throughout the III-N LED community but the exact cause of the phenomenon remained a controversial topic. Conclusions on the matter often fell into three main branches: carrier delocalization \cite{19, 20}, carrier overflow \cite{21, 22}, and Auger recombination \cite{23, 24, 25}. 

7
The argument for carrier delocalization is often presented as a consequence of random alloy fluctuations that can exist in InGaN alloys, the material that comprises the active regions of GaN LEDs. This effect has been measured directly by atom probe tomography (APT) [26]. These alloy fluctuations create a potential landscape that can localize carriers within the indium rich regions. It was argued that this effect localizes carriers preventing them from reaching non-radiative recombination centers such as point defects or dislocations and explains the unusually high $\eta_{IQE}$ of III-N LEDs given the relatively high defect density in the semiconductor crystal structure [27]. Efficiency droop is then explained as being due to the delocalization of carriers from these indium rich regions at sufficient carrier concentrations. In this case the indium rich regions are fully occupied by carriers and any additional carriers are free to reach non-radiative recombination centers. Further efficiency losses can occur by Auger recombination because of the very high concentration of carriers within the confines of the indium rich regions [28].

Another proposed mechanism to explain efficiency droop is the idea of carrier overshoot. Carrier overshoot occurs when electrons or holes fail to be captured by the InGaN QW active region of the device. Instead they pass over these heterostructures and recombine non-radiatively in their respective minority carrier regions [29].

The third proposed mechanism for efficiency droop is Auger recombination. Auger recombination is a scattering event involving three carriers, either two electrons and one hole (eeh) or two holes and one electron (ehh). In this process, an electron and hole recombine, and the energy of transition is transferred to a nearby carrier, either an electron or hole.

To produce efficient, high brightness LED based lighting solutions many manufacturers resorted to using arrays of LEDs operating at relatively low current densities [30, 31]. By integrating many LEDs into a single bulb the cost of these devices has been comparatively high vs the alternatives (compact fluorescent and incandescent), and in turn has
stunted the adoption of these products over less expensive lighting solutions.

Along with efficiency droop, III-N LEDs suffer from another well known efficiency loss issue, thermal droop (figure 1.3). Thermal droop is the decrease in $\eta_{IQE}$ as temperature increases, a phenomenon that is not unique to LEDs. Temperature dependent efficiency changes are common among organic semiconductor material devices, phosphors, and solar cells as well [32, 33, 34]. The explanation for this phenomenon has remained an open question in the scientific community for many years with some of the claims being: thermally-activated impurity tunneling [35], temperature dependent Auger recombination [36], increased Shockley-Read-Hall recombination, and reduced carrier injection efficiency ($\eta_{inj}$) [37]. Most studies of thermal droop in the literature today also rely on indirect measurement of carrier lifetimes and recombination rates by EL or photoluminescence (PL) and have inherent limitations requiring several assumptions in the analysis and interpretation.

The efforts to understand efficiency droop and other carrier transport and recombination mechanisms in III-N LEDs rely almost entirely upon measurements of EL or PL combined with the current-voltage characteristics of a particular device. Typically the analysis involves curve fitting a polynomial (ABC) rate equation to a measured $\eta_{EQE}$ as a function of applied current density ($J$). The rate equation contains terms for the relevant radiative ($B$) and nonradiative recombination ($A$ & $C$) rates, each being a function of carrier concentration ($n$) and is described by the following system of equations.

$$J = qd(An + Bn^2 + Cn^3)$$

$$\eta_{IQE} = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

Here, $q$ is the elementary charge, $d$ is the active region thickness, $B$ is the radiative
recombination rate coefficient, and $A$ and $C$ are the nonradiative Shockley-Read-Hall (SRH) and Auger rate coefficients respectively.

Unfortunately this system contains 4 unknowns and only 2 equations, leaving the system underdetermined. To acquire a fit and determine values for the rate coefficients, several assumptions must be made. The first of which being that extraction efficiency ($\eta_{\text{ext}}$) is a constant. This is necessary to determine $\eta_{\text{IQE}}$. This approximation is decent for blue LEDs as the index of refraction of blue light (450 nm) in GaN changes very little for most operating temperatures [38]. Extraction efficiency is typically determined through numerical modeling of LED designs with ray tracing [39].

Figure 1.3: Thermal droop is the decreasing electroluminescence efficiency at elevated temperatures and effects all current densities somewhat equally.
The next assumption to consider is how to define $d$, the active region volume. While it is possible to define an active region volume simply on the layer thicknesses and LED dimensions, this ostensible approach does not accurately describe this quantity. Effects like current crowding, non-uniform injection, differences in electron/hole mobilities, and compositional fluctuations all contribute to a higher carrier density at a given current density than would be calculated from a simple geometric approach.

After making both of these assumptions we are still left with an underdetermined system of equations. To determine unique values for the recombination coefficients it is typical to assume a value for $B$. A best guess for $B$ is still problematic in many cases because the radiative rate coefficient depends on many sample specific parameters (QW thickness, indium composition, etc.). For an accurate value of $B$ one would need to measure or calculate this value for every different active region design.

Finally an assumption of carrier density needs to be made as well. Because of the complex relationship between carrier density ($n$) and current density ($J$) this is not a trivial problem. Trying to determine the recombination rate coefficients without specifying a carrier density still leaves an infinite number of solutions that can produce the same EQE curve. In the end, because we have an underdetermined system of equations there is no unique solutions for $A$, $B$ and $C$, making the ABC model a poor representation of the actual efficiency loss mechanisms present in III-N LEDs.

With all that being said, it is still true that the ABC rate equation model does provide a useful model for understanding the relevant carrier recombination dynamics in LEDs but must be used with a clear understanding of the limitations of this analysis.
1.2 Negative Electron Affinity

The process of emitting electrons into vacuum from materials plays a critical role in a myriad of technologies. Specifically, photoemission, secondary electron emission and thermionic emission of electrons have found uses in image intensifiers, photomultiplier tubes, Geiger counters, televisions, cameras and high powered radar systems to name a few.

In 1965, J. J. Scheer and J. Van Laar showed that p-type GaAs-Cs would have exceptional properties as a photocathode [40]. They explain that the adsorption of an electropositive metal (cesium in this case) can decrease the electron affinity by the formation of a dipole layer at the surface (figure 1.4). In the early 1970’s, the concept of negative electron affinity began to receive a lot of attention in both the scientific and commercial communities. Negative electron affinity is the condition that can be created in a p-type semiconductor in which electrons that have been excited in to the conduction band can simply spill out into vacuum.

Figure 1.4: The deposited cesium monolayer creates surface dipole that can act on electrons, pushing them towards the surface.
In a semiconductor, the emission of electrons is prevented by a potential barrier equal to the materials particular electron affinity ($\chi$). The value of the electron affinity for GaN, Silicon, GaAs and InAs are in the 4-5 eV range \cite{41}. Applying a very thin layer of cesium or cesium oxides, the electron affinity can be reduced to 0.5 eV above the conduction band minimum. To further reduce this energy barrier it is necessary to take advantage of the band bending region (BBR) near the semiconductor surface\cite{1.5}. In a p-type semiconductor, the free charge carriers (holes) can reside in surface states causing a surface depletion region that bends the bands downwards. This downward band bending further reduces the vacuum level with respect to the bulk conduction band energy position. With the combination of the adsorbed cesium as well as the downward BBR it is possible to decrease the vacuum level below the bulk conduction band energy position producing a surface with an effective, negative electron affinity (NEA).

Another way to think about this is that we have some effective electron affinity ($\chi_{eff}$) which is equal to the difference of the actual electron affinity and the amount of surface band bending ($V_{BBR}$).

\[
\chi_{eff} = \chi - V_{BBR}
\]

From this expression it is easy to see that if the surface $V_{BBR}$ is larger than $\chi$ then \(\chi_{eff}\) is negative and no barrier remains to prevent electrons from being emitted into vacuum directly from the conduction band \cite{1.5}.

It is still not possible to give a complete explanation of NEA semiconductor surfaces due to the complexities in the monolayer, electronegative-electropositive, surface dipole induced by the adsorption of an alkali metal. The problem becomes even more intractable when considering the several-monolayer configurations. A complete understanding of these details, although interesting is not a necessity for using NEA semiconductor surfaces for electron spectroscopy experiments.
Figure 1.5: The relevant energy levels for a cesiated p-GaN cold cathodes including the vacuum level \( E_{\text{vac}} \), side-valley conduction band minimum \( L_{CB} \), Γ-valley conduction band minimum \( \Gamma_{CB} \), band gap energy \( E_g \), valance band maximum \( \Gamma_{VB} \), material work functions \( \phi \), and Fermi level \( E_F \).

### 1.3 Band Structure

Deciphering EES measurements relies heavily on an understanding of the energy band structures of semiconductors. A formal derivation of band structure can be done in several methods, for simplicity I will only discuss the tight binding method (sometimes referred to as linear combination of atomic orbitals, LCAO) and a matrix method.

For the tight binding method we start by imagining neutral separated atoms and calculate the changes in the atomic energy levels as the atoms are brought together to form an ordered crystalline lattice. It is easiest to consider two hydrogen atoms, each only containing one electron in the 1s ground state. The wavefunctions of these two atoms will be denoted \( \psi_A \) and \( \psi_B \). Because we start with two individual electron wavefunctions
we only need to consider the combinations $\psi_A \pm \psi_B$.

The symmetric state, $\psi_A + \psi_B$ will have a slightly lower energy than $\psi_A - \psi_B$ because the electron spends a finite time in region between the two atoms where it experiences the attractive positive potential of both nuclei. Because there is an energy difference between $\psi_A + \psi_B$ and $\psi_A - \psi_B$, as the two atoms are brought together, to separated energy levels are formed. This generalizes for N atoms forming N energy levels. As the two free atoms are brought together, the coulomb interaction between the electrons and atomic cores splits the energy levels spreading them into bands. The width of the band is proportional to the magnitude of the wavefunction overlap. A new band of energies will form for each atomic orbital (s,p,d). This method of calculating energy bands is fairly good valence bands but often fails at describing the conduction bands accurately.

Matrix methods have also been developed for computing band structure and are based on the equivalence of matrix eigenvalue/eigenvector problems with that of solutions to the Schrödinger equation. In this framework, the determination of the energy levels in a periodic potential (lattice of atomic nuclei) is done by choosing a complete set of wavefunctions with the requirement that they are eigenstates of the Hamiltonian describing the system. For example a set of wavefunctions can be written as follows.

$$\psi_{nk}(r) = \sum_j C_{nj}(k) \phi_j(k, r)$$

These wavefunctions must also satisfy Bloch’s theorem, meaning that the wavefunction is composed of the product of a plane wave component and a periodic component.

$$\phi_j(k, r + R) = \exp^{ik \cdot R} \phi_j(k, r)$$

Where $R$ is the lattice vector.
With a suitable set of wavefunctions it is then possible to solve the Schrödinger equation for this system giving a set of eigenvalues (energies) for each specific value of crystal momentum ($k$). The band structure is then obtained by performing this calculation for all of the allowed values of $k$ and plotting the eigenvalues vs $k$.

$$H_{ij}(k) = \int \phi_i^*(k,r)H(r)\phi_j(r)dr$$

The accuracy of the matrix method described above is limited by the choice of functions and the number of terms taken into account in the expansion. It is therefore important that the choice of functions be based on the type of material.

The majority of publications calculating band structure use density-functional theory (DFT), a first-principles theory of condensed matter physics that attempts to solve the many body problem of electrons in a periodic potential. Even with the substantial amount of computing power needed to converge on a solution for DFT calculations of band structure, band diagrams generated with this method still do not predict experimental results. This is most evident in DFT calculations of band gap, deviating from experimental values by 30-40%.

The x-axis of this diagram shows varying wavevector ($k$). At each $k$ a vertical line intersects the various bands at very specific points. These points are the energy eigenvalues for that particular choice of $k$. The high symmetry points in reciprocal space are shown with vertical lines and the energy scale in most band diagrams is referenced to the valance band maximum.

The energy of the band diagram is referenced to the valance band maximum (VBM) with the top portion of this diagram depicting the excited electron energy states that make up the conduction bands. Electrons occupying these states are weakly bound to a particular atom in the material and can freely move throughout the crystal structure.
and participate in current flow. The bottom portion of the diagram shows valance band states. These lower energy electron states correspond to electrons that are still bound to atoms and do not freely travel through the material.

The lowest allowed energy state in the conduction bands occurs on the abscissa of the figure at the $k$-value marked $\Gamma$. States residing near the $\Gamma$ point comprise what is called the $\Gamma$-valley. There are also several other pseudo-parabolic regions at higher energy positions indicated with vertical lines. These are conduction band side-valleys (SV). Electrons can reside in these excited states for relatively long times, a feature that is essential in the analysis of EES data.

Angle-resolved photoemission spectroscopy (ARPES) is a technique designed to directly measure material band structure. The central goal of ARPES is to relate the
binding energy and momentum of electrons measured in vacuum to the electron dis-

tension relation $E(k)$ for electrons in the solid $[43]$. An important point here is that

ARPES experiments typically use photoexcitation energies of 10-150 eV. It is for this

reason ARPES is primarily used for determination of valance band structure and is not

particularly well suited to capture information about the conduction bands.

![Figure 1.7: Band diagram of an LED structure in the absence of applied bias.]

Because LEDs are comprised of a combination of semiconductor heterostructures

combined with a diode homojunction it is often helpful to calculate a ‘device band dia-

gram’ for a specific device structure prior to growth. This is done to optimize doping

parameters, alloy composition, and layer thickness prior to growth and fabrication.

An example of a device band diagram for an LED with two quantum wells and an

AlGaN electron blocking layer (EBL) is shown in figure 1.7. This band diagram was

calculated using SiLENSe at zero bias. Software modeling of device structures also allows

\footnote{A device band diagram does not mean the detailed “spaghetti” diagram shown earlier but instead refers to a schematic showing the energy positions of the conduction band minimum and valance band maximum through a cross section of the device.}
for calculation of electron/hole wavefunctions and will predict emission wavelengths as well as wavefunction overlap inside the quantum wells. That being said, the limitations of device modeling are many, and conclusions based on computer generated device band diagrams should be made with caution.

1.4 Electron Emission Spectroscopy

The field of cold cathode emitters has long been studied as a possible replacement for other filament (hot) cathodes typically used in electron microscopes and cathode ray tube displays. Cold cathodes have been demonstrated as early as 1961 (prior to any knowledge of NEA), with what was described in the paper as a “Tunnel-Emission Device” [44]. In this work by C. A. Mead, he demonstrates a controlled electron sources with the use of a metal-insulator-metal diode. Then in 1969 (after the advent of NEA cathodes) B. F. Williams and R. E. Simon were able to use cold cathodes to measure hot electron-phonon processes in GaP [45]. The progress of cold cathodes would continue to improve and transition across several different semiconductor materials including gallium arsenide (GaAs), silicon (Si) and finally GaN p-n diodes [46, 47].

The principle of NEA, p-n diode, cold cathodes is straightforward. After applying a bias to the device electrons are injected from the n-contact (cathode) to the p-contact (anode). Some of these electrons will pass beyond the depletion region into the p-type material as minority carriers and subsequently diffuse to the semiconductor-vacuum interface. If the p-type semiconductor surface has been activated with an electropositive metal, then conduction band electrons near the surface can be emitted into vacuum. In these simple structures, all emitted electrons will have transited the p-type GaN region of the device in the Γ-valley CBM.

It is for these reasons that EES measurements from p-n diodes show only a single peak.
The low energy threshold of this peak is the semiconductor vacuum level. The position of the vacuum level at the semiconductor-vacuum interface depends on the quality of the cesium layer deposited on the surface and can depend on many factors, some still not well understood. This peak is the direct measurement of electrically injected electrons that have transited the entire thickness of the device before being emitted. As these electrons pass through the surface (downward) band bending region many will lose energy before being emitted. The resultant peak shape can be described as an exponentially modified Gaussian (EMG) peak function and is written explicitly as follows.

\[ f(x) = y_0 + \frac{A}{t_0} \exp \left[ \frac{1}{2} \left( \frac{w^2}{t_0} - \frac{x - x_c}{t_0} \right) \right] \int_{-\infty}^{z} \frac{1}{\sqrt{2\pi}} \exp \left[ -\frac{y^2}{2} \right] dy \]

This function can be thought of as a weighted function of a shifted exponential with the weight being a Gaussian distribution.

The same process is true for cesiated LED structures however there are the additional complications of the various LED heterostructures (superlattice, QW, EBL) that can effect the energy distribution of emitted electrons.

Identically to p-n diodes, EES measurements from LEDs is done by applying a forward bias electrons are injected into the n-contact. In efficient LEDs the majority of these electrons will be captured in the quantum wells and recombine with holes in the valence band and emitting a photon in the process (radiative recombination). However, these devices are not 100% efficient at converting electrical power into optical power. Some of the injected carriers transit the device without generating light (non-radiative). The EES technique measures electrons initially occupying states in the conduction bands of the p-GaN. This means that EES can directly collect information on any non-radiative recombination mechanisms or transport phenomenon that involves electrons that do not participate in radiative recombination and end up in the p-type conduction bands.
EES measurements from LEDs typically contain 4 distinct peaks. Two low energy peaks that are below the energy of the Γ valley peak measured in p-n diodes, and two higher energy peaks. The aim of these measurements is to glean information about the internal processes occurring in these devices by measuring the relative intensities of these peaks.

The EES technique is at the forefront of expanding our understanding of the specifics of electron transport and recombination and how they relate to these non-radiative carrier pathways.

\(^2\)The analysis of these measurements is often limited to plausibility arguments but is reasonably rigorous in terms of determination of the energy positions and identification and onset conditions of hot-electron generating processes.
Chapter 2

Photoemission

It probably goes without saying that the salient feature of LEDs is the emission of light. However, for EES measurements, the emission of light complicates the measurement. Photoemission of electrons is a fairly efficient process from both cesiated metal and semiconductor surfaces, both of which are present in the vicinity of the electrostatic analyzer EES measurements. This means that for any EES measurement from LEDs there is the possibility of additional peaks that are due to photoemission processes. It is important to understand the physics of this process completely as it aids in the understanding of electroemission measurements as well.

2.1 3-Step Model of Photoemission

The photoemission of electrons from solids is most completely described by a three-step process: (1) Absorption of a photon and creation of an electron-hole pair, (2) Transport of the electron to the surface, and (3) Emission of the electron from the surface [48].
2.1.1 Step 1: Optical Excitation of Electron Within a Solid

This step requires the computation of the transition probability \( W_{f,i} \) from the \( N \) electron ground state to the \( N-1 \) electron excited state. This is approximated using Fermi’s Golden Rule,

\[
W_{f,i} = \frac{2}{\hbar} |\langle \Psi^N_f | H | \Psi^N_i \rangle|^2 \delta(E^N_f - E^N_i - \hbar)
\]

where \( H \) is the Hamiltonian describing the interaction of an electron with the electromagnetic vector potential \( A \) of the incident photon.

\[
H = -\frac{e}{2mc} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) + \frac{e^2}{2mc} \vec{A}^2
\]

The quadratic term is negligibly small compared to the linear term in this expression and can be ignored for most situations. Applying the commutation relation \( [p,A] = -i\hbar(\nabla \cdot \vec{A}) \) along with the dipole approximation \( \nabla \cdot \vec{A} = 0 \), simplifies the Hamiltonian to the following.

\[
H = -\frac{e}{mc} (\vec{A} \cdot \vec{p})
\]

The calculation of Fermis Golden Rule can be further simplified with the sudden approximation. This means there is no interaction between the system and the photoelectron, and no relaxation during the photoemission process itself. We can then write the total wavefunction as a product of a one electron orbital \( k \) which represents the photoelectron, and \( \Psi^{N-1} \) the wavefunction of the \( N-1 \) electron system. The Hartree-Fock method allows the initial and final wavefunctions to be approximated by a single Slater determinant.

\[
\psi^N_i = A\phi_i^k \phi^{N-1}_i, \quad \psi^N_f = A\phi_f^k \phi^{N-1}_f
\]
Where $A$ is an antisymmetric operator to properly express the $N$ electron wavefunction to satisfy the Pauli Exclusion Principle. These assumptions allow us to write the matrix element $\langle \Psi_f^N | H | \Psi_i^N \rangle$ in Fermi’s Golden Rule as follows.

$$\langle \Psi_f^N | H | \Psi_i^N \rangle = \langle \phi_f^k | H | \phi_i^k \rangle \langle \Psi^N_{f-1} | \Psi^N_{i-1} \rangle$$

The sum over all possible transition probabilities $W_{f,i}$ from Fermi’s golden rule then gives the following expression for total photoemission intensity.

$$I = \frac{2\pi}{\hbar} \sum_{i,j} |\langle \phi_f^k | H | \phi_i^k \rangle|^2 \sum_j |\langle \Psi^N_{f-1} | \Psi^N_{i-1} \rangle|^2 \delta(E_{\text{kinetic}}^N - E_{j}^{N-1} - E_{i}^{N} - \hbar \nu)$$

With $|\langle \Psi^N_{f-1} | \Psi^N_{i-1} \rangle|^2$ giving the probability that the removal of an electron from the initial state will leave the $N-1$ electron system in the excited state $j$.

2.1.2 Step 2: Transport to Surface

Once the electron is excited, the likelihood of the electron reaching the surface is dependent on the mean free path in the material. This is a very complicated topic and is covered in detail in the paper by Berglund and Spicer [49]. The calculation involves determining emission probabilities of electrons, which depends on the average number of inelastic scattering events taken to reach the surface. If the elastic scattering length is of comparable size to the inelastic scattering length then it too must be considered. Other phenomena include optical transition probabilities, scattering due to plasmon creation, and effects due to Auger processes. These calculations are too lengthy to include in this document.
2.1.3 Step 3: Escape into Vacuum

The escape of a photoexcited electron into vacuum generally is described by a transmission or escape probability, which depends on the work function of the material and the kinetic energy of the electron. The perpendicular component of momentum must be large enough to satisfy the following inequality for transmission to occur.

\[
\frac{\hbar^2 k^2}{2m} \geq V_0 + \phi
\]

2.2 Photoemission Spectroscopy Experiments

The earliest photoemission experiments we performed were aimed at quantifying the \( \Gamma \)-SV conduction band energy separation via a series photoemission measurements taken from GaN p-n diodes. These devices were grown with 200 nm of p-GaN to ensure sufficient thickness to optically absorb all incident light in this region. In these experiments the photon energy was varied and the resultant electron energy distribution curves were measured. This work was done to confirm earlier results on the \( \Gamma \)-SV energy separation [50] using a different electrostatic analyzer geometry. The premise of these experiments was to begin at sub-bandgap photon energies and gradually increase the photoexcitation energy. At sufficiently high photon energy it becomes possible for electrons to scatter from their initial momentum state in the valance band (likely near the \( \Gamma \) point) into the high energy \( SV \approx 1\text{eV} \) above the CBM.

The typical photoemission EDC from p-type GaN appears as a single peak. As mentioned earlier the low energy onset of this peak identifies the vacuum level at the semiconductor-vacuum interface. The high energy threshold of this peak depends pri-
marily on the incident photon energy. The highest energy electron we can measure in a photoemission measurement is an electron excited from the highest energy state in the valance band (Γ) and emitted from the surface quasi-ballisticly (loosing little to no energy). Thus, as photoexcitation energy is increased, the high energy threshold of the peak increases to higher energies accordingly.

At sufficiently high energy it is possible for photoexcited electrons to scatter from the Γ-valley to excited states in conduction band SVs, a process known as intervalley scattering. The incident photon energy required for intervalley scattering to occur is substantially higher than the energy difference of the valley minimums. Because of momentum conservation the initial and final states of the electron absorbing the incident photon must have the same k (crystal momentum). Thus the energy required for an electron to scatter into a SV is the sum of the energy difference of the valleys and changes in the initial energy due to valance band dispersion.

EDCs taken at energies high enough for intervalley scattering to occur (> 4.6eV) do not look markedly different than EDCs at lower energies. How is it possible to verify that intervalley scattering has occurred? The answer is the data does contain information that intervalley scattering has occurred but it requires a more subtle data analysis involving examination of the derivative electron distribution curves (DEDCs) measured directly with a lock-in amplifier.

Analysis of DEDCs is also challenging because of the relatively noisy signal. The DEDCs measured in photoemission initially spike to positive values and immediately drop to negative values. The negative portions of the plot are where the analysis of bulk conduction band energy positions can be made. At sufficiently high photoexcitation energies several linear portions (with positive slope) that can be extrapolated to the x-axis. The intercept of these lines with the x-axis corresponds to the high energy threshold

\[1\] Details on lock-in amplifiers and using these instruments is included in appendix C.
of each peak in the photoemitted EDC. The inter-valley energy separation is then the
difference in energy of these points. If done correctly, there will be a point associated
with the Γ-valley and high energy SV peaks. To properly resolve the SV peak it was
necessary to go to high enough photoexcitation energy that a separate ballistic electron
emission signal is observed above the SV high energy accumulation point. These ballistic
electrons appear as the highest energy linear regime and the extrapolated intercept of
this line varies with photoexcitation energy differing from the other features.

Following the work of Piccardo et. al. we performed the same differential PES
measurements to quantify the energy separation of the Γ and SV peaks [50]. In the
original experiments, the electrostatic energy analyzer being used was configured with
a double cylindrical geometry for measuring electron spin as well as energy. This is an
unnecessary complication that reduces the emission intensity. Our recent measurements
done at UCSB were done on a spherical sector electrostatic analyzer and confirm that
the energy separation measured previously is independent of analyzer geometry.

The following spectra show the DEDCs measured from a GaN p-n junction with a 200
nm thick p-GaN region. This relatively thick p-type region was chosen to give sufficient
thickness to absorb any incident light. Because of the built in potential in a p-n junction,
any carriers absorbed in the depletion region or n-type material would experience a force
pushing them away from the p-type surface where emission would occur.

Following the analysis described above the linear portions of the DEDCs were fit
and the x-intercept was determined for each of them. The three linear portions show
each of the spectral contributions from the various conduction band valleys. The lowest
energy line shows the energy position of the electrons that have accumulated in the Γ-
valley conduction band minimum and transited the surface BBR quasi-ballistically. [51] At
sufficiently high photoexcitation energy (> 4.6eV), the mid-energy linear accumulation
appears in the plots and corresponds to electrons that have been photoexcited high
enough into the conduction band to scatter into the first conduction band SV. The energy separation of the Γ-SV lines was measured to be 0.9 eV, in agreement with the previous PES measurements as well as those done by time-resolved differential reflection and transmission measurements [52, 53].

2.3 Cesiation Experiments

As discussed in the introduction, application of cesium to the surfaces of the samples measured in photoemission or electroemission is necessary to achieve NEA. To better understand the limitations of our NEA procedure and the limits of cathode efficiency we measured the effect of thermal annealing on Cs:p-GaN photocathodes.

The first series of measurements we performed included measuring the photoemitted EDCs from p-n diodes with sufficient p-GaN to absorb nearly all of the incident light. However, in these measurements we aimed to see what impact thermal annealing had on the emission spectra.

The first of these devices showed that there is a strong dependence on the vacuum level position as the annealing temperature is adjusted. Two EDCs are shown in figure 2.1.

The black curve shows the room temperature spectra taken shortly after cesium was deposited on the surface of the sample using a photoexcitation wavelength of 225 nm ($\approx 5.51eV$). The vacuum level position in the sample without thermal annealing is $\approx 2$ eV from the Fermi level and is a similar value of NEA achieved in other PES and EES measurements.

The red curve shows the photoemitted EDC after annealing the sample at 360 °C for 20 minutes. There is a very large shift in the vacuum level position after annealing the sample, increasing from $\approx 2$ eV, to $\approx 2.8$ eV. The high energy portion of the spectra
remains relatively unchanged$^2$ with the high energy threshold still corresponding to quasi-ballistic emission of photoexcited electrons$^3$.

These EDCs also elucidate some details of the cesium behavior on the surface of the sample. Because the initial deposition of cesium contains approximately 1 monolayer of material, it is expected that if any cesium is lost from the surface then there would need to be areas on the sample that do not have cesium. The surface in this situation would have cesium confined to areas of near monolayer coverage and regions of bare p-GaN. If this were the case the low energy onset of the emission spectra would be expected to broaden as we would have a large distribution of different vacuum level positions across the surface.

But as we can see from the data, there is no broadening of the low energy onset of the photoemission spectra. This suggests that the cesium on the surface is able to reconfigure and spread out uniformly across the surface even at sub-monolayer concentrations giving a clearly defined effective vacuum level position.

The other important measurements done to improve our understanding of the cesium monolayer on our samples was to determine the photocathode efficiency changes as a function of temperature. Photocathode efficiency is quantified via a measurement of quantum yield (QY).

QY is also important when measuring multiple samples for the same experiment as it becomes necessary to quantify the differences in cathode efficiency between devices. Variation in cesiation conditions can result in very different spectra and makes comparison of internal processes difficult (or impossible) sample-to-sample. QY is defined as the

$^2$This spectra was substantially lower intensity than the room temperature measurement. The data was normalized using the changes in quantum yield at this specific wavelength to isolate the analysis to changes in vacuum level position.

$^3$The high energy threshold is approx 20% lower than the photon energy due to valance band dispersion.
Figure 2.1: The photoemitted EDCs from a cesiated p-GaN surface. Spectra were taken at room temperature.

The following formula represents the quantum yield (QY) of a material:

\[
\text{QY} = \frac{\text{# of emitted electrons}}{\text{# of incident photons}}
\]

and is a measurement of cathode efficiency vs. wavelength.

The experimental setup for QY measurements consisted of a broadband light source focused onto the entrance slit of a monochromator. In our experiments, the broadband light source used is a laser-driven light source (LDLS) paired with an Oriel 1/8 m monochromator with holographic gratings making it suitable for narrow linewidth (< 2 nm) and is capable of selecting wavelengths into deep ultraviolet range (≈ 200 nm). The output of the monochromator passes through a UV transparent window in the UHV analysis chamber and is focused on a sample inside the chamber. A bent wire is biased with +92 V. A schematic of the quantum yield experimental apparatus described above is shown in figure 2.2.

\footnote{Large enough positive bias must be supplied for any measured current to saturate and not increase further as voltage increases.}
Figure 2.2: Experimental schematic for QY measurements. All electrons are collected by highly biased wire that. These experiments does not resolve electron energy, only total emission current.

There is an enormous interest in quantifying the actual Auger rate coefficient experimentally and initially it seemed that EES would be able to accomplish this task. Ideally, to determine the Auger rate coefficient we would need to account for the eventual fate of every electron that entered the device via the metal contacts. In EES measurements however the measured current is on the order of $10^{-6}$ lower than the injected current. To try to improve the EES efficiency and reduce the difference between the measured emission signal and the injected current it was necessary to try to maximize QY and thus optimize cathode efficiency.

A series of QY experiments were done to identify the optimal doping for photoemission of electrons. These measurements also included several annealing cycles to determine the effects of temperature on QY.

A very low doping concentration ([Si] $\approx 5 \times 10^{18} cm^{-3}$) sample was first measured following the idea that minority carrier lifetime is inversely proportional to doping concentration (figure 2.3). Thus a very low doping concentration would facilitate long lived
Figure 2.3: QY measurement of p-GaN with low magnesium content.

electrons in the p-type material and maximize their chance for emission.

That being said, the measured QY of this sample was actually very poor ($\approx 6\%$) but to accurately understand the effects of doping on QY it was necessary to measure higher doping samples. Following this surprisingly poor result of this first, low doping sample we proceeded to increased the Si concentration in the next sample to $\approx 1 \times 10^{19} \text{cm}^{-3}$ and repeat the measurements (figure 2.4).

Perhaps not surprisingly, this higher doping sample showed even worse performance. This is in agreement with the argument framed above suggesting that increased dopant concentrations limits minority carrier lifetimes and results in lower QY.

To push the doping experiment to the limits we attempted one more round of measurements, this time on a very highly doped sample ($[Si] \approx 5 \times 10^{19} \text{cm}^{-3}$) (figure 2.5).

This highest doping sample was the biggest surprise of this series of measurements. The QY curves measured from this sample were far higher than either of the two lower doping samples. This suggests perhaps there is some non-linear behavior in carrier life-
The other important result covered in this series of experiments is that as annealing temperature is increased, QY decreases at all photoexcitation wavelength by a similar factor. This suggests that the deposited cesium monolayer used to bring the surface of the devices into NEA sublimes or decomposes in some way when temperature is increased.

Also it is worth mentioning that there is a marked decrease in the dependence of QY on photon energy when the photon energy is near the bandgap of GaN. This feature is present in all of the room temperature measurements. This dip coincides with approximately the band gap energy and is suggestive of an Coulombic potential between the newly created electron-hole pair. As photon energy is increased beyond the bandgap the energy imparted to the electron frees it from this bound state.
2.4 Origins of Low Energy Peaks

Until recently the origin of two low energy peaks in EES measurements from LEDs was not unambiguously understood. It was clear from early EES measurements that these peaks were likely due to a photoemission process because of the high energy threshold of these features was almost exactly equal to the LED emitted photon energy.

The only plausible surfaces that would be able to participate in photoemission of electrons during EES measurements is either photoexcitation of electrons in the semiconductor near the p-GaN surface or from the exposed p-contact metals.

Ostensibly, photoemission from the p-GaN surface would be impossible because the energy of photons emitted by the LED quantum wells would have to be less than the band gap energy of the p-type material. By the possibility was that these low energy peaks could be due sub-bandgap absorption of photons in the surface band bending region via the Franz-Keldysh effect [54, 55]. The Frans-Keldysh effect is the change in the optical
absorption of a semiconductor due to an electric field. The surface band bending region of a p-type semiconductor has a relatively strong electric field and in this region optical absorption of sub-bandgap light is possible due to the electron wavefunctions extending into the forbidden gap. In the surface BBR the electron wavefunctions are no longer plane waves but Airy functions because they are spatially confined to the surface of the material. These airy functions have a relatively long decay tail that extends into the gap and facilitates recombination of electrons and holes at sub-bandgap energies.

Alternatively, these low energy peaks are the result of photoemission from the exposed p-contact metals described in detail in the 3 step method.

To resolve this outstanding issue on the low energy peak origin we did PES measurements from two different metal samples as well as EES from a commercially grown MOCVD LED sample.

The metal samples included: a palladium sample, 30 nm of Ti followed by 300 nm of Pd deposited on a (0001) sapphire substrate; and a gold sample, 30 nm of Ti followed by 300 nm of Au deposited on a (0001) sapphire substrate. These samples were cleaned with the standard 30 seconds in acidic piranha solution (H\textsubscript{2}O\textsubscript{2} : H\textsubscript{2}SO\textsubscript{4}, 1 : 4) followed by 30 seconds in hydrochloric acid (HCl).

The LEDs used in EES measurements were grown by Seoul VioSys using metal organic chemical vapor deposition (MOCVD) on (0001) sapphire. The epitaxy structure of the samples consisted of a p++ GaN contact layer, p-GaN (100nm, [Mg] $2 \times 10^{20} cm^{-3}$), Al\textsubscript{0.2}Ga\textsubscript{0.8}N EBL (10nm, [Mg] $2 \times 10^{20} cm^{-3}$), In\textsubscript{0.18}Ga\textsubscript{0.82}N/GaN ($5 \times 10^{-19}$ QW/barrier region, 25nm), low indium content InGaN (150 nm), Si doped n-type region.

In the metal sample photoemission experiments a 450 nm laser was chosen as the photoexcitation source to match the emission wavelength of the LED used for the EES measurements.

The gold photoemission EDCs are shown in figure 2.6. The high energy threshold
Figure 2.6: Temperature effects on the photoemission intensity of gold are negligible at temperatures up to 150 °C of the peak matches the expected photoexcitation energy (2.75 eV). The peak shape is not Gaussian but this is also to be expected and reflects the valance band density of states (DOS). The temperature of the sample was also varied between 21 °C and 145 °C showing little to no change in photoemission intensity at all measured temperatures.

Similarly, palladium photoemission EDCs are shown in figure 2.7. The high energy threshold of the peak also matches the expected photoexcitation energy (2.75 eV). Of interest here is that the palladium vacuum level is noticeably higher than that of the gold sample. This indicates that the cesium may react with or alloy into the palladium during cesium deposition. We also measured the temperature dependence of photoemission from this sample between 21 °C and 165 °C. The photoemission intensity decreases
dramatically at all measured temperatures above 21 °C. This is further evidence that the cesium-palladium interaction is unstable and could be due to a reaction or alloying mechanism occurring at the metal cesium-palladium interface.

![Palladium Photoemission](image)

**Figure 2.7:** The temperature dependence of palladium photoemission. At all measured temperatures the photoemission intensity decreases and is vanishingly small at 165 °C.

The EES measurements from a blue LED are similar to previous works and show the expected 3 peaks plus an additional low energy peak. The spectra now includes two low energy peaks that we aim to resolve and two higher energy peaks describing electrons that have transited the device and been emitted from the p-type semiconductor surface. Shown in **figure 2.8** are the room temperature photoemission measurements overlaid with the LED EDC taken at a diode current of 25 mA. The intensity of the photoemission
measurements is much higher than that of the electroemission measurement because the laser light source being used in the PES measurements is far more luminous than the optical emission from the LED. To better compare the PES and EES spectra, two different y-axes were used.

![Figure 2.8](image.png)

Figure 2.8: Comparison of both metal photoemission peaks taken individually (peaks 3 and 4) and a typical EDC form an LED. Peaks 1 and 2 correspond to electrons emitted from the semiconductor surface while peaks 3 and 4 are clearly due to the various exposed metal surfaces near the p-contact apertures.

Our analysis of the 4 peaked spectra measured from the commercial LED agrees with previous EES measurements. We believe that the high energy peak (labeled 1) must be due to a hot electron generating mechanism (some form of Auger) occurring in the LED active region. We also agree that the mid-energy peak (labeled 2) must correspond to electrons that have leaked past carrier confinement regions and transited the p-GaN to the surface in the Γ-valley CBM. Some of this mid-energy peak may be due to electrons that have scattered back into Γ from the high energy SV but this effect seems minimal.
To ensure that current crowding was not significantly affecting the surface potentials within the aperture regions the p-contact electrical characteristics were measured. The contact resistance and resistivity were measured using the circular transmission line method (CTLM). The linear IV characteristics of these measurements indicated that the contacts were ohmic. The p-GaN resistivity and sheet resistance was measured to be 0.18 \( \Omega \cdot cm \) and 18 \( k\Omega/\square \) respectively. These values correspond to a characteristic current spreading length (Ls) between 3-14 \( \mu m \) for the range of currents measured (1-25 mA). Because the current spreading length is equal to or greater than the aperture radius for the reported current densities, the surface potential across an aperture will at most vary by a factor of \( 1/e \).

Our observation of the new low-energy peak is primarily due to the new p-contact aperture design, as well as optimization of the cesiation process for achieving NEA. The new p-contact design decreases the size and increases the number and density of apertures compared to our previous works. These changes increase the amount of exposed metal at the aperture perimeter leading to an increase in the intensity of photoemitted electrons from the p-contact metals. The increase in measured metal photoemission may also be due to the increased efficiency of the hemispherical sector analyzer geometry.

To summarize, we observe four peaks measured in LED EES. Two low-energy peaks that are due to photoemitted electrons from the p-contact metals, and two high-energy peaks corresponding to electrons emitted from the semiconductor surface which have transited the device and relaxed into a high-energy side valley or the \( \Gamma \)-valley conduction band minimum. Reduction of aperture size to improve p-GaN current spreading and surface potential uniformity within the aperture regions allows for measurement of a new, low intensity gold photoemission peak. These photoemission measurements also show that the previously measured low-energy peak corresponds to photoemitted electrons from the exposed palladium p-contact metal at the aperture perimeter.
These measurements resolve ambiguities in the interpretation of previous EES measurements and demonstrate the results of EES measurements in multiple analyzer geometries are repeatable and reliable and eliminates the possibility that spectral features are an artifact of analyzer geometry.

2.5 In-Situ monitoring of Light Output Power

To accurately identify nonradiative recombination mechanisms in III-N devices it is vitally important to correlate changes in the measured electroemission spectra to changes in the optical output of the device. In the past this was accomplished by external electrical measurements of light vs current vs voltage (L-I-V). And then making comparisons of the L-I-V vs the EDCs.

The issue with this is that the experimental parameters may not be captured by the external measurements. For example, device cooling may be significantly different in the external measurements due to the presence of atmosphere providing convection cooling.

During our analysis of the metal photoemission experiments it became clear that the gold photoemission peak is a perfect candidate for the indirect measurement of light output power as the intensity of the photoemission peak depends only on the optical photoexcitation intensity and is robust against changing temperature. The solution to the problem was already built-in to the device, we now just had to quantify the gold photoemission intensity for each EDC measured.

There are some subtleties that need to be accounted for when measuring the gold photoemission intensity, the first of which is that the palladium photoemission peak overlaps about half of gold photoemission peak. In this situation a partial integral of the gold peak may be sufficient by integrating between specific data points where the gold photoemission peak is uniquely resolved. As long as the data points chosen are
the same for subsequent EDCs the relative changes in photoemission intensity should be representative of light output of the device (figure 2.8).

![Gold Photoemission vs Temperature](image)

Figure 2.9: The integrated photoemission intensity from the gold peak (4). This data indirectly represents relative changes the light output of an optoelectronic device.

The other possibility involves taking advantage of the thermal instability of cesiated palladium. By thermally annealing the sample the palladium photoemission peak can be attenuated. At temperatures $\approx 150 \, ^\circ C$ the palladium peak should be completely removed from the EDCs. After this annealing procedure it is straightforward to take a complete integrated intensity of the gold photoemission peak.

The advantages of this in-situ technique are profound for future EES measurements. It is now possible to plot efficiency droop directly from EES data. It should be noted that future EES device designs should put some effort into improving the gold photoemission intensity to better quantify the total light output power of the devices being measured.
2.6 Photoemission from n-type GaN

All of the work discussed thus far involved either electroemission or photoemission from III-N devices terminated with a p-type GaN surface. As mentioned in the introduction the downward BBR at the surface of p-type semiconductors is an essential component in achieving NEA. It is however of some interest to understand the emission characteristics of semiconductors terminating in n-type material.

Semiconductors terminating in n-type material have a similar depletion region forming at the surface but this time the majority carrier is electrons, not holes like in p-type semiconductors. The additional electrons in the n-type material near the surface can occupy surface states and depleting the first few nanometers of the material.

![Energy diagram for n-type photoemission measurements. The high energy threshold of the photoemission measurements suggests absorption from the conduction band.](image)

The EDCs shown in figure 2.11 are PES measurements from a highly doped ([Si] = 5 × 10^{19}cm^{-3}) n-GaN terminated sample. One of the most significant details of this plot is that the vacuum level for all peaks is roughly the same, and this value shows exactly the magnitude of the upward band bending at the surface.

Another surprising detail is the energy position of the high energy threshold of these
peaks. It appears that the high energy threshold walks out with photon energy exactly. This is an unexpected result for an n-type sample. In photoemission we expect that the conduction band is weakly absorbing and the initial states of all emitted electrons would be in the valence bands. If that were true, we should only be able to extract electrons from the surface with a photon energy equal to the sum of the bandgap and the height of the upward band bending region at the surface \( E_g + E_{BBR} \approx 4.9 \text{eV} \). This is not the case however. We measure appreciable electron emission at energies far lower than the band gap \( (500 \text{ nm} = 2.48 \text{ eV}) \) and the high energy threshold of these peaks correlates directly with the photon energy suggesting that the electrons being measured here were photoexcited directly from the conduction band\(^5\).

The next experiments we did were to see if the vacuum level could be decreased by the

---

\(^5\) Again, the Fermi level in this sample is approximately at the conduction band because it is highly doped n-type material.
inclusion of an n-type InGaN region at the surface. The hope was that this lower bandgap material would experience less upward band bending and by extension also improve the emission of electrons and the signal-to-noise ratio in these measurements (figure 2.12).

This second round of PES measurements from n-GaN with a 10 nm InGaN capping layer show a similar single peak that broadens in conjunction with photoexcitation energy. The energy position of the high energy threshold of these spectra suggest that the electrons being measured were initially occupying states near the Γ-valley CBM instead of the valance band maximum (VBM) as expected.

Markedly in this sample there is an improvement in the signal to noise ratio for the high photon energy measurements (< 300nm). Also, it is worth noting that the vacuum level position in the sample with the InGaN cap is ≈0.2 eV lower than the sample without this capping layer. This suggests that the upward band bending region at the surface is
decreased due to the addition of the smaller bandgap of the InGaN layer and is likely responsible for the improved signal to noise we see in this set of spectra.
Chapter 3

EES of p-n Junctions

Modern GaN-based LEDs are composed of several different kinds of semiconductor heterostructures and bulk materials. To understand the impacts of each feature on the emitted electron energy distribution, we studied their individual contributions to a known test structure, the p-n diode. The p-n diode is an ideal test structure for EES experiments because all LEDs have, at their core, a p-n diode. A device band diagram for a p-n diode is shown in figure 3.1 with the associated emitted electron energy distribution shown on the right.

A p-n diode is a junction a p-type and an n-type semiconductor. In the absence of applied bias a p-n diode, the Fermi level is uniform throughout the device and perhaps unsurprisingly, there is no net current. However, at the junction of the two materials, mobile majority carriers (holes for p-type, electrons for n-type) flow from their respective regions across the junction due to the differences in carrier densities across the junction via diffusion. Nearly all of the carriers that transit the junction will recombine, holes with electrons, and vice versa. As a result, a region near the junction becomes depleted of both kinds of charge carriers. this results in the n and p-type regions becoming positively and negatively charged respectively. The electric field created by this potential difference
EES of p-n Junctions Chapter 3

Figure 3.1: Device band diagram for a p-n diode. The associated emitted electron energy distribution is shown on the right and contains only one peak associated with electrons transiting the p-GaN and being emitted form the Γ-valley conduction band minimum.

sweeps out any charge carriers that enter the depletion region, electrons towards the n-side and holes towards the p-side. There are two competing currents in this situation: the drift current and the diffusion current. The diffusion current is movement of charge carriers caused by variation in the carrier concentration and is in the direction of decreasing slope of the carrier concentration profile. The drift current is caused by the electric field of the depletion region. Because we are describing the condition of no external bias, the sum of these two currents must be 0.

\[ J(x) = q \left[ \mu n \mathcal{E}(x) - D \frac{\partial n}{\partial x} \right] = 0 \]

In the above expression, q is the elementary charge, n is the carrier concentration, \( \mu \) is the mobility, \( \mathcal{E} \) is the electric field, and D is the specific diffusion constant for the material and carrier in question.
The most important feature of the p-n diode is that the apparent barrier to both electrons and holes can be adjusted by changing the applied bias to the device. To proceed with an analysis of the biased p-n diode it is common to make the following assumptions:

1. We assume that the change in carrier densities is small and localized mainly within the depletion region.
2. Electron and hole distributions are described by Boltzmann statistics.
3. The applied potential drop is contained mainly within the depletion region.

These are reasonable approximations for typical diode operating conditions.

Moving forward with these assumptions in place an equation describing the current-voltage (I-V) characteristics of a p-n diode can be derived.

\[ I = I_0 \left( \exp \left( \frac{qV}{k_B T} \right) - 1 \right) \]

Where \( I_0 \) is the reverse bias saturation current.

In the unbiased case, a Boltzmann distribution of free carriers exists in both the p and n-type regions. As bias is applied, the quasi-Fermi levels of both electrons and holes are separated causing a reduction of the potential barrier in the depletion region. At sufficiently high bias the potential barrier becomes lower than part of the thermal distribution of carriers and these carriers flow across the junction. Because we are assuming the thermal distribution of carriers is described by Boltzmann statistics as bias is further increased there is an exponentially larger number of carriers that are of sufficient energy to flow across the junction.
3.1 Diffusion Length

In a p-n diode, as electrons transit the device from the n to the p contacts they transition from being majority carriers (while in the n-type material) to minority carriers (while in the p-type material). As minority carriers, electrons have a relatively short lifetime $10^{-8}$s because of an abundance of unoccupied, low energy states in the valence band. Electrons transiting the p-type material as minority carriers will recombine with holes either radiatively or non-radiatively at a particular rate. The average distance a minority carrier travels before recombining is a quantity known as the minority carrier diffusion length, typically denoted $L_p$ for holes, and $L_e$ for electrons.

Minority carrier lifetime in semiconductors depends on the non-radiative recombination mechanisms present in the material. In bulk materials this is often limited to Shockley-Read-Hall (SRH) recombination, due to the absence of carrier confinement regions where carrier concentrations can be large enough to facilitate multi-carrier scattering processes. The measurement of minority carrier lifetime or diffusion length is often a challenging experimental procedure considering on average the carrier lifetime for semiconductors is on the order of nanoseconds (or shorter).

Formally, the minority carrier diffusion length is obtained by solving the diffusion equation in the context of minority carriers.

$$\frac{d^2 \Delta n_p}{dx^2} = \frac{\Delta n_p}{D_n \tau_n} = \frac{\Delta n_p}{L_e^2}$$

This type of differential equation has solutions of the form,

$$\Delta n_p(x) = A_1 e^{x/L_e} + A_2 e^{-x/L_e}$$

This ansatz of the form of the solution to the equation can be solved in the usual way
by applying the relevant boundary conditions.

In the case of electrons traversing a p-type region as minority carriers the positive exponential solution drops away and we are left with an exponential decay proportional to the ratio of the distance traveled divided by a constant (the characteristic, minority carrier diffusion length).

In this study of diffusion length, five p-i-n diodes were grown with varying p-GaN thickness from 50 to 500 nm. The intrinsic region of these devices was \( \approx 125 \, \text{nm} \) thick, the same thickness of a typical intrinsic region in an LED. The goal being to make an LED structure while omitting the quantum wells. The n-type doping was \([Si] \approx 5 \times 10^{19} \, \text{cm}^{-3}\), however, the p-type doping was extremely high \(([Mg] \approx 2 \times 10^{20} \, \text{cm}^{-3})\). This unusually high doping was an unfortunate oversight during sample growth because minority carrier lifetime and diffusion length are both directly related to the donor \((N_d)\) and acceptor \((N_a)\) concentrations.

Of the five different thickness samples grown only three yielded working EES devices. The EDCs from the 75, 100, and 150 nm p-n diodes is shown in figure 3.2. Each of the devices were measured at 1 mA \((\approx 0.6 \, \text{A/cm}^2)\) of injected current. This plot shows that the highest intensity electroemission was from the sample with 75 nm of p-GaN. The other EDCs plotted in this figure show that the EES signal intensity decreases rapidly with increased p-GaN thickness. The thickest sample (150 nm) was so small it needed to be plotted separately in an inset of the figure.

Another important detail of these spectra is that the high energy threshold occurs at \(\approx 3.4 \, \text{eV}\), exactly at the \(\Gamma\)-valley position.

As is typical with EES analysis, to determine quantitative information about the relative intensities of EDCs requires calculating the area under these curves. Fortunately, because these spectra are single peaked, it is very easy to do a simple numerical integration of the raw data without the need for exponentially modified Gaussian (EMG) curve
fitting.

From the solution to the diffusion equation for minority carriers we would expect that the number of electrons that are emitted from the surface would decrease exponentially with p-GaN thickness. The plots of total emission intensity vs p-GaN thickness along with an exponential fit to the data is shown in figure 3.3.

The exponential fitting yields a quantity $I_0$ which should be equal to the injected current. Depicted in the data shown in red, the calculated injection current is too high by roughly a factor of two. We believed this was due to differences in cathode efficiency between the different samples. As discussed in the chapter on photoemission, it is possible to use QY data to correct for cathode efficiency variations between samples. These QY measurements were done and the QY at 365 nm was recorded. This value was then used to normalize the data between the different spectra and then the data was re-plotted and
a new fit calculated. The new fit is again off by a factor of two but this time predicts it to be too low, instead of too high. The reported diffusion length was calculated by taking the ratio of the exponential functions for different samples as follows.

\[
\frac{I_{75\text{nm}}}{I_{100\text{nm}}} = e^{-\frac{100 - 75}{L_e}}
\]

\[
L_e = \frac{75 - 100}{\ln(I_{100\text{nm}}/I_{75\text{nm}})}
\]

Plots of diode current vs this calculated diffusion length are included in figure 3.4. The calculated diffusion length is changing as a function of applied current (changing diode bias as well). This is likely due to the changing thickness of the diode depletion region as the diode bias is changed.

As a proof of concept this experiment was a huge success but these experiments could not be used in a publication due to the remarkably high p-type doping. As discussed previously, the minority carrier lifetime is proportional to dopant concentration. Thus the calculated diffusion length for these samples was not representative of typical p-GaN because the doping was nearly an order of magnitude higher than typical Mg concentra-
Figure 3.4: The calculated p-GaN minority carrier diffusion length is shown here. The changing diffusion length is likely due to non-linear diode effects such as changes in the depletion region thickness with diode bias.

In the literature minority carrier lifetimes (figure 3.5) have... It is for this reason another round of experiments is needed before this work is published.
Figure 3.5: This plot from the literature shows the decreased diffusion length with doping, likely the cause of the very low value for the calculated diffusion length.

Chapter 4

Thermal Droop Mechanism

In a variety photoluminescent or electroluminescent materials and devices (semiconductor, organic LEDs, phosphors, etc.), the efficiency of light emission decreases with increasing temperature [32, 33, 56]. In bulk semiconductors materials, the observation of reduced photoluminescence efficiency at elevated temperatures is often attributed to Shockley-Read-Hall (SRH) non-radiative (NR) recombination [57, 58]. However, in electrically-injected diodes containing heterostructures, the decrease in internal quantum efficiency (IQE) with increasing temperature can be a result of many different competing processes including: thermally-activated impurity tunneling [35], temperature dependent Auger recombination [36], increased SRH recombination [37], and a reduction in carrier injection efficiency ($\eta_{\text{inj}}$) [37]. The unambiguous identification of the dominant thermal droop mechanism is challenging due to the simultaneous effects of the interplay of both electrical and optical phenomena.

To understand the electrical processes of thermal droop it is necessary to consider all possible transport phenomena including: electrical injection into the optically-active region, and carrier escape from that region. The optical processes are no less complicated, including linear, quadratic and third order radiative and NR recombination processes.
As a result, the origin of thermal droop in LEDs has not been clearly identified.

Figure 4.1: Device band diagram for a MQW LED and the associated recombination mechanisms. (1) Radiative recombination, (2) eeh Auger recombination, (3) TAAR, and (4) carrier escape.

Understanding the mechanism of thermal droop would open a pathway to engineering mitigation through improved heterostructure design and materials growth. This chapter summarizes recent electron emission spectroscopy (EES) measurements from LEDs and p-n diodes, and identifies the mechanism responsible for the efficiency droop at elevated temperatures. This work directly builds off previous results identifying third-order Auger recombination as the mechanism responsible for efficiency droop [59]. Utilizing the same technique, we were able to collect spectroscopic signatures of electronic processes and unambiguously identify carrier overshoot as the main mechanism for thermal droop in InGaN/GaN LEDs. In the process of conducting these measurements we were also able to demonstrate the impact of electron blocking layers (EBLs) on NR recombination and carrier overshoot processes.

As is standard for EES measurements, the electron energy in these experiments was measured by application of a scanning potential to the p-contact metal. As per usual, the Ohmic voltage drop across the metal-semiconductor junction appears as a shift in energy as diode current is increased.
Applying a similar approach to previous EES measurements, it is often helpful in the interpretation of the electron energy distribution curves (EDCs) it is advantageous to consider the integrated intensity of the peaks. In the case of full LED structures this is difficult because all four of the peaks overlap with one another to some degree. This issue can be overcome by fitting the semiconductor emitted electron peaks with an EMG, using non-linear least squares fitting. The area of the fitted curve can then be used to determine each peaks integrated intensity. The shape of the $\gamma$ and SV peaks is closely matched by an exponentially modified Gaussian because electrons thermalize as they transit the p-surface band bending region (BBR). Plotting this integrated intensity vs temperature, or diode current, facilitates a clearer interpretation and quantification of the data.

4.1 AlGaN Electron Blocking Layers

Thermal droop has been reported in previous literature to mitigate some of the effects of thermal droop.

Two p-i-n structures were grown, one with and one without an AlGaN electron blocking layer (EBL). These samples were grown at UCSB by metal organic chemical vapor deposition (MOCVD). The devices consisted of a 3 $\mu$m n-GaN region, $[Si] = 5 \times 10^{18} cm^{-3} // 125$ nm UID GaN // 10 nm $p - Al_{0.20}Ga_{0.80}NEBL^*, [Mg] = 6 \times 10^{19} cm^{-3} // 70$ nm p-GaN, $[Mg] = 6 \times 10^{19} cm^{-3} // and a 10 nm p-GaN contact layer. The p-i-n structures included a 125 nm UID region to mimic the active region thickness in a typical LED. In addition, two samples were LED structures, one with and one without an AlGaN EBL (figure 4.2).

To accurately measure the dominant, temperature dependent efficiency loss mechanism in LEDs, we performed a series of control experiments to understand the spectral
contribution of each of the heterostructures in a typical LED. The first experiments were to establish a baseline electron emission spectrum from a simple p-i-n device and compare this to a p-i-n device containing a p-AlGaN EBL. The second set of control experiments were done to determine the effects of temperature on the low-energy photoemission peaks.

EES measurements from a p-i-n structure are shown in Fig. 3a. Spectra from this device were single peaked with a high energy threshold near the expected Γ-valley minimum position ($\approx 3.4eV$ from $E_F$). The intensity of the peak increased linearly with applied diode current, consistent with the expected electrical characteristics of a diode. This control experiment shows that a simple p-i-n structure operates as expected with most electrons transiting the device as minority carriers in the p-GaN. The absence of any low energy features indicates that the light output of this device was below the threshold for measurable photoemission from the metal contacts, as expected for a device without any carrier confinement regions.
The second p-i-n device included a 10 nm, p-AlGaN EBL at the end of the UID region. Figure 3b shows the EDCs for this device at varying diode current. Two peaks are observed at all applied currents. A low-energy peak with a high energy threshold at the expected Γ-valley position. And a high energy peak with a high energy threshold roughly 1 eV above the high energy threshold of the low-energy peak. The low-energy Γ-valley peak increased linearly in intensity with increasing current, like the p-i-n device without the AlGaN layer. In contrast, the high energy peak intensity increases sub-linearly with diode current. This difference in behavior suggests that the emitted electrons of the two peaks have very different origins and mechanisms. It is likely that the low-energy peak is due to electrons that have transited the p-AlGaN layer by tunneling or percolative pathways towards the p-type surface.\[60, 61\] Due to the sub-linear increase in intensity shown by the high energy peak we believe that the likely mechanism responsible for these hot electrons is a trap-assisted Auger recombination (TAAR) occurring due to the presence of the AlGaN EBL. For electron-electron (ee) TAAR, an electron is captured from the conduction band to a trap state in the within the forbidden gap via concurrent generation of a second hot electron. A similar TAAR has observed in InGaN-based QW LEDs and is the subject of forthcoming work. It is reasonable that the number of traps which are available to participate in TAAR processes is finite, and it would be expected that this peak would reach a maximum integrated intensity regardless of applied diode current.

Schrödinger-Poisson simulations of the p-i-n structures show that there is no region which should be accumulating electrons in these devices. The AlGaN/GaN heterostructure should produce a two-dimensional hole gas on the p-side of the barrier heterostructure. The lack of a high electron density region suggests that the probability of a standard, electron-electron-hole (eeh) Auger recombination occurring would be very small. Furthermore, it would be expected that an eeh Auger mechanism would produce a peak
that had a super-linear increase in peak intensity with increasing diode current; instead of the sub-linear dependence that was measured. It is also worth mentioning that there are other non-radiative processes that generate hot carriers such as electron-hole-hole (ehh) Auger recombination but holes cannot be detected in an EES measurement.

4.2 LED Experiments

In addition to the p-i-n devices, two different LED structures were studied one containing an AlGaN EBL and one without. These LEDs were grown by an industrial partner by MOCVD and consisted of a Si doped n-GaN region with a low indium content InGaN region, an AlGaN EBL*, [Mg] = 2 × 10^{20} cm^{-3}, a p-GaN, [Mg] = 2 × 10^{20} cm^{-3}, and a p++GaN contact layer. The AlGaN region is marked with an asterisk to denote the experimental variable being modified between samples.

After having done the background control experiments on p-i-n devices we proceeded to measure the temperature dependent EDCs from forward biased LEDs (Fig. 4a). The first of these experiments was from a simplified LED that did not contain an AlGaN EBL. The EE spectra showed the expected four peaks, two low-energy peaks due to photoemission from the p-contact metals a mid-energy peak that aligned with the expected Γ-valley position, and a high-energy peak generated by Auger recombination in the LED active region. Examination of the integrated intensity of the semiconductor emitted peaks (Fig. 4b), the mid-energy, Γ-valley peak intensity remained relatively constant at temperatures below 75 C. And at temperatures above 75 C the intensity of the Γ-valley peak increased rapidly. Because the Γ-valley peak increase does not coincide with a corresponding, rapid decrease in SV emission it is unlikely this effect is due to intervalley scattering from SV to Γ. The only mechanism remaining to explain this increase in Γ-valley emission is an
increase in electrons that have leaked past or escaped from the active region and ended up in the \( \Gamma \)-valley of the p-GaN.

Temperature dependent EES measurements from an LED that includes an AlGaN EBL again showed the expected four peaks and have some similarities to the simplified LED. The mid-energy, \( \Gamma \)-valley peak emission from this device also showed an increase at temperatures above 75 °C. Surprisingly, the changes in the SV integrated peak intensity with either changing current or temperature differ from those of the simplified device. At temperatures below 130 °C, the high-energy peak shows decreasing intensity and then suddenly begins to increase at temperatures over 130 °C. This again agrees with the interpretation that leakage and/or overshoot is playing a dominant role at increased temperatures. Similar to the high energy peak observed in p-i-n + EBL experiments, an LED operated at high enough temperatures experiences significant overshoot and/or leakage, causing electrons to interact with the p-AlGaN layer and can subsequently generate additional hot electrons (Fig. 5).

![Figure 4.3: a. Temperature dependent EDCs of a MQW LED without EBL. These spectra show a large increase in \( \Gamma \)-valley emission at temperatures above 75 °C. b. These plots of the integrated intensity of the \( \Gamma \) and SV peaks clearly show the onset of some loss mechanism (likely carrier escape) occurring at temperatures over 75 °C.](image)

Another surprising result comes from the comparison of the total integrated intensity
of the SV peak from LEDs with and without EBLs. LEDs that contain no EBL emit 5 more hot electrons than LEDs with the AlGaN EBL which suggests that along with mitigating some of the efficiency losses due to electron leakage or overshoot, the EBL may also increase the scattering probability of hot electrons in the SV. The increased scattering of SV electrons would likely be due to the SV conduction band discontinuities from the GaN/AlGaN/GaN heterostructure barrier. This measured decrease in SV emission occurring in samples containing an AlGaN EBL is consistent across several devices.

Figure 4.4: Temperature dependent EDCs of a MQW LED with an AlGaN EBL. These spectra show a large increase in Γ-valley emission at temperatures above 75 °C as well as an additional change in SV emission occurring at 130 °C. b. The integrated intensity of the Γ and SV peaks clearly show the onset of some loss mechanism (likely carrier escape) occurring at temperatures over 75 °C. At temperatures over 130 °C the additional electrons interacting with the EBL due to carrier escape make it possible for TAAR to occur and are evidenced as additional intensity in the SV peak.

Additionally, we compared the temperature dependence of the LED electroluminescence (i.e., thermal droop), as measured by the metal photoemission integrated intensity, for both types of LEDs (Fig. 6). LEDs that did not contain an AlGaN EBL showed a relatively large decrease in EL intensity (30%) as temperature is increased to 165 °C. Most of the decrease in electroluminescence occurs at temperatures above 75 °C in agreement with the carrier overshoot or leakage measured as an increased Γ-valley emission
at these same temperatures. EES-based thermal droop measurements from LEDs with an AlGaN EBL showed a much smaller electroluminescence decrease of only 5%. Most of this decrease in electroluminescence occurred at temperatures above 130 C, coinciding with the sudden increase in SV emission, likely due to a trap-assisted Auger process. The measured $F_{HC}$ of the LED with the EBL is similar in magnitude to current, commercially produced LEDs with values ranging from 0.95-0.82.

In conclusion, we have directly observed for the first time the generation of hot electrons generated in a semiconductor barrier heterostructure by the analysis of the energy distribution of electrons emitted into vacuum from electrically injected LEDs and p-i-n diodes. In both types of device, the presence of an AlGaN EBL provides a pathway for hot electron generation, likely a TAAR process. Also, our analysis of the temperature dependent emission spectra from LEDs unambiguously identifies leakage or overshoot as the mechanism for thermal droop for InGaN/GaN LEDs and demonstrates the effectiveness of the AlGaN EBL at mitigating the loss of electroluminescence efficiency at elevated temperatures.
Chapter 5

Trap-Assisted Auger Recombination in InGaN QWs

High efficiency (>70%), InGaN/GaN LEDs are widely available today and are produced by metal organic chemical vapor deposition (MOCVD) \[11\]. Another widely used semiconductor growth method, molecular beam epitaxy (MBE), but InGaN/GaN LEDs produced by MBE typically have radiative efficiencies of only a few percent, despite excellent current-voltage (I-V) characteristics.\[10\] This low efficiency behavior of MBE LEDs is generally attributed to point defects or native impurities that act as non-radiative recombination centers. There have been studies to identify these potential impurities, but the low efficiency of MBE produced LEDs remains an open question \[62\].

Again, it is important to recognize previous work on understanding non-radiative recombination mechanisms present in high efficiency InGaN/GaN LEDs. It is generally accepted that at low carrier densities the dominating nonradiative recombination mechanism is Shockley-Read-Hall (SRH). SRH recombination is described as a successive carrier capture of either an electron or hole (depending on the nature of the trap) by a phonon-assisted process,\[58, 63\] followed by a subsequent capture of the opposite
sense carrier, again by a phonon-assisted process.

At high carrier densities it is generally accepted that Auger recombination is the dominant non-radiative recombination mechanism and is responsible for the phenomenon known as “efficiency droop” \[64, 65, 66\]. Interband Auger recombination is a three-body carrier recombination process that either involves either two electrons and one hole (eeh) or one electron and two holes (ehh). For eeh recombination, an electron in the conduction band recombines with a hole to the valance band and the energy of this transition is transferred to a second electron in the conduction band producing a high energy electron. Similarly, an ehh interband recombination produces a hot hole.

The EES data in figure 5.1 shows a significant number of hot carriers are emitted from low efficiency ammonia MBE LEDs, normally a signature of eeh Auger recombination occurring in the LED active region. We measure the electroluminescence efficiency of these devices and show that these devices do not droop. The combination of data showing hot carrier generation, no efficiency droop, and very low efficiency, suggests that there must be another mechanism capable of generating hot electrons occurring in these devices.

The design constraints of EES devices prevents them from being useful for absolute measurement of electroluminescence efficiency. Separate devices were also fabricated, singulated, and encapsulated LEDs using a standard process, from the same epitaxial material that was used for the EES LEDs, and measured their absolute EQE in an integrating sphere. The EQE of these devices reached a maximum value of 0.2%. Because of the low light output power of these low efficiency LEDs, the measurements in the integrating sphere had a low signal-to-noise ratio, even with exceptionally long integration times. Therefore, the maximum absolute EQE of 0.2% was used to scale much less noisy measurements of the relative EQE performed on a third set of devices fabricated from the same MBE LED epitaxial material. These devices were left on-wafer, and their rela-
Figure 5.1: EDCs of a single QW LED grown by ammonia MBE. The spectra is two peaked showing both the $\Gamma$-valley peak as well as a high energy SV peak. This high energy peak is surprising due to the abysmally low EQE of this sample.

tive EQE was measured using a setup equipped with an actively temperature-controlled stage and a Si photodiode amplified by a FEMTO high-gain current amplifier (set to 108 V/A gain). Both the geometry of the on-wafer LEDs and the measurement setup are described elsewhere [67]. The EQE measurements will also appear in a forthcoming article [68] and are reproduced here (figure 5.2) to show the lack of efficiency droop in these MBE grown LEDs.

Based on the data collected, we believe that the origin of these hot electrons in MBE LEDs is likely a trap-assisted Auger recombination (TAAR) process [69, 70, 71, 72, 73].
Figure 5.2: External measurements of EQE done in conjunction for this work as well as another publication [68]. This EQE shows the complete lack of efficiency droop (due to eeh Auger recombination) and thus should not have any measurable SV peak.

For electron-electron (ee) TAAR, the capture of an electron from the conduction band directly into a trap state within the forbidden gap, occurs concurrently with the generation of a second hot electron. Unlike SRH where this energy of transition is conserved by the emission of phonons. The hot electron generated in a TAAR event has sufficient energy to scatter into the high energy SV where it can be emitted into vacuum and measured by EES. This process is shown schematically in figure 5.3. A similar TAAR mechanism occurring AlGaN heterostructure barriers is the topic of a forthcoming paper [78].

The EQE measurements show that over a wide range of carrier densities the radiative
efficiency remains constant and at a very low value (Figure 5.2). To explain this data, we consider the different non-radiative recombination mechanisms that could contribute to this EQE behavior. Because radiative recombination has a quadratic dependence on carrier density and SRH is linear, the LED efficiency would scale as $Bn/A$ and increase linearly with carrier density. Thus, if SRH recombination was the dominant efficiency loss mechanism in MBE LEDs, we would expect that efficiency would increase with carrier density. A similar argument can be made for interband Auger recombination. If interband Auger recombination was a significant non-radiative recombination mechanism occurring in this device then efficiency droop should occur at sufficiently high carrier densities. The cubic dependence of interband Auger recombination would yield efficiency that scales as $B/Cn$ and would decrease with increasing current density.

This above argument is completely at odds with the observation of hot carriers in the EES measurements. Because interband eeh Auger recombination would cause efficiency
to droop, there must be another hot carrier generating mechanism occurring in these devices. We believe that this process is TAAR.

To see this, a modification can be made to the, admittedly simplified, ABC model discussed above, adding a term to the total recombination rate, \( B_{n2} \), to represent the non-radiative TAAR process, where \( n \) is the carrier density, and \( B \) is the TAAR rate coefficient (note that, in contrast to \( B \), \( B \) is not an intrinsic parameter and will vary proportional to the concentration of TAAR inducing impurities). Now the radiative efficiency in the QW is given by \( B_{n2}/(A + B_{n2} + B_{n2} + C{n^3}) \), where \( A \), \( B \), and \( C \) are the SRH, radiative, and interband Auger coefficients, respectively. Choosing values for the \( A \), \( B \), \( B \), and \( C \) coefficients in the InGaN QW\(^{[68]} \) of \( 5.3 \times 10^8 \) 1/s, \( 5.0 \times 10^{12} \) 1/cm\(^3\)/s, \( 5.1 \times 10^{-10} \) 1/cm\(^3\)/s and \( 6.4 \times 10^{32} \) 1/cm\(^6\)/s, respectively, and assuming that the light extraction efficiency in the singulated LEDs is 34%, the EQE curve in figure5.2 is well reproduced by this model.

The EDCs we measured from the low efficiency MBE LEDs showed two distinct peaks at drive current densities as low as 8.75 A/cm\(^2\) (figure5.1). The EDCs show a low energy peak, consistent with the expected energy position of electrons emitted from the -valley conduction band minimum, and a high energy peak 1 eV above the -valley peak, the expected energy position of the SV peak, thus demonstrating that a hot electron generating process must be occurring within the device. Due to the lack of significant efficiency droop, and the very low efficiency of these devices, interband Auger recombination cannot be the source of the hot electrons. The alternate explanation we propose for this high energy peak is TAAR. TAAR is a strong candidate for the efficiency limiting mechanism in these devices due to the abundance of point defects or impurities in MBE grown III-N LEDs, taken in conjunction with the observation of hot electrons.

The abrupt cutoff of the low energy portion of the -valley peak is due to the vacuum level at the surface preventing emission of electrons from lower energy states. The effec-
The relationship between the diode current density and the hot electron generation rate by TAAR was extracted from the EES data by integrating the area under the SV peaks in the EDCs. The peaks were fit with the standard EMG functions by non-linear least squares. The integrated SV peak area is plotted in Figure 5.4. The error bars in Figure 5.4: Plot of the integrated peak intensity with associated ABC+B’ fitting used in the external measurements of EQE. The scaling needed to be adjusted for this data because the measurement is of electrons instead of electroluminescence. The model is in close agreement with the integrated intensity vs drive current.

tive vacuum level position at the surface is 2.4 eV above the Fermi level in the p-GaN. These EDCs lack the typical low energy photoemission peaks due to the poor electroluminescence intensity of the MBE LEDs. These low energy peaks arise from photoemitted electrons from the deposited metal p-contacts.
The dashed line in Figure 4 shows the expected relationship between the TAAR recombination current \((Bn2)\), and the observed integrated SV peak area, as a function of total drive current. The model shows agreement with the EES data. The TAAR recombination current is calculated using the modified ABB’C model described above (with the parameter values in given in the text), and scaled as a whole to match the magnitude of the data (the EES measurements provide only a relative, and low efficiency, measure of the total hot carrier generation rate within the device). The slow turn-on of the TAAR component of the current in the model is due to the dominance of conventional SRH recombination at low drive currents; in the measured integrated SV peak areas this manifests as the apparent offset of the linear portion of the data to 15 mA.

To summarize, we have determined that the poor efficiency characteristics of MBE LEDs are linked to a mechanism that generating hot electrons, likely an Auger-type process, such as TAAR, occurring in the InGaN quantum wells. This is evidenced by the presence of hot electrons in the absence of efficiency droop (usually due to interband Auger). The integrated area under the SV peaks (proportional to the hot electron generation rate within the device) scales linearly with the total current, as would be expected in very low efficiency devices where the dominant recombination mechanisms is a hot electron generating process such as TAAR.
Chapter 6

Current & Future Work

As part of this dissertation I wanted to commit some effort to guiding future EES work at UCSB. Based on some of the partial results I obtained throughout my PhD work I believe there are several avenues of research that should be pursued and published as soon as possible. The following sections detail some of the partially complete work that I conducted at UCSB along with my preliminary conclusions on these topics.

6.1 Long Wavelength LEDs

Nearing the last half of my graduate studies there began a big push to understand the efficiency issues that continue to plague InGaN based LEDs when pushed to longer wavelengths. Specifically this effect is most notably discussed in literature as the phenomenon of the ‘green-gap’. Shown in figure 6.1 the ‘green gap’ is the lack of high efficiency LEDs that emit within the range of 500-600 nm. At lower energy emission, the phosphide material system becomes viable for higher efficiency devices and GaN is no longer necessary.

This efficiency problem in green seemed like it was an easy target for the next push
Figure 6.1: The green gap phenomenon is the lack of high efficiency green optoelectronic devices in both the nitride and phosphide material systems.

of EES experiments after Justin Iveland’s findings on blue LEDs in 2013 [64]. However, in those earlier experiments one of the main advantages was that the LED wafers being examined in EES were produced commercially and represented the contemporary “state of the art” technology. The use of industry supplied epi is invaluable in EES measurements because of the direct comparison and applicability of the data to the industry as well as the consistency between samples and relatively high quality of the devices makes analysis of the EDCs a much more tractable problem. For most of my graduate career we did not have any commercially produced LED wafers that emitted in the ‘green gap’ regime; so it was necessary that any green LED EES experiments that would be done would need to be grown at UCSB. The difficulties that many crystal growers can attest to do not go away when trying to perform spectroscopy measurements on the same epi. Wafer uniformity, efficiency, run-to-run variations and many different users growing dif-
Different structures are just a few of the complications that can arise when growing devices in house.

Our first round of LEDs we managed to run successful EES measurements on are shown in figure 6.2. Remarkably, these spectra show the expected 4 peaks that are expected in EES measurements from LEDs. The low energy peaks align with the expected energy positions of the metal photoemission peaks. The high energy threshold of the photoemission peaks coincides with the emitted photon energy (which is substantially lower in these devices as compared with previous experiments on blue LEDs.

Figure 6.2: EDCs from a green LED grown at UCSB. These spectra show several similarities to commercially produced blue LEDs. Specifically the low energy photoemission peaks as well as the high energy SV peak. The unusually high Γ-valley peak is indicative of an excess amount of carrier escape, possibly the cause of decreased EQE in longer wavelength nitride LEDs.

The mid-energy Γ-valley peak is in the expected energy position as well (≈ 3.4 eV
from the p-contact Fermi level). And the high energy SV peak is $\approx 1$ eV above the $\Gamma$ valley CBM. Because of this close agreement with previous EES experiments from industry epi, it makes the analysis of the EDCs fairly straightforward. Perhaps the most interesting thing about this spectra is that the $\Gamma$-valley peak is quite pronounced, even at very low current densities (much less than $1 \text{ A/cm}^2$). This large emission from the $\Gamma$-valley indicates that the injection efficiency in these devices may be much poorer than the analogous LED emitting at 450 nm. Carrier escape from the QWs directly impacts the intensity of the $\Gamma$-valley peak. Along with the uncharacteristically large $\Gamma$-valley peak, these EDCs also show a strong emission from the high energy SV. This high energy peak, although large, is not very different than the kinds of SV peaks we see in blue LEDs. This is surprising because many papers suggest that the 'green gap' is due to an enhanced Auger rate. This data suggests that the Auger rate for green LEDs is nearly identical to that of blue LEDs. This is very interesting because of the large differences in efficiency of blue and green LEDs.

If Auger recombination is not the cause of the 'green gap' then what could the possible explanation be? The answer seems to present itself clearly in these spectra that additional losses of efficiency are due to an excess amount of carrier escape from the QWs in the devices active region.

Although very promising, this single set of data is not sufficient to make such grand conclusions. Additional measurements from green LEDs need to be made to fully understand the radiative and non-radiative recombination dynamics in these devices.

### 6.2 Semipolar LEDs and p-n Junctions

UC Santa Barbara was one of the pioneering institutions in regards to examination of optoelectronic devices grown on different crystallographic orientations of the wurtzite
Ga\nN crystal structure. Because GaN is a polar material (a result of it’s point group) devices grown on the (0001) C-plane of the crystal are impacted the hardest by the spontaneous electric field present in the material.

In quantum mechanics, the shifting and splitting of energy levels in the presence of an electric field is known as the Stark effect. This is analogous to the Zeeman effect (the analogous energy level shifting and splitting from the application of magnetic fields). Because we have a spontaneous electric field in the (0001) direction in GaN based semiconductor devices, as well as a dimensionally constrained system (quantum wells), the net effect on the electronic structure in the quantum wells is described by the quantum confined stark effect (QCSE). QCSE causes the bands to have a slope instead of being flat within the quantum wells. The sloped bands spatially separate the wavefunctions of both electrons and holes to opposite sides of the quantum well. This directly impacts all of the aforementioned (electron-hole) recombination mechanisms.

One creative solution to dealing with the detrimental effects of QCSE is to grown on a different crystal axis. For example, the m-plane is orthogonal to the (0001) C-plane and does not experience any effects of QCSE, however, m-plane LEDs have many other challenges in terms of indium uptake and morphological issues [79].

Another mitigation tactic would be to use a crystal orientation that is nearly free of the effects of the spontaneous electric field. These ‘in-between’ crystal planes were dubbed semipolar planes and UCSB has seen much success in the implementation of both LEDs and laser diodes using semipolar planes (typically 2021 and 20211) [80, 81, 82, 83]. These previous publications demonstrate the efficacy of semipolar plane optoelectronic devices to mitigate the effects of efficiency droop. A diagram of the Brillouin zone bisected by polar (0001) and semipolar (2021) planes are illustrated in figure 6.3.

These ‘droop free’ devices are of particular interest for EES measurements because of their sensitivity to both the thermal escape of electrons as well as non-radiative recom-
Current & Future Work

Chapter 6

6.3 EES from Tunnel Junction Devices

Another technology that UC Santa Barbara was at the forefront of innovation and development was the inception of the tunnel junction contact for GaN optoelectronic devices. Specifically, the pioneering work of Erin C. Young and her development of MBE grown tunnel junctions on top of MOCVD grown LED structures [84, 85, 86, 87, 88]. This hybrid tunnel junction design marked a huge advance in LED designs and ease of production.

In concept, the tunnel junction is fairly simple. It is the subsequent growth of highly doped n-type material on top of the highly doped p-type contact layer. The homojunction of these two different layers forms an extremely narrow depletion region where it is possible for electrons in the n-type layer to tunnel directly to valance band states without the need for recombination with the opposite charge carrier (holes in this case).
result is a device where both electrical contacts are to n-type material.[1] This means that all of the metal contacts can be deposited in the same lithography step, in most cases substantially reducing the time needed to fabricate devices.

For EES devices, tunnel junctions devices are interesting for different reasons. As shown in figure 6.4 the tunnel junction on the surface of the device creates a very large electron launching structure. After transiting the device, many electrons reside in the p-GaN Γ-valley, or high energy SV. In a tunnel junction device these electrons leave the p-GaN $\approx 3.2$ eV from the n-type CBM. This extra energy could allow for EES to probe much higher into the conduction bands of GaN further mapping the electronic structure of this material system.

Figure 6.4: Device band diagram for a tunnel junction LED. This device has no applied bias but illustrates the benefits of the tunnel junction in injecting electrons to very high energy states ($3.2$ eV) above the n-GaN CBM.

During my time at UCSB we attempted this experiment twice, neither time yielded

[1]In the case of GaN n-contacts have orders of magnitude lower contact resistance.
results. That being said this study is of huge importance and should be done in the future.
Appendix A

UCSB Electron Energy Analysis System

The electroemission chamber has two distinct ultra-high vacuum (UHV) sections. The load-lock, and the main analysis chamber. The load-lock is a small spherical chamber attached to two pumps, a turbomolecular pump and an ion pump. Inside the load lock is a 120 Watt, halogen lamp for baking out the load-lock and a K-type thermocouple to monitor the internal temperature of the load-lock. The final component attached to the load-lock is a magnetically coupled transfer arm for transferring samples from the load-lock to the analysis chamber. The end of the transfer arm is fitted with a custom designed fork that engages with the sample holder. The tines of this fork have very shallow groves machined into them to help keep the sample holder from sliding off unintentionally. The fork freely rotates about a central rod with a slot similar to a screwdriver to interface with the screw mount on the sample holder. Rotation of the transfer arm while the sample holder is inserted into the stage in the analysis chamber twists this central rod allowing for the screw mount to be manipulated without changing the orientation of the sample holder.
The main analysis chamber is equipped with three different pumping apparatus. A large ion pump, a titanium sublimation pump and a passive getter pump. This chamber is always under vacuum under normal operation. In the event of power failure the passive getter pump is capable of maintaining a pressure of $10^{-9}$ Torr for several days. The ion pump is configured to resume pumping automatically once power is restored and the chamber will return to the $10^{-11}$ regime within a few hours.

A.1 Sample Design

To accommodate the design of the sample holder and analyzer entrance slit, the design of devices must take several special considerations that are very different than a typical LED fabrication process.

The first of these is that any device design must have some region of exposed semiconductor surface for electrons to be emitted from without obstruction of metal contacts, dielectric layers, or transparent conducting oxides. This is challenging for GaN based optoelectronic devices due to the relatively high resistivity of p-GaN. Because lateral current spreading away from the deposited metal contacts is very poor in p-GaN, it is difficult to have exposed semiconductor regions without causing significant current crowding effects.\cite{89}

Another constraint that must be considered is the entrance slit of the analyzer. The entrance slit at the front of the analyzer is a protruding copper tube ($\approx 1$ cm in diameter) with a small, 1 mm hole in the front. It is necessary that the sample be as close to this entrance slit as possible without coming in direct contact. To bring a sample close enough to the entrance slit for reliable EES measurements the p and n contacts must be separated by nearly 1 cm as well to allow clearance to keep the probes from touching the entrance slit during measurements.
The device geometry is shown in figure A.1. As shown in the image, the p-contact is in the center of the device and contains an array of densely packed hexagonal apertures. Surrounding the p-contact is a dielectric layer composed of an equal thickness of $SiO_2$. This dielectric layer insulates the p-pad from the p-GaN surface and allows for the probes to be placed far away from the p-contact. Finally, the n-contact is arranged in a semi-annulus around the entire device. This was done to prevent the electric fields between the p and n contacts from effecting the emitted electrons.

A final consideration is that the p-type material must have uniform current spreading. This is typically not an issue because the devices we use for EES experiments are grown by commercial suppliers. However there have been instances when we needed to use home-grown epi where the contact resistances are not necessarily competitive with industry. In these situations we use a different p-contact mask with smaller apertures. Decreasing the aperture size reduces the lateral distance current needs to spread form the deposited metal (figure A.1).

### A.2 Ultra-High Vacuum

To achieve pressures in the ultra-high vacuum range ($< 10^{-8}$ Torr) there are several conditions that must be satisfied. These include: making sure that the base pressure of the vacuum pump is a factor of 10 lower than the desired chamber pressure, choosing materials for the vacuum chamber that are optimized for minimum outgassing and have appropriate surface finish, chamber segments should be connected with metallic gaskets (typically CF flange connections), all parts must be solvent cleaned with toluene-acetone-methanol-isopropanol and installed with grease free gloves, helium leak check chamber using quadrupole mass spectrometer (typically called a residual gas analyzer or RGA for short), and finally the chamber must be baked out.
A bake-out is the heating of a vacuum chamber to temperatures above 100 °C once it has reached a base pressure of $< 10^{-5}$ Torr. This process significantly increases desorption and diffusion rates resulting in significantly shorter pumping times. For stainless steel chambers, bake-out temperatures of 120 °C and heating times of approximately 48 hours are sufficient to reach pressures of $10^{-10}$ Torr. Bake-out should continue until the base pressure of the chamber is 100× higher than the desired, ultimate pressure. At this point the chamber should be ready to cool-down to ambient temperatures and the desired ultimate pressure should be achieved. For chambers with large surface areas escaping interstitial hydrogen from the chamber walls becomes significant at pressures of less than $10^{-10}$ Torr. In these situations it is advantageous to use a gas-binding pump (titanium sublimation for example) that pumps hydrogen at high volume flow rates.

### A.3 EES System Standard Operating Procedures

It is important to consider a few things before moving the manipulator arm around the analysis chamber.

1. Check and make sure that the collection wire is disconnected from any battery. Accidentally touching any part of the stage with a biased collection wire can result in damage to the current amplifier.

2. Rotating the manipulator arm should be done only at $\approx Z = 3$ in. If the Z position of the manipulator arm is too far inserted or retracted the stage can come in contact with the chamber walls.

3. Complete rotations of the manipulator arm should be avoided. The wires that lead to the stage can become entangled around the manipulator arm and can damage the wiring. So sample annealing should always be done by rotating clockwise from 12:00 position to 6:00 position. And cesiation and quantum yield measurements should be
aligned by rotating the manipulator counter-clockwise to the 3:00 position. The stage should at no time be turned through the 7:00 or 8:00 positions.

Sample Loading/Unloading

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Turn OFF load-lock ion gauge</td>
<td>Top shelf beneath glove box</td>
<td>Ion gauge will burn out</td>
</tr>
<tr>
<td>2</td>
<td>CLOSE ion pump gate valve</td>
<td>Black handle on manual gate valve</td>
<td>Turn clockwise firmly until end</td>
</tr>
<tr>
<td>3</td>
<td>Turn ON turbopump</td>
<td>Button on bottom unit of server rack</td>
<td>Wait for load-lock pressure to reach $&lt;5 \times 10^{-4}$ mbar</td>
</tr>
<tr>
<td>4</td>
<td>OPEN turbopump gate valve</td>
<td>Mechanical switch in server rack</td>
<td>immediately proceed to next step</td>
</tr>
<tr>
<td>5</td>
<td>Turn OFF turbopump</td>
<td>Button on bottom unit of server rack</td>
<td>System will vent through turbopump at $&lt;400$ Hz</td>
</tr>
<tr>
<td>6</td>
<td>Open screw latch on load-lock</td>
<td>Black knob on load-lock in glove bag</td>
<td>unscrew and shift knob to the side to prevent overpressure</td>
</tr>
<tr>
<td>7</td>
<td>Retrieve sample holder from load-lock</td>
<td>End of the transfer arm</td>
<td>Do not drop sample holder</td>
</tr>
<tr>
<td>8</td>
<td>Remove or mount new sample</td>
<td></td>
<td>Do not over tighten or over loosen probes</td>
</tr>
</tbody>
</table>
### Table A.1 continued from previous page

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Replace sample holder</td>
<td>Place sample holder back on transfer arm fork</td>
<td>face sample away from heater lamp</td>
</tr>
<tr>
<td>10</td>
<td>Close load-lock door</td>
<td>Black knob on load-lock in glove bag</td>
<td>Once closed turn grey regulator CCW to stop venting</td>
</tr>
<tr>
<td>11</td>
<td>Turn on turbopump</td>
<td>Button on bottom unit of server rack</td>
<td>Wait for load-lock pressure to reach $&lt;5 \times 10^{-4}$ mbar</td>
</tr>
<tr>
<td>12</td>
<td>Turn ON load-lock ion gauge</td>
<td>Top shelf beneath glove box</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Load-lock bakeout</td>
<td>Coiled grey wire near roughing pump</td>
<td>Heat load-lock $&gt;115$ °C</td>
</tr>
<tr>
<td>14</td>
<td>OPEN ion pump gate valve</td>
<td>Black handle on manual gate valve</td>
<td>Turn CCW until end</td>
</tr>
<tr>
<td>15</td>
<td>CLOSE turbopump Gate valve</td>
<td>Mechanical switch in server rack</td>
<td>Check ion gauge for pressure stability</td>
</tr>
<tr>
<td>16</td>
<td>Turn OFF turbopump</td>
<td>Button on bottom unit of server rack</td>
<td>Turbopump will vent at $&lt;400$ Hz</td>
</tr>
</tbody>
</table>

**Sample Transfer**
<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Position stage for sample transfer</td>
<td>Manipulator on main analysis chamber</td>
<td>Approximate positions are $Z = 1.35$ in, $Y = 1.392$ in</td>
</tr>
<tr>
<td>2</td>
<td>CHECK load-lock pressure</td>
<td>Ion gauge beneath glove box</td>
<td>Load-lock pressure should be $&lt; 7.5 \times 10^{-8}$ Torr</td>
</tr>
<tr>
<td>3</td>
<td>OPEN chamber gate valve</td>
<td>Mechanical switch in server rack</td>
<td>Do not flip the wrong switch CHECK LABEL</td>
</tr>
<tr>
<td>4</td>
<td>INSERT transfer arm into chamber</td>
<td>Long tube next to server rack</td>
<td>Do not push past marked line on transfer arm until aligned</td>
</tr>
<tr>
<td>5</td>
<td>CHECK through windows to verify alignment</td>
<td>Either window on side or top of chamber</td>
<td>Iterate as necessary to align transfer arm with stage</td>
</tr>
<tr>
<td>6</td>
<td>INSERT sample holder or fork into stage</td>
<td>Main chamber</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Screw or unscrew sample holder</td>
<td>Long tube next to server rack</td>
<td>Turn transfer arm CW to tighten CCW to loosen</td>
</tr>
<tr>
<td>8</td>
<td>Fully retract transfer arm</td>
<td>Long tube next to server rack</td>
<td>Take care not to drop anything in chamber</td>
</tr>
<tr>
<td>9</td>
<td>CLOSE chamber gate valve</td>
<td>Mechanical switch in server rack</td>
<td>Make sure transfer arm is fully retracted before closing valve</td>
</tr>
</tbody>
</table>
Sample Cesiation

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Position sample for anneal</td>
<td>Manipulator arm</td>
<td>Rotate arm CW to 6:00 position</td>
</tr>
<tr>
<td>2</td>
<td>Anneal sample</td>
<td>DC power supply underneath glove box</td>
<td>Check calibration plot to determine current</td>
</tr>
<tr>
<td>3</td>
<td>Degas Cs source</td>
<td>DC power supply next to chamber ion pump</td>
<td>Set to 4.5 A for 30-60 seconds then return to 2.0 A</td>
</tr>
<tr>
<td>4</td>
<td>Position sample for cesiation</td>
<td>Manipulator arm</td>
<td>Rotate arm CCW to 9:00 position near cesiation viewport</td>
</tr>
<tr>
<td>5</td>
<td>Align sample</td>
<td>Cesiation viewport</td>
<td>Align laser to exposed semiconductor surface to monitor cathode activation</td>
</tr>
</tbody>
</table>
| 6    | Set up measurement (hardware) | Cesiation viewport and amplifier | -Connect collection wire to (+) terminal of battery  
-Connect (-) terminal to input of amplifier  
-Set amplifier to $10^6$ V/A  
-Connect amplifier output to computer input  
-Ground sample |
### Table A.3 continued from previous page

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Set up measurement (software)</td>
<td>Computer</td>
<td>Change file names</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Update notes section</td>
</tr>
<tr>
<td>8</td>
<td>Turn ON Cs source</td>
<td>DC power supply next to chamber ion pump</td>
<td>Increase Cs source current to 4.5 A</td>
</tr>
<tr>
<td>9</td>
<td>START cesiation program</td>
<td>Computer</td>
<td>Labview</td>
</tr>
<tr>
<td>10</td>
<td>Monitor cesiation</td>
<td>Computer</td>
<td>Occasionally cycle photoexcitation source or Keithley to check emission response</td>
</tr>
<tr>
<td>11</td>
<td>Turn OFF Cs source</td>
<td>DC power supply next to chamber ion pump</td>
<td>Resting current for Cs source is 2.0 A</td>
</tr>
<tr>
<td>12</td>
<td>STOP cesiation program</td>
<td>Computer</td>
<td>Monitor photoemission decay for as long as desired</td>
</tr>
</tbody>
</table>

### Quantum Yield Measurement

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Position sample for QY measurement</td>
<td>Manipulator arm</td>
<td>*Rotate arm CCW to 9:00 position at cesiation viewport</td>
</tr>
<tr>
<td>Step</td>
<td>Task</td>
<td>Location</td>
<td>Notes</td>
</tr>
<tr>
<td>------</td>
<td>-------------------------------</td>
<td>------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>2</td>
<td>Align sample</td>
<td>Cesiation viewport</td>
<td>Align monochromator optical fiber to exposed semiconductor surface (use lens to focus)</td>
</tr>
</tbody>
</table>
| 3    | Set up measurement (hardware) | Cesiation viewport and amplifier | -Connect collection wire to (+) terminal of battery  
-Connect (-) terminal to input of amplifier  
-Set amplifier to $10^6$ V/A  
-Connect amplifier output to computer input  
-Ground sample  
-Set up LDLS and monochromator  
-Close blackout curtain |
| 4    | Set up measurement (software) | Computer               | -Set I/O to GPIB-4  
-Set gain to 1  
-Update file names and notes |
| 5    | START QY program              | Computer               | Choose wavelength range and step size, typically (195-550 nm, 1nm step) |
Table A.4 continued from previous page

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Take calibration measurements</td>
<td>Cesiation viewport wand, photodiode</td>
<td>Measure the light output from optical fiber into photodiode</td>
</tr>
</tbody>
</table>

EDC Measurement

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Laser alignment</td>
<td>Raised optical tabel</td>
<td>Align 520 or 450 nm laser through analyzer slits</td>
</tr>
<tr>
<td>2</td>
<td>Sample alignment part 1</td>
<td>Manipulator arm</td>
<td>Use X,Y,θ adjustments to align sample with laser</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(check for reflected diffraction pattern for EES devices)</td>
</tr>
<tr>
<td>3</td>
<td>Sample alignment part 2</td>
<td>Manipulator arm</td>
<td>Use Z adjustment wheel to ≈ Z = 5.8 in</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(check that diffraction pattern is maintained, adjust x,y as necessary)</td>
</tr>
<tr>
<td>4</td>
<td>Set up measurement hardware</td>
<td>Electrical feed thrus and amplifier</td>
<td>-Set amplifier to $10^{-11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Connect Keithley to device</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Connect cathode potential to p-contact</td>
</tr>
</tbody>
</table>
Table A.5 continued from previous page

<table>
<thead>
<tr>
<th>Step</th>
<th>Task</th>
<th>Location</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Set up measurement</td>
<td>Computer</td>
<td>- Update file name</td>
</tr>
<tr>
<td></td>
<td>software</td>
<td></td>
<td>- Record important values in notes section</td>
</tr>
<tr>
<td>6</td>
<td>Check analyzer potentials</td>
<td>Potentiometer box</td>
<td>Set sufficient voltage on power supply, and set</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_{\text{inside}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_{\text{outside}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_{\text{top/bottom}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_{\text{entrance}}$</td>
</tr>
<tr>
<td>7</td>
<td>Adjust Einzel lens</td>
<td>Potentiometer box</td>
<td>- Run spectra acquisition in labview and stop program at</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>cathode potential of interest</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Connect Keithley to amplifier output and maximize signal</td>
</tr>
<tr>
<td>8</td>
<td>Acquire spectra</td>
<td>Computer</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Analyze data</td>
<td></td>
<td>- Convert cathode potential to energy using analyzer work function</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>- Check integrated EDC vs entrance slit current for linearity (normalize if necessary)</td>
</tr>
</tbody>
</table>
# A.4 EES Process Flow

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
<th>Details</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activation &amp; Dice</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activate</td>
<td></td>
<td>600 C, 15 min</td>
<td>No indium on sample</td>
</tr>
<tr>
<td>Surface treatment</td>
<td>Acid bench</td>
<td>HNO3+HCl 1:3 boil 140 C, 10min</td>
<td>Improves contact resistance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Repeat 3x</td>
<td></td>
</tr>
<tr>
<td>SiO2 deposition</td>
<td>PECVD #1</td>
<td>10 min SiO2 clean, 300 nm SiO2</td>
<td>Clean &quot;_10CLNSO&quot;, Deposit &quot;_SIO30&quot;</td>
</tr>
<tr>
<td>Dice</td>
<td>Dicing saw</td>
<td>11 x 11 mm</td>
<td>Use heater to apply adhesive</td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
<tr>
<td><strong>Mesa (-)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesa lithography</td>
<td>Spin bench</td>
<td>PR: nLOF 2020 30 sec 3000 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Soft bake</td>
<td>Spin bench</td>
<td>Hot Plate, 110C, 90 sec</td>
<td></td>
</tr>
<tr>
<td>Expose</td>
<td>Contact aligner</td>
<td>10 sec, 7.5 mW/cm2</td>
<td></td>
</tr>
<tr>
<td>Post exposure bake</td>
<td>Spin bench</td>
<td>Hot Plate, 110C, 60 sec</td>
<td></td>
</tr>
<tr>
<td>Develop</td>
<td>Developer bench</td>
<td>AZ300MIF, 50 sec</td>
<td></td>
</tr>
<tr>
<td>UV ozone descum</td>
<td>PR-100</td>
<td>15 min + 30 sec warmup</td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td>Location</td>
<td>Details</td>
<td>Notes</td>
</tr>
<tr>
<td>----------------------</td>
<td>-------------</td>
<td>----------------------------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>Wet etch</td>
<td>HF bench</td>
<td>BHF 60 sec</td>
<td>Calibrate with Si monitor</td>
</tr>
<tr>
<td>Mesa etch</td>
<td>RIE #5</td>
<td>SiCl4 GaN etch ~30 nm / min</td>
<td>Clean &quot;DMYERS01&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Etch &quot;DMYERS02&quot;</td>
</tr>
<tr>
<td>Water dip</td>
<td>Solvent bench</td>
<td></td>
<td>Water removes residual Cl</td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
<tr>
<td>*PR Removal</td>
<td>Acid bench</td>
<td>H2SO4:H2O2 3:1 (add peroxide to acid)</td>
<td>*Only if PR does not come off</td>
</tr>
<tr>
<td>Remove SiO2</td>
<td>HF bench</td>
<td>BHF, 120 sec</td>
<td>Make sure all SiO2 is removed</td>
</tr>
<tr>
<td>Measure etch depth</td>
<td>Profilometer</td>
<td></td>
<td>make sure etch is to required depth</td>
</tr>
<tr>
<td>SiO2 deposition</td>
<td>PECVD #1</td>
<td>10 min SiO2 clean, 150 nm + H2O + 150 nm</td>
<td>Clean &quot;.10CLNSO&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Deposit &quot;.SIO15&quot; x2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>n-contact (+)</strong></td>
</tr>
<tr>
<td>n-Contact Lithography</td>
<td>Spin bench</td>
<td>PR: SPR 220-3.0, 30 sec 3500 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Soft bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115C, 90 sec</td>
<td></td>
</tr>
<tr>
<td>Expose</td>
<td>Contact aligner</td>
<td>25 sec, 7.5 mW/cm2</td>
<td></td>
</tr>
</tbody>
</table>
### Table A.6 continued from previous page

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
<th>Details</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post exposure bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115C, 60 sec</td>
<td></td>
</tr>
<tr>
<td>Develop</td>
<td>Developer bench</td>
<td>AZ300MIF, 50 Sec</td>
<td></td>
</tr>
<tr>
<td>UV ozone descum</td>
<td>PR-100</td>
<td>15 min + 30 sec warmup</td>
<td></td>
</tr>
<tr>
<td>Wet etch</td>
<td>HF bench</td>
<td>BHF 60 sec</td>
<td></td>
</tr>
<tr>
<td>HCl Dip</td>
<td>Acid bench</td>
<td>HCL, 30 sec, DI Rinse</td>
<td></td>
</tr>
<tr>
<td>n-contact Deposition</td>
<td>E-Bean #3</td>
<td>Ti/Au, 30/300 nm</td>
<td></td>
</tr>
<tr>
<td>Liftoff</td>
<td>Solvent bench</td>
<td>NMP, 80C, 10 min</td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
<tr>
<td><strong>p-contact (+)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-contact underlayer</td>
<td>Spin bench</td>
<td>PR: LOL-2000, 30 sec 3500 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Remove edge beads</td>
<td>Spin bench</td>
<td>Razer Blade</td>
<td></td>
</tr>
<tr>
<td>Bake</td>
<td>Spin bench</td>
<td>Hot Plate, 200C, 5 min</td>
<td></td>
</tr>
<tr>
<td>p-contact lithography</td>
<td>Spin bench</td>
<td>PR: SPR 220-3.0, 30 sec 3500 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td>Location</td>
<td>Details</td>
<td>Notes</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------</td>
<td>--------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Remove edge beads</td>
<td>Spin bench</td>
<td>Razer Blade</td>
<td></td>
</tr>
<tr>
<td>Soft bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115C, 90 sec</td>
<td></td>
</tr>
<tr>
<td>Expose</td>
<td>Contact aligner</td>
<td>25 sec, 7.5 mW/cm²</td>
<td></td>
</tr>
<tr>
<td>Post exposure bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115C, 60 sec</td>
<td></td>
</tr>
<tr>
<td>Develop</td>
<td>Developer bench</td>
<td>AZ300MIF, 50 Sec + 10 sec</td>
<td>for LOL undercut</td>
</tr>
<tr>
<td>UV ozone descum</td>
<td>PR-100</td>
<td>15 min + 30 sec warmup</td>
<td></td>
</tr>
<tr>
<td>Wet etch</td>
<td>HF bench</td>
<td>BHF 60 sec</td>
<td></td>
</tr>
<tr>
<td>HCl Dip</td>
<td>Acid bench</td>
<td>HCL, 30 sec, DI Rinse</td>
<td></td>
</tr>
<tr>
<td>p-contact deposition</td>
<td>E-Bean #4</td>
<td>Pd/Au, 30/300 nm</td>
<td></td>
</tr>
<tr>
<td>Liftoff</td>
<td>Solvent bench</td>
<td>NMP, 80C, 10 min</td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
<tr>
<td>p-pad (+)</td>
<td>Spin bench</td>
<td>PR: SPR 220-3.0, 30 sec 3500 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Soft bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115C, 90 sec</td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td>Location</td>
<td>Details</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------</td>
<td>------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Expose</td>
<td>Contact aligner</td>
<td>25 sec, 7.5 mW/cm²</td>
<td></td>
</tr>
<tr>
<td>Post exposure bake</td>
<td>Spin bench</td>
<td>Hot Plate, 115°C, 60 sec</td>
<td></td>
</tr>
<tr>
<td>Develop</td>
<td>Developer bench</td>
<td>AZ300MIF, 50 Sec + 10 sec</td>
<td>for LOL undercut</td>
</tr>
<tr>
<td>UV ozone descum</td>
<td>PR-100</td>
<td>15 min + 30 sec warmup</td>
<td></td>
</tr>
<tr>
<td>HCl Dip</td>
<td>Acid bench</td>
<td>HCL, 30 sec, DI Rinse</td>
<td></td>
</tr>
<tr>
<td>n-pad deposition</td>
<td>E-Bean #3</td>
<td>Ti/Au, 30/300 nm</td>
<td></td>
</tr>
<tr>
<td>Liftoff</td>
<td>Solvent bench</td>
<td>NMP, 80°C, 10 min</td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
<tr>
<td>Aperture lithography</td>
<td>Spin bench</td>
<td>PR: nLOF 2020, 30 sec 3000 RPM, 20000/sec</td>
<td></td>
</tr>
<tr>
<td>Soft bake</td>
<td>Spin bench</td>
<td>Hot Plate 110°C, 90 sec</td>
<td></td>
</tr>
<tr>
<td>Expose</td>
<td>Contact aligner</td>
<td>10 sec, 7.5 mW/cm²</td>
<td></td>
</tr>
<tr>
<td>Post exposure bake</td>
<td>Spin bench</td>
<td>Hot Plate, 110°C, 60 sec</td>
<td></td>
</tr>
</tbody>
</table>
Table A.6 continued from previous page

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
<th>Details</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Develop</td>
<td>Developer bench</td>
<td>AZ300MIF, 50 sec</td>
<td></td>
</tr>
<tr>
<td>UV ozone descum</td>
<td>PR-100</td>
<td>15 min + 30 sec warmup</td>
<td></td>
</tr>
<tr>
<td>Wet etch</td>
<td>HF bench</td>
<td>BHF 180 sec</td>
<td></td>
</tr>
<tr>
<td>Clean</td>
<td>Solvent Bench</td>
<td>3 min Sonicate: ACE, ISO, Liquinox, DI</td>
<td></td>
</tr>
</tbody>
</table>

A.5 Analyzer Details, Calibration, and Problems

Calibration of the analyzer’s effective work function is necessary to convert from the applied cathode potential to the electron kinetic energy. Electrons that are transmitted through the analyzer can be thought of as those that would enter a grounded electrode of work function $\phi_A$ (analyzer work function) with zero kinetic energy.

To determine the analyzer work function ($\phi_A$) and energy resolution ($\Delta E$) we perform a series of PES measurements from a cesiated gold sample with a known photon energy (typically a 450 or 405 nm laser). The incident photons can photoexcite any electron they encounter in the gold, however, only the electrons occupying states within a photon energy of the vacuum level can be emitted and measured by the spectrometer.

The electron occupancy in the gold obeys Fermi-Dirac statistics and takes the form of a step function that is broadened as temperature increases.

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1}$$
where \( \mu \) is the chemical potential, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. During a photoexcitation process, the highest energy electrons that can be measured are electrons very near the surface and have an energy very near \( \mu \). This is why we would expect that the high energy portion of an EDC to have a similar shape as the Fermi-Dirac distribution.

The analyzer work function \( (\phi_A) \) can then be determined by the following relationship:

\[
qV_c + h\nu = \phi_A
\]

The analyzer energy resolution, \( \Delta E \), was determined by measuring the width of the high-energy threshold of the Au-Cs photoemitted EDCs. The broadening of the high-energy threshold is a combination of thermal broadening of the Fermi step, the analyzer resolution, and the linewidth of the photoexcitation source [Fig. 2(b)]. The analyzer resolution, \( \Delta E \), was then calculated by taking \( 4kT \) for the thermal broadening and the full width half maximum of the light source \( (\Delta \nu_{exc}) \). The experimental width of the Fermi step was determined using a differential analysis of the EDCs. Considering the other contributions, the measured analyzer resolution is 0.8%. For the measurements presented in this paper, \( \Delta V = 5 \) V gives an analyzer energy resolution of approximately 90 meV.

Electron energy was measured using a Comstock AC-901 spherical sector analyzer. This analyzer differs from previous EES studies which used a cylindrical analyzer geometry. Electrons that are at the analyzer transmission energy \( E_T \), defined by the equation below will pass through the analyzer and be collected in a Faraday cup.

\[
E_T = \frac{e(V_{in} - V_{out})}{\frac{r_2}{r_1} - \frac{r_1}{r_2}} = \frac{e\Delta V}{\frac{r_2}{r_1} - \frac{r_1}{r_2}}
\]
Here, $\Delta V$ is the potential set between the inside and outside selector plates, and $r_1$ and $r_2$ are the inside and outside selector plate radii respectively. All analyzer potentials are referenced to a common ground. For the measurements presented in this paper, the analyzer dimensions are 32.5 mm and 40.5 mm for $r_1$ and $r_2$ respectively. This gives a transmission energy in the range of 6.7-13.5 eV depending on choice of $V$ and an energy resolution in the range of 50-150 meV. The inside and outside selector plates are set to positive potentials and are symmetric about the set pass energy (ET).

The electrostatic energy analyzer can be operated in two different modes, fixed field and fixed transmission energy. In a fixed field mode configuration, the pass energy is adjusted by changing the potentials of only the inside and outside selector plates while all electric fields outside the analyzer remain constant. Unfortunately, the energy resolution and transmission efficiency of the analyzer change during the measurement. In a fixed transmission energy mode the selector potentials are left constant and the selected electron kinetic energy is controlled by changing the cathode potential ($V_c$). Because the analyzer potentials remain constant throughout a measurement in the constant transmission energy configuration, the energy resolution of the analyzer does not change. It is for this reason that the preferred analyzer configuration is fixed transmission energy mode. All measurements presented in this paper were conducted using a fixed transmission energy configuration.

The electrons transmitted through the analyzer are those which would enter a grounded electrode of work function $\phi_A$, the analyzer work function, with zero kinetic energy. Calibration of the analyzer work function ($\phi_A$) and energy resolution ($\Delta E$) was done by photoexcitation of a cesiated gold sample with a known photon energy. The high-energy threshold in the measured EDC corresponds to electrons excited from the highest occupied states in the cesiated gold sample (i.e. the Fermi level). This defines the position of the high-energy threshold referenced to the Fermi level as being equal to the pho-
ton energy. The analyzer work function ($A$) can then be determined by the following relationship.

$$ qV_c + h\nu = \phi_A $$

The analyzer energy resolution $\Delta E$, was determined by measuring the width of the high-energy threshold of the Au-Cs photoemitted EDCs. The broadening of the high-energy threshold is a combination of thermal broadening of the Fermi step, the analyzer resolution, and the linewidth of photoexcitation source. The analyzer resolution $\Delta E$, was then calculated by taking $4kT$ for the thermal broadening and the full width half maximum of the light source ($\Delta h\nu_{exc}$). The experimental width of the Fermi step was determined using a differential analysis of the EDCs. Considering the other contributions, the measured analyzer resolution is 0.8%. For the measurements presented in this paper, $\Delta V = 5 \text{ V}$ gives an analyzer energy resolution of approximately 90 meV.

### A.6 Possible Problems

For optimal analyzer performance all surfaces that interact with electrons must have a uniform potential. Additionally an electron that collides with these surfaces should have near 100% absorption as reflected electrons would be problematic. The Comstock analyzer is composed of polished copper and to reduce field distortion and reflection effects, all of these copper surfaces were coated with a thin layer of Aerodag-G colloidal graphite. This graphite is applied with an aerosol spray and subsequently all parts were placed under heat lamp for 1 hour before re-assembly.

It is also possible that spectral distortion may occur if the cathode current becomes too high. Sufficiently high electron fluxes can cause electrons to interact during transit
to the analyzer. These space charge effects can cause a blooming of the electron beam. Taking this into account, the maximum electron current that can pass through a given volume is proportional to the three halves power of the electron energy. To prevent operating in a space charge limited current regime, the maximum electron current is given by:

\[ I_{\text{max}} \approx 38.5 \left( \frac{D}{s} \right)^2 E^{3/2} [\mu A] \]

Cleaning the coaxial contacts is of particular importance when measuring small electron currents. It is possible for a coaxial connector to become contaminated and its contact resistance between the inner contact and outer (ground) shield be reduced. This increase in resistance is particularly important when a large bias is applied to extract electrons. For instance: a 100 V bias with a 1 MΩ resistance will result in 100 microamps of parasitic current, this can be as much as 100 times larger than the typical electron currents measured (nanoAmps). In addition, poorly shielded cables can add noise to the data via vibrations by introducing charges by electrostatic or triboelectric effects. Faraday cup and cesiation currents are monitored using EOC CAB-LN1 low noise cables, whose insulation resistance is measured to be \( > 10^{14} \Omega \). To avoid any issues with coaxial connectors they should be cleaned with ultra-pure isopropanol and dried completely.

When measuring low energy electrons, special care must be taken to reduce all stray magnetic fields. This includes Earths magnetic field, which ranges from 250 to 650 milliGauss. A 10 eV electron, traveling perpendicular to earths magnetic field has a bend radius of approximately 16 cm. A 1 eV electron has a bend radius of around 5cm. These dimensions are on the order of the total path length of the electron from the sample, through the analyzer, to the Faraday cup. The analyzer is enclosed in a 0.062 inch thick mu-metal box to reduce the effects of Earths magnetic field. \( \mu \)-metal is a soft,
nickeliron, ferromagnetic alloy with high magnetic permeability, often used for shielding sensitive electronic equipment against static or low-frequency magnetic fields.

It is also possible for stainless steel parts to become magnetized through cold working in machining processes. If any magnetized hardware is found the reduction of the magnetic field in a magnetized steel part can be reduced by annealing. The parts should be heated to 1075 °C and quenched. This effect of annealing and subsequent quenching removes the magnetic Martensite (BCT) domains and results in a non-magnetic Austenite (FCC) stainless. After thermal treatment a surface oxide can be removed using 2% HF by volume in a 20% nitric acid solution. This solution should be heated to 60 °C.

For the fixed transmission energy measurements, voltage differences between the applied cathode potential and the local surface potential where an electron is emitted will influence the measured energy of that electron. These voltage drops can occur at each element of the structure between where the cathode potential is applied (the p-contact) and the surfaces which are emitting electrons. It is for this reason any voltage drops in the bulk n-GaN, and n-contact do not influence the measured electron energy distributions.

The first voltage drop occurs at the metal-metal interface of the probe used to contact the sample and the gold p-contact metal deposited on the semiconductor surface. This potential drop is neglected because it is typically small, and voltage differences between the probe and p-contact metals will uniformly shift photoemitted electrons from the metal surfaces as well as semiconductor emitted electrons from the aperture regions. In most cases, the analysis of the EDCs focuses on the measuring of the separation of the high-energy thresholds of each feature and the relative intensity of peaks 1 and 2. Neither the energy difference nor the intensity of peaks 1 and 2 are influenced by this voltage drop.

The second voltage drop occurs at the metal-semiconductor junction between the palladium p-contact metal and the p-GaN surface. This voltage drop will shift the energy
position of electrons emitted from the semiconductor surface relative to the photoemitted
electron features (peaks 3 and 4). Assuming ohmic behavior of the contact, this voltage
drop will also scale linearly with injected current.

The third and last voltage drop which can influence the spectrum occurs within
the exposed p-GaN region inside the p-contact apertures. Because current must spread
laterally across bare p-GaN it is important to make sure any voltage drops in this region
are minimized by decreasing the aperture radius to within the current spreading length.
If the spreading resistance of the p-GaN is too large, the surface potential across the
aperture region can vary significantly from the applied cathode potential.
Figure A.1: 3d model of EES device geometry. Apertures are not to scale.
Figure A.2: To minimize current crowding effects, the aperture diameter should be less than the current spreading length. To accommodate variances in p-GaN conductivity several p-contacts were designed to ensure optimal current spreading across the open areas.

Figure A.3: (a) Energy diagram of the analyzer-sample system at a cathode potential ($V_C$). This potential is the energy required for electrons excited from the Fermi level to an energy $E_f + h\nu$ to be collected in the analyzer with work function $\phi_A$. (b) Spectral broadening of the Fermi step corresponding to the analyzer resolution $E$, thermal broadening $4kT$ and the spectral width of the excitation source ($\Delta h\nu_{exc}$).
Appendix B

Photolithography

Photolithography is a ubiquitous component of any semiconductor fabrication process and it is for this reason I wanted to provide a comprehensive tutorial on semiconductor fabrication processing, from mask design to finished device.

Photolithography is the process of applying a light sensitive polymer to the surface of a semiconductor. This polymer is then selectively exposed to ultraviolet light. Depending on choice of photoresist, positive or negative, the solubility of the regions exposed to light are either enhanced (positive) or diminished (negative). Once the polymer has been exposed it is placed in a solution that selectively etches the more soluble regions leaving exposed semiconductor surface in the desired pattern. Once this has been done, the subsequent processing can take place usually consisting of etching away the exposed regions of the semiconductor or deposition of a material onto the exposed surface. This process is repeated, layer by layer, until the device is complete. A common metric for determining the complexity of a given device is the number of photolithography steps required to fabricate it.

For most LED processing, contact photolithography provides sufficient alignment and resolution; but some devices, such as transistors, and edge emitting lasers, can have fea-
ture size and alignment tolerances that are beyond the capabilities of the contact aligner. These kinds of devices require the use of stepper photolithography or in some cases e-beam lithography. These more precise techniques require the use of specific tools that (at UCSB) must be reserved in advance and are beyond the scope of this tutorial. As a general rule, if feature size is greater than 3 \( \mu m \) and alignment tolerances are 5 \( \mu m \) or larger, then the process is compatible with contact photolithography. I recommend the use of contact lithography whenever possible because tool can generally be used whenever needed, decreasing processing time substantially over non-contact photolithography techniques. Contact lithography is not without fault however. Because it is a contact process, the mask will actually touch the photoresist layer that have been painstakingly applied to the sample. This can lead to damage of the mask and/or the photoresist may be compromised and will need to be reapplied. Both of these drawbacks can be avoided by following the procedures outlined in Section B.2.

B.1 Mask Design

The mask design program I will be discussing is L-edit. This program has some quirks that I will explain but overall is a good program for the job. The first thing we will cover is layers. Layers in L-edit are analogous to colors in a primitive drawing program such as MS Paint. The layer selection window is (by default) on the left side of the screen and appears as a 2d array of color coded boxes. After installing L-edit there is typically quite a few layers shown in this window and most can be ignored. There are a few layers that should be regarded as mandatory or else they will make using the software difficult or impossible. These layers are called: Grid Layer, Drag Box Layer, Origin Layer, Cell Outline Layer, Icon/Outline, and Error Layer. The rest of the preconfigured layers can be deleted or used with discretion.
Layers can be configured by right clicking on any one of the layer buttons and selecting “Setup” from the drop down menu to. This opens the ‘setup layers’ window where one can edit the color, pattern, name, order, and something called a 'GDSII number' for each layer. It is necessary to first decide how many lithography steps are needed for the devices and make a layer for each one with the appropriate name (e.g. Mesa Etch, n-contact, p-contact, etc.) and assign each of them a unique GDSII number. This number is necessary when exporting a mask which will be covered in more detail later.

The fundamental building block in L-edit is called a cell. Cells are simply sketch areas where one can draw and edit objects. Cells can contain any combination of layers, made into shapes of arbitrary complexity. Cells can also contain other cells by creating an ‘instance’ of cell-2 inside cell-1, for example. The most important thing to remember when making a mask is to organize cells hierarchically. This means, start from making

Figure B.1: L-Edit design environment showing the ‘setup layers’ window.
individual cells for each type of device which I will refer to as level 1 cells. The next cell level (level 2) should be cells that contain a combination of the level 1 cells, and so on. Finally, the mask should have a top level cell, called 'Main' or 'Final' that contains only instances of lower level cells and is a representation of the final mask layout.

![Diagram of cell hierarchy]

Figure B.2: Example cell hierarchy for a L-edit file.

Once the layers are defined for the process, it is time to begin by sketching a drawing in the first cell, in this example, this cell will be called ‘device’ and will be a typical 0.1 mm$^2$ LED. In the hierarchy this cell is a level 1 cell, one of the fundamental building blocks of our mask. To draw a shape it is often easiest to begin by making an arbitrary sized object and then edit the object to the appropriate size and position. For example, to draw a circle with a radius of 63 µm, draw a circle of any size and then press $ctrl + E$. This will open the ‘edit object(s)’ widow, update the radius field to 63 µm and also specify the center point of the circle in terms of ‘x’ and ‘y’.

For more complex shapes one will need to become familiar with L-edit’s Boolean operations. By selecting one or more objects and pressing the ‘B’ a list of these operations will pop up. I would argue this is a very non-intuitive method of drawing shapes but they are actually quite a powerful set of tools.
General rules for Boolean operations:

- **Or** ⇒ Union of objects
- **And** ⇒ Keep only overlap of two objects
- **Xor** ⇒ Remove overlapping regions
- **Not** ⇒ Negative of the selection
- **Grow** ⇒ Increase size of object
- **Shrink** ⇒ Decrease size of object
- **Subtract** ⇒ Cookie cutter removal

Figure B.3: (left) drawing of a typical LED device with a 0.1 mm$^2$ footprint. (right) the corresponding unit cell that will be tiled to create the full mask with the desired dimensions to cover the typical processing sample size.

The individual cells are combined by instancing them within other cells by pressing 'I' and selecting the desired cell from a list. The instance will appear as a new drawing object that has all of the detail of the cell that has been instanced, but acts as 1 object. Editing an instance only allows adjustment to the objects proportions and arrange it in
1D or 2D arrays. If further corrections need to be made to the geometry of the object, it must be done in the original drawing. This is in fact what I believe to be the most convenient thing about L-edit.

![Figure B.4: A 2D array of the instance in the previous figure forming the final mask.](image)

The general guideline is as follows. The first cells should only contain drawings of each of the devices. The next level is a unit cell. This unit cell contains instances of all devices arranged in a small array or pattern. The final step is to make an array or pattern composed of instances of the unit cell. This final level of cell is what is exported and made into the mask and contains all devices and is exactly as they should appear on the mask.

### B.2 Tutorial on SUSS MJB-3 Contact Aligners

In the UCSB Nanofabrication Facility we have two mask aligners for contact exposure processes. The resolution (depending on contact mode, optics and exposure wavelength and operator technique) can be in the sub-micron regime, however, typical use of contact lithography results in a minimum features size of 2 $\mu$m. Black chucks should be used for transparent materials (such as GaN and sapphire) to prevent reflected and guided light from exposing regions of photoresist that are not intended.
When using the contact aligners it is important to understand the controls. There are 4 micrometers that adjust the x,y,z,\( \theta \) positions of the stage. There is also a large lever arm on the left side that is used only to bring the z position of the stage within a working distance for alignment.

When arriving at the tool it is important to lower the z position of the stage with the micrometer (typically 10-15 twists) to ensure that the stage is sufficiently far away from the mask after using the z height adjustment lever. Previous users may have samples that are significantly thinner than the material being processed and if adjustments are not made the stage z-adjustment lever will crash the sample into the mask and can damage the mask or sample.

Make sure the settings and on the contact aligner are configured prior to loading a sample into the tool. This will prevent using the wrong exposure conditions by accident. Check that the exposure time is correct and the center dial is selecting the correct magnitude (typically \( \times 10 \) seconds). Also check that there is no optical filter in the tool. The i-line filters in the UCSB nanofab have many scratches in them and these scratches will appear as features in the photoresist after development.

The only difficult part of the alignment procedure is aligning the angle (\( \theta \)) of a sample relative to the mask. One of the most important things to remember to make this process easier is that adjustments to the \( \theta \) micrometer rotates the stage about the center of the chuck. When placing the sample onto the chuck it is important that one of the alignment marks in the corner of the sample is close to the center of the chuck. This will make aligning \( \theta \) much easier later on.

After placing the sample on the chuck, slide the chuck underneath the mask and then use the large z adjustment lever to bring the sample within a working distance of the mask. At this point the sample may still be too far away from the mask to resolve the features on the mask and on the sample at the same time. Slowly bring the sample up
to a height where both the mask and sample features are visible (to some degree) at the same microscope focal position while taking care to avoid making contact with the mask. The sample should now be ready for alignment.

The sample should be in a random position relative to the features on the mask so simply by eye, use the x and y micrometers to get the mask roughly aligned with the appropriate features on the sample. Next is to begin the alignment algorithm as follows.

1. Move microscope view to alignment mark at center of chuck.
2. Align only the x and y position of this alignment mark.
3. Move microscope view to any distant alignment mark.
4. Align only $\theta$ position of this alignment mark.
5. Check if aligned, if not go to step 1.

If these steps are followed the alignment should converge within 3-4 cycles. If alignment tolerances are especially tight, increase microscope magnification at this point and iterate through the alignment algorithm a couple more times.

Once alignment is complete, the final step is to bring the sample into direct contact with the mask. The best way to do this is to gently twist the z micrometer until the micrometer gives some resistance. Stop advancing the micrometer at this point and visually inspect the sample under the microscope. If the sample is in contact with the mask there will be at least one area that interference fringes are visible. A ‘perfect’ outcome here is that the interference fringes appear as a rainbow of color evenly distributed across the entire surface of the sample. This is only possible if the edge beads have been removed completely and the photoresist is extremely flat. Having the thickness fringes spread across the entire sample surface is the goal for having a “perfect” exposure.

Exposure and baking were some of the frequent mistakes I made in the cleanroom. It is for this reason I recommend that the exposure time on the contact aligner prior to loading a sample, and *don’t forget the post exposure bake.*
Lock-In Amplifiers: Theory and Operation

Lock-in amplifiers sometimes referred to as phase sensitive detectors, are basically just AC voltmeters. The basic operation of one of these amplifiers requires an input signal that is of interest and a periodic reference signal that is generated with the lock-in itself, or by an external source. The lock-in amplifier responds only to the portion of the input signal that occurs at the reference frequency while rejecting everything else. With a little clever experimental design it’s possible to make measurements that would normally be too noisy to collect useful data.

The specifics of how a lock-in amplifier operates can be understood by considering an input signal of interest $V_0$ and applying a sinusoidal modulation to this signal, and a sinusoidal reference signal.

$$V_{in}(t) = V_0 \sin (\omega_{in} t + \phi_{in})$$

$$V_{ref}(t) = \sin (\omega_{ref} t + \phi_{ref})$$
In a lock-in amplifier, these two functions are multiplied together as follows:\(^1\)

\[
V_{\text{in}}(t)V_{\text{ref}}(t) = \frac{V_0}{2} \left( \cos \left( (\omega_{\text{in}} - \omega_{\text{ref}})t + \phi_{\text{in}} - \phi_{\text{ref}} \right) - \cos \left( (\omega_{\text{in}} + \omega_{\text{ref}})t + \phi_{\text{in}} + \phi_{\text{ref}} \right) \right)
\]

It is clear now that the product of two sinusoidal functions can be broken down into a linear combination of two fundamental frequencies, one at the difference frequency \(\omega_{\text{in}} - \omega_{\text{ref}}\), and the other at the sum frequency \(\omega_{\text{in}} + \omega_{\text{ref}}\).

However, in the special case when the reference signal and input signal have the same frequency \(\omega_{\text{in}} = \omega_{\text{ref}} = \omega\) then we are left with a sinusoidal output that is offset by a phase dependent, zero frequency (DC) component.

\[
V_{\text{in}}(t)V_{\text{ref}}(t) = \frac{V_0}{2} \left( \cos (\phi_{\text{in}} - \phi_{\text{ref}}) - \cos (2\omega t + \phi_{\text{in}} + \phi_{\text{ref}}) \right)
\]

If at this point the output is passed through a low pass filter, the AC component will be discarded and only the DC component that is proportional to the signal amplitude will remain.

\[
V_{\text{in}}(t)V_{\text{ref}}(t) = \frac{V_0}{2} \left( \cos (\phi_{\text{in}} - \phi_{\text{ref}}) \right)
\]

It is important to remember that the output of the lock-in amplifier is proportional to \(V_{\text{in}} \cos \phi\), where \(\phi = \phi_{\text{in}} - \phi_{\text{ref}}\). This means that by adjusting \(\phi_{\text{ref}}\) it is possible to make \(\phi = 0\) making the output of the lock-in simply \(V_{\text{in}}\) however, it is also possible to make \(\phi = \pi/2\), making the output 0. This problem is most often overcome by implementing a second phase-sensitive detector that multiplies the signal with the reference oscillator shifted by \(\pi/2\) as follows.

\[
V_{\text{in}}(t) = V_0 \sin (\omega_{\text{in}}t + \phi_{\text{in}})
\]

\[
V_{\text{ref}}(t) = \sin (\omega_{\text{ref}}t + \phi_{\text{ref}} + \pi/2)
\]

\(^1\)Making use of the identity \((\sin \alpha)(\sin \beta) = \frac{1}{2} \left( \cos (\alpha - \beta) - \cos (\alpha + \beta) \right)\).
Working through the algebra and assuming again we are in the special case where $\omega_{in} = \omega_{ref}$, we are left with a similar expression as we derived earlier.

$$V_{in}(t)V_{ref}(t) = \frac{V_0}{2} \left( \cos (\phi_{in} - \phi_{ref} + \frac{\pi}{2}) - \cos \left( (\omega_{in} + \omega_{ref})t + \phi_{in} + \phi_{ref} + \frac{\pi}{2} \right) \right)$$

Finally, we need to recognize here that $\cos ((x + \pi/2)) = \sin (x)$ giving us the following expression after passing it through a similar low pass filter to remove the AC component.

$$V_{in}(t)V_{ref}(t) = \frac{V_0}{2} \left( \sin (\phi_{in} - \phi_{ref}) \right)$$

We now have two outputs from our lock-in amplifier, one proportional to $\cos \phi$ and the other proportional to $\sin \phi$. It is hopefully clear at this point that these two quantities represent the input signal as a vector relative to the lock-in reference signal. In typical lock-in amplifiers one can select between the following outputs.

$$X = V_{in}\cos \phi$$

$$Y = V_{in}\sin \phi$$

$$R = (X^2 + Y^2)^{1/2}$$

$$\phi = \tan^{-1} \left( \frac{Y}{X} \right)$$
References


