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Sputtered Gallium Nitride Tunnel Junction Contacts

A Thesis submitted in partial satisfaction of the
requirements for the degree Master of Science
in Electrical and Computer Engineering

by

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June 2019

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Koosha Daneshi

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ABSTRACT

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Koosha Daneshi

Gallium nitride LEDs produced for commercialization currently use indium tin oxide (ITO) as both a current spreading layer (CSL) and a contact to p-GaN. ITO is known to absorb wavelengths in the UV and visible light regions, the primary spectrum of GaN devices [20]. Tunnel junctions (TJ) have been proposed as an alternative p-contact and CSL which would transmit more light from the active region [20] while generating holes, from the electron tunneling, to reach the quantum wells of the LEDs for additional radiative recombination [18]-[21]. The fabrication process would also be simplified because the top layer of both the p- and n-contacts would be n-GaN and the metal contacts to both could be deposited at the same time. However, until now all GaN TJs have been deposited by MOCVD or MBE systems despite sputtering machines offering a lower cost and easier to use method of depositing GaN [12] [13]. This thesis explores the application of two sputtering techniques, the electron cyclotron resonance (ECR) and radio frequency (RF) magnetron, to the creation of TJs on blue GaN LEDs.

Both sputtering methods utilized silicon doped n-GaN targets with the intention of depositing the n-GaN layer of the TJs. The films were examined for their transmissivity of 440 nm light as well as their resistivity. The ECR system was observed to produce GaN that

lost around 5% of the emitted light when N₂ in conjunction with argon was used in the sputtering gas. Substrate heating did not meaningfully affect the transmissive property of the deposited GaN. Despite the good optical quality, the GaN remained resistive. Secondary ion mass spectrometry (SIMS) of the n-GaN target found it contain many impurities. High amounts of carbon, hydrogen, oxygen, magnesium, and calcium among other elements were discovered to be within the target. This stopped the research to produce a tunnel junction with the ECR system, but with a cleaner target it could still be a viable option.

The RF magnetron machine also relied upon nitrogen within the sputtering gas mixture to produce transparent GaN films. In general, the higher the rate of N₂ the less absorption of the tested 440 nm light. Substrate heating did improve the transparency of the GaN when sputtered with the RF magnetron machine. For a gas mixture of 38:25 sccm of N₂:Ar and a temperature of 800 °C, the GaN layer absorbed less than one percent of the blue wavelength. Hall-effect measurements showed greater substrate heating also increased the carrier concentration with films reaching the high 10¹⁹ and low 10²⁰ cm⁻³ ranges.

During the course of this work the RF magnetron system was modified and the maximum substrate temperature was lowered to 650 °C. Some previous films had been grown at 600 °C and this temperature was kept for continuity, but a silicon target was co-sputtered with the n-GaN target to raise the carrier concentration of the GaN. Hall measurements of these samples presented them to have higher mobilities compared to the GaN sputtered with only the GaN target. Sputtering the silicon target at 35 W of power was determined to give the highest carrier concentration of 1.137x10¹⁸ cm⁻³.

A tunnel junction was created utilizing the RF magnetron sputtering system on a UCSB blue LED structure deposited on a sapphire substrate with a MOCVD machine. Silicon was co-sputtered at 35 W and the nitrogen and substrate temperature were set to 38 sccm and 650

°C, respectively, to create the n-GaN layer of the TJ. LEDs with an area of 0.1 mm² were fabricated and required only two photolithography steps compared to the three steps necessary for ITO GaN LEDs. After a chlorine etch performed by a RIE machine to create the LED mesas, the MOCVD n-GaN around the mesas was noted to be rough in some areas of the wafer. When metal contacts were deposited on these areas, the metal did not stick to the n-GaN. Many LEDs were created in the smoother regions and were observed to emit blue light. These were tested for their current-voltage relationships and were found to have turn-on voltages of approximately 6.5 V with the least resistive devices reaching almost 5 mA at 10 V. These are the first reported GaN tunnel junctions deposited onto LEDs with a sputtering system.

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I. Introduction

A. Epitaxial Gallium Nitride

The III-V Nitride semiconductors consisting of InN, GaN, AlN, and their ternary and quaternary alloys have been the focus of intense research for the last few decades because of their direct and wide band gaps. The nitrides system band gaps can be engineered in a continuous range from 0.8 (InN) to 3.4 (GaN) to 6.2 eV (AlN) which allows for devices emitting from the infrared to ultra-violet (UV) range, respectively [1]. GaN, in particular, has been essential in creating high-brightness blue light-emitting diodes (LEDs) and laser diodes (LDs) [2]. The wide band gap also allows the nitrides to be used to create electronics, such as the high electron mobility transistor (HEMT), which can withstand high temperatures, powers, and frequencies [3].

The research done on the III-Nitrides started early in the 20th Century with more intense focus and attention given to the system as the century wore on. AlN was reported in 1907. In 1937, the crystal structure of GaN was described [2]. Maruskas and Tietjen grew GaN films on sapphire using hydride vapor phase epitaxy (HVPE) in 1969 [4]. Growth of GaN using metal-organic chemical vapor deposition (MOCVD) was achieved in 1971 [2]. Due to its high throughput, MOCVD is the most common commercial method of growth for GaN today [1]. 1974 showed the growth of GaN using molecular beam epitaxy (MBE), another popular growth method, by Akasaki and Hayashi. Yoshida used MBE to deposit an AlN buffer layer between sapphire and GaN in 1983. By depositing the buffer layer, his GaN film showed better optical performance than previous growths. Amano and Akasaki then used an

AlN buffer film to subsequently grow smooth GaN films in 1986 which yielded further increases to the optical and electrical properties of the epitaxy [2].

Throughout this time magnesium was used as a dopant in an attempt to create p-type GaN. However, due to its incorporation as a Mg-hydrogen complex the acceptors were electrically passivated and the resulting films showed resistivities on the order of $\sim 10^4 \Omega \text{ cm}$ [1] [5]. Akasaki and Amano activated the Mg using low energy electron beam irradiation (LEEBI) in 1989 [1] and produced p-GaN with a hole density in the range of 10^{16} cm^{-3} [2]. In the same year, they created a p-n junction blue LED using GaN [2]. Nakamura achieved a larger hole concentration of $3 \times 10^{17} \text{ cm}^{-3}$ with a resistivity of $2 \Omega \text{ cm}$ by thermal annealing with nitrogen in 1992 [2] [5] [23].

Nakamura went on to create InGaN/AlGaIn double heterostructure blue LEDs allowing Nichia Chemical Industries to produce them for the public by 1994. He also created green single quantum well InGaIn LEDs the next year diversifying the applications of GaN devices in the visible spectrum. These devices have been found to have lifetimes of at least 50,000 hours. Further broadening nitride optoelectronics in 1996 were Nakamura's blue-violet electrically injected laser diodes (LDs) under both pulsed and continuous wave conditions [2]. Epitaxial lateral overgrowth (ELO) was used by him to reduce threading dislocations (TDs) in GaN which led to lifetimes reaching 10,000 hours for the lasers in 1997 [1].

Devices fabricated from the III-Nitrides have found a variety of applications, both potential and realized, with many taking advantage of their direct and wide band gaps. UV LEDs, LDs, and photodetectors have been demonstrated. UV LEDs can be utilized in biological particle detection, water and air purification, and medical treatment and diagnosis. UV LDs can also be adopted within medical equipment. AlGaIn UV photodetectors are sensitive in the range 200-365 nm depending on the amount of aluminum incorporated

allowing for ozone and solar UV detection. Also, the atmosphere absorbs solar radiation under 300 nm which allows for the spectrum range 250-300 nm to be monitored by the photodetectors without background noise from the sun. This allows for the photodetectors to sense fires and missile launches or other combustion [1].

Optical storage is another application for the short wavelength lasers fabricated using the nitrides. Optical discs store data using spots limited by the wavelength (λ) of the light used to read them [1] [2]. Smaller wavelengths mean higher storage densities, increasing by λ^{-2} , and faster reading [2]. LDs used to read DVDs have a wavelength of 780 nm [2] and were created with AlGaAs [1]. Violet InGaN lasers with a wavelength of 405 nm are currently being used in Blu-ray discs which can store 27 GB of data on a single-layer side [1]. Laser printers can also utilize shorter wavelengths to achieve higher resolutions [2].

Most notably, nitride LEDs can be used to replace incandescent and fluorescent lamps. In 2003, the world used around 20% of its electricity to keep the lights on. White light from LEDs can be used to bring down the cost [1]. White light is created by mixing blue, green, and red light. This is generally achieved with LEDs by covering a blue LED with a yellow phosphor [1] [2]. However, red, green, and blue LEDs can also be packaged together to create any color by varying the intensity of each color [2]. Traffic lights can also benefit from LEDs [1] [2]. Traffic lights using filtered incandescent lamps to create red light lose 85% of the light and green and amber lose about 30%. These lamps also need to be switched out several times a year. LEDs can solve both problems by using less energy to create the desired wavelength and with their lifetimes above 5 years [2]. Other applications for nitride LEDs are color displays and panel lighting [1] [2].

Increasing wireless applications such as cellphones, satellites, and the internet require better microwave transistors and amplifiers [3]. The nitrides can be used to fabricate

electronics necessary for high power, high temperature, and harsh environments [1] [3] [5]. This is possible because the nitrides are non-reactive, radiation resistant, have high saturation drift velocities, high breakdown fields, and high thermal stability [5]. The high breakdown field and high electron velocities resulting from wide band gaps are especially important for achieving higher powers and frequencies [3]. Silicon carbide could also be used for its wide band gap, but GaN can form heterojunctions giving it preference in many applications [1] [3]. GaN/AlGaIn heterostructures are used to fabricate HEMTs [1]. HEMTs have high carrier concentration and high electron mobility which translate to high current density and low channel resistance, both being critical for higher powers and frequencies. The high output power density leads to smaller devices outputting the same amount of power and higher voltage operation leads to more efficiency than transistors made from GaAs [3]. GaN HEMTs can also withstand high temperatures [1] [3]. They have been shown to operate at 500 °C. These advantages of GaN transistors over current ones made from Si and GaAs can lead to incorporation in aerospace and automobile manufacturing [1].

Homoepitaxial growth, growth of a thin film material on a substrate of the same material, is not possible on a large scale with GaN because of the lack of large bulk single crystals [1] [2] [4]. This is due to the high vapor pressure of nitrogen at GaN's melting point. High temperature and high pressure growth is utilized to grow single crystal GaN of only around 1 cm² [1]. In order to produce GaN epitaxy on a commercial scale, heteroepitaxy, growth of a thin film on a substrate of a different material, is used [1]-[5]. As stated previously, MOCVD is the most common method of nitrides growth. The most widely used precursors are trimethyl-gallium, -aluminum, and -indium as the group III source and ammonia as the nitrogen source [2] [3] [5]. Growth of device quality GaN requires high

temperatures, a large partial pressure of ammonia, and methods to prevent mixing of the precursors before deposition [1] [5].

The general procedure for nitride epitaxy using MOCVD is as follows: the substrate undergoes nitridation, a nucleation (buffer) layer, usually AlN or GaN, is deposited at low temperature, the buffer layer is annealed, and epitaxial growth is started [1] [4] [5].

Depending on the substrate used or the specific nitride being grown, steps could be added or modified in the process. Unfortunately, heteroepitaxy of the nitrides comes with problems. Some examples are: high inherent n-type doping in films, high temperatures necessary for growth, high pressures needed for nitrogen incorporation, reactions between the precursors before deposition, lattice mismatches with substrates, and threading dislocations [1] [5]. Two of the issues that will be discussed here are finding a proper substrate and threading dislocations.

The substrate used in GaN deposition can have consequences upon the properties of the epitaxial film. Some examples include: crystal orientation, polarity, polytype, smoothness of the surface, amount of strain, threading dislocation densities, inversion domain boundaries, and stacking faults [4]. Lattice constant mismatch is usually the guiding property used to pick the substrate [1] [4] [5], but other traits, such as: crystal structure, surface, composition, reactivity, chemical, thermal, and electrical, are also relevant [4]. Cost of the substrate can also be a defining factor [1] [3]-[5]. Many materials including metal oxides, metals, metal nitrides, and semiconductors have been researched to find a perfect substrate, but it remains elusive [4]. Sapphire, silicon carbide, and silicon will be discussed here.

Sapphire (Al_2O_3) is the most commonly used substrate for GaN epitaxy [1] [2] [4] [5]. However, there are many problems associated with it. The mismatch between the lattice constant (~15%) [4] and thermal expansion coefficient of sapphire and GaN causes a large

amount of dislocation densities (10^9 - 10^{11} cm^{-2}) [1]. This leads to lower mobilities, minority carrier lifetime, and thermal conductivity in the film causing decreased device operation. Stress is also caused in the GaN due to the difference in thermal expansion coefficients [4]. Thicker films relieve neither the stress, in fact cracking is observed [4], nor the dislocations [1]. Additionally, sapphire does not dissipate heat well, is an insulator requiring contacts to be made on the epilayer, and can cause n-type doping with its oxygen. Sapphire continues to be used partly because the most amount of time has been spent developing processes for deposition on it than other substrates [4]. It is also less expensive than some other substrates [3]. C-plane (0001) GaN on c-plane sapphire is the most widely grown film and substrate orientation combination [4].

The general procedure for GaN epitaxy on sapphire is treatment of the substrate surface, nitridation of the substrate, growth of a nucleation layer, heating of the buffer layer, and high temperature epitaxial deposition [1] [4]. Sapphire substrates can be rough from polishing damage when obtained. Root-mean-square (RMS) values of 0.8-2.1 nm over 1 mm^2 are observed. Thus, the substrate needs to be smoothed before deposition. This is usually achieved by annealing the sapphire under flowing hydrogen at temperatures 1000-1100 °C [4]. Nitridation occurs by exposing the substrate to either ammonia [1] or an ammonia/hydrogen mixture in MOCVD [4]. The usual process is the use of ammonia at a temperature of 1050 °C [1]. Temperature and duration of the nitridation are both important and can affect epilayer properties. When using high temperatures (\sim 1000 °C) shorter times of less than 3 minutes are preferred. Nitridating for lengths above 3 minutes can lead to decreased electron mobility, increased yellow luminescence from defects, and worse surface morphology. However, when nitridating at low temperatures (\sim 400 °C) longer durations seem to increase film quality. When the substrate is nitridated properly increased electron

mobility, decreased defects, decreased yellow luminescence, and better wetting of the epilayer are observed [4]. The buffer layer is typically GaN or AlN and is grown at temperatures between 450 and 600 °C [1]. The layer is thin, usually between 10 and 100 nm [4]. The deposition of a low temperature nucleation layer causes smoother epitaxial films [4], lower dislocation densities, and helps with uniform coverage of the substrate [1]. The buffer layer is annealed at the growth temperature around 1050 °C [1]. The heating changes the layer from amorphous to a c-plane film when using c-plane sapphire and reduces the number of low-angle grain boundaries [4]. The epitaxial layer is then deposited at 1050-1080 °C. Hall measurements place electron concentrations in the 10^{16} cm^{-3} range for undoped epitaxy [1] [5]. Threading dislocation densities of 10^{10} cm^{-2} are observed [1] [4] [5].

The preceding procedure described the steps for 2D growth of GaN on sapphire. 3D growth can be achieved by adding a step of flowing silane and ammonia above the substrate after the nitridation and before the buffer layer deposition. Hydrogen gas must also be used during the annealing of the nucleation layer. These additions cause the buffer layer to coalesce into islands and when epitaxial growth occurs the epilayer grows both laterally and vertically from these islands. Using this method, TD densities can be reduced to the 10^8 cm^{-2} range [1].

Silicon Carbide (SiC) is another popular substrate for the nitrides and has especially found a niche in GaN transistor growth [3]. There are several advantages to using specifically 6H-SiC: the lattice constant is much closer to GaN with a mismatch of ~3%, its thermal conductivity is higher than sapphire, and it is electrically conductive allowing for contacts to be made to the substrate leading to easier device processing [1] [4]. SiC can have either a silicon or carbon face [4], but research has shown that growth on the silicon face has better surface morphology [1]. Unfortunately, there are several reasons why the substrate is

not more widely used. Silicon carbide wafers are more expensive than sapphire [1] [3] [4] [5]. Making it worse, the wafers exhibit rough surfaces [2] with an RMS of 1 nm [4] and can have bad structure quality [5]. A buffer layer of either AlGaN or AlN is also a requirement when growing GaN because of poor wetting between the materials [1] [4]. This leads to an increase in resistance between devices and substrate. Additionally, SiC's thermal expansion coefficient is lower than both GaN's and AlN's causing the epilayer to be under stress [4]. This tensile stress can cause cracks propagating through all layers [1]. Finally, the threading dislocation densities of 10^9 cm^{-2} are not much better than GaN/sapphire [1] [4].

The procedure for nitride deposition on SiC is simpler than sapphire: the surface is prepared, a buffer layer is grown, then epitaxial deposition occurs. Substrate preparation is critical for SiC because, as stated previously, the surface is very rough upon reception. The amount of threading dislocations and epilayer roughness is dependent on the surface morphology of the substrate. Etching using hydrogen at high temperatures ($\sim 1600 \text{ }^\circ\text{C}$) can remove all scratches. Any oxides on the substrate must also be removed [4]. The nucleation layer is usually composed of AlN or AlGaN [1] [4]. The deposition process for the buffer layer varies from system to system, but if AlN is used a high temperature growth above $1100 \text{ }^\circ\text{C}$ seems best [4]. If a thickness between 30 and 100 nm is deposited, the AlN will not have any domains or low-angle boundaries [1]. Annealing the buffer layer can also improve the structure of the epitaxial film [4]. Finally, the epitaxial deposition of GaN occurs at $950 \text{ }^\circ\text{C}$ using an MOCVD system. Undoped GaN on 6H-SiC typically has a carrier concentration around 10^{16} cm^{-3} . Red-shifted luminescence is observed due to the tensile stress from the substrate. The dislocation density is 10^9 cm^{-2} , but can be reduced with thicker films [1].

Silicon is a highly desirable substrate because of the large-scale manufacturing system already in place for the material. This system can produce large, inexpensive silicon wafers

with crystal qualities and surface morphologies better than all other substrate candidates [1] [4]. Silicon also has thermal stability during GaN deposition [4]. If this technology is sufficiently advanced, it could lead to integration of devices made from silicon and GaN on the same chip [4] [6]. Unfortunately, the quality of the epitaxial films on silicon is lacking compared those on sapphire or SiC [1] [4]. The difference in thermal expansion coefficients causes GaN layers to be stressed and can crack if grown thicker than approximately 800 nm making the deposition of a buffer layer a necessity [1]. The substrate has been observed to create silicon nitride when coming into contact with nitrogen. Non-radiative recombination centers are also a problem with nitrides grown on silicon [4].

The procedure for epitaxial deposition on silicon is the same as SiC: substrate preparation, buffer layer growth, and epilayer deposition. Research has been done for growth on both (001) Si and (111) Si [4]. Both wurtzite and zincblende GaN have been deposited on (001) Si [4]-[6]. Using MBE, GaN buffer layers between 300 and 900 Å were grown in a temperature range of 175-400 °C. Subsequently, approximately 1 µm of epitaxial GaN was deposited at 600 °C. It was found that the buffer layers grown at higher temperatures were single crystalline while those deposited at low temperatures were either amorphous or polycrystalline [6]. Furthermore, the epilayers deposited on the single crystalline buffers were single crystalline zincblende GaN while those deposited on the amorphous or polycrystalline buffers were polycrystalline wurtzite GaN [5] [6]. 3C-SiC layers on (001) Si have been deposited with the intention of growing zincblende GaN on top. This epitaxial stack has poor surface morphology and crystal quality which, again, leads to the growth of wurtzite GaN. The low growth temperature of MBE has been observed to be advantageous when growing zincblende GaN on 3C-SiC/(001) Si compared to the high temperatures of MOCVD. However, growth of cubic GaN on (001) Si continues to be a work in progress.

Separate buffer layers of sapphire, AlN, and AlGaN have all yielded wurtzite gallium nitride [4].

(111) Silicon has both problems of SiN formation and cracking of the epilayer. A variety of buffer layers have been attempted to fix the problem. An AlN buffer layer can be used to stop the SiN from occurring [4]. Multiple layers of AlGaN and GaN can help with the cracking [1]. Surface treatments of the silicon must also be implemented to improve crystallinity and optical properties of the epitaxial films. Despite these problems, (111) Si remains the plane of choice and devices such as LEDs, photodetectors, and transistors have been shown using this substrate [4].

Threading dislocation densities have been a consistent problem for the nitrides due to deposition using heteroepitaxy. TD densities are around 10^9 - 10^{10} cm^{-2} for GaN growth on sapphire or 6H-SiC. It is remarkable that devices created from the nitrides can even work with such high dislocation densities [1] [4]. Optoelectronic devices fabricated from other III-V semiconductors would not operate at those densities [1]. The consensus used to be that optical devices would not be efficient with densities of 10^6 cm^{-2} and above [4]. As an example, blue lasers using a II-VI semiconductor had been created with TD densities around 10^5 cm^{-2} , but they would fail due to more TDs being created while emitting light [1].

Despite early III-nitride devices working with such high dislocation densities, lowering the number of TDs can result in higher efficiency and better performance [1]. In fact, complex devices, such as laser diodes, require lower amounts of dislocations. One method of decreasing TDs is to use homoepitaxy. As an example, homoepitaxial silicon has close to zero dislocations and GaAs homoepitaxy has densities between 10^2 and 10^4 cm^{-2} [1] [4]. Homoepitaxy on small bulk GaN crystals has been performed with results showing TD densities of 10^5 cm^{-2} and below [2] [4]. However, as stated before, homoepitaxial GaN on a

large scale is not feasible because of the lack of the ability to produce bulk single crystal wafers for substrates [1] [2] [4]. Thus, additional growth steps must be utilized during heteroepitaxial growth to decrease TD densities [1] [4]. Nitridation and buffer layers have decreased dislocation densities to 10^8 cm^{-2} and optimized 3D growth of GaN can reduce them further to 10^7 cm^{-2} , but more complex methods such as epitaxial lateral overgrowth or pendeoepitaxy are needed for lower values [1].

Epitaxial Lateral Overgrowth uses a selective area epitaxy process to decrease dislocation densities by depositing a masking material on top of portions of previously grown GaN and then growing a new GaN layer on top of that template. The general procedure for ELO has four steps. First, a GaN film several micrometers thick is grown as normal on the substrate being used. Second, a dielectric material, usually silicon dioxide or silicon nitride, is grown on top of the GaN layer. Third, parallel strips of the dielectric are etched away using photolithography thus exposing strips of the underlying GaN next to strips with the dielectric still on top. Fourth, GaN growth is started again with GaN only growing on top of the strips of exposed GaN. Once the GaN has reached the surface level of the dielectric, GaN grows laterally from the exposed strips and covers the mask. Vertical growth also continues as normal while lateral growth occurs. Vertical epitaxial deposition does not occur on the dielectric before lateral growth because the supersaturation of the growth nutrients should be low on the mask. The rate of lateral growth is controlled by many factors, some examples are: planar orientation of the GaN epitaxy, temperature during deposition, pressure, V/III vapor ratio, and chemical mixture of the carrier gas. For instance, research has shown that using a 1:1 ratio of H_2 and N_2 for the carrier gas leads to the fastest growth rate while maintaining a smooth surface morphology [1].

While threading dislocations propagate as normal through the vertically grown film on top of the exposed GaN, the dislocations do not occur in the laterally grown film on top of the mask. The mask stops the propagation of the dislocations in the epitaxy beneath it and thus lowers the dislocation density. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) analyses of GaN grown using this ELO method have shown TD densities as low as $5 \times 10^6 \text{ cm}^{-2}$ [1].

The previously described procedure is known as one-step ELO. Multiple growths using ELO is possible and can achieve lower TD densities. A variety of procedures have been created for two-step ELO. After following the normal steps for one-step ELO, one procedure calls for stripes of a second deposition of the dielectric to be etched at an angle, 60° or 90° , with respect to the strips of the original mask. Lateral growth will then occur as in the original step. Another method calls for the second set of mask strips to be placed on top of the strips of exposed GaN in the first ELO growth. Again, lateral growth will occur as before. Nichia has even developed a three-step ELO process for GaN/sapphire. First, one-step ELO deposition using MOCVD is utilized. Above this template, GaN is grown using HVPE. The sapphire is polished away to expose the GaN epitaxy. Finally, one-step ELO is utilized on top of the exposed film. This method has reduced TDs to $7 \times 10^5 \text{ cm}^{-2}$. Using ELO, reverse bias leakage current and dark current have been reduced in LEDs and photodetectors, respectively. The three-step procedure has allowed Nichia to create LDs with lifetimes of 15000 hours [1].

Pendeoepitaxy is a modified version of the epitaxial lateral overgrowth procedure. Again, the first step is GaN growth on a substrate. However, at this point parallel stripes of the epitaxy along with some of the substrate beneath them are etched away. This creates ridges and troughs with the bottom of the troughs being the exposed substrate and the sides

being composed of epitaxial film on top of the substrate. The remaining GaN is covered by a dielectric mask. GaN is then grown laterally from the walls of the troughs and once a bridge has been created by the film over the exposed substrate vertical growth occurs. When the growing material reaches the dielectric surface, lateral growth occurs again to cover the mask. Just like ELO, by masking parts of the originally grown GaN and allowing lateral growth, TD densities are reduced. Multistep pendeoepitaxy can be achieved by repeating the procedure with a film previously grown using pendeoepitaxy. Despite additional steps in both ELO and pendeoepitaxy resulting in lower dislocation density material and thus better performing devices, this must be balanced with the increased time and resources put into growing such films [1].

B. Sputtered Gallium Nitride

Sputter deposition is another method that can be used for gallium nitride deposition. Sputtering involves directing molecules of a gas to bombard a target, the material for which deposition is desired, causing the atoms or molecules of the target to be dislodged. Some of these freed particles will settle on the substrate placed within the chamber and become the deposited layer. The material being deposited can be constituted from solely the target material or from chemical bonding of the atoms of the target with the atoms of the gas. The substrate is loaded before the sputtering process begins.

Sputter deposition of GaN is a less widely used procedure compared to MOCVD, MBE, and HVPE [7], but there are benefits inherent to the method which have the possibility of opening a variety of new applications for GaN. The technique allows for deposition at low temperatures [7]-[13] especially compared to the usual MOCVD requirement of 800 °C or above [14]. Low temperature growths can lead to better III-Nitride electronic devices such as

AlGaIn/GaN HEMT biosensors [8] while room temperature deposition can allow for integration of GaN layers with silicon complementary metal oxide semiconductor (CMOS) devices [10]. Room temperature deposition is desirable for pre-grown silicon devices because they could become defective if they are heated during the GaN deposition [10]. Electronic devices also require low free electron concentrations in undoped material. Samples with concentrations in the 10^{14} cm^{-3} range have shown this is achievable with sputtering [9]. Although GaN deposition by sputtering mainly results in polycrystalline material [12] [13], applications such as transistor displays and solar cells do not need single-crystalline quality [14]. Persistent photoconductivity has also been observed in sputtered gallium nitride layers which could be utilized to record information optically [11].

The most attractive feature of sputter deposition is the low cost compared to conventional epitaxial methods [7] [10] [12] [13]. This gives the ability to deposit layers on large area substrates and subsequently fabricate devices in large quantities. When coupled with inexpensive substrates such as silicon or glass, the cost to commercially produce GaN optical and electronic devices can be reduced further [7] [10] [13]. Ease of use is another desirable trait of the sputter process [8] [12] [13]. This trait leads to improved control of film thickness [8] and properties, tailoring them to specific needs of the application [12] [13]. High growth rate [7], reduced toxicity, and subsequent deposition of different materials are other benefits of the method [8].

Two different approaches to sputtering GaN are using gallium as the target and using GaN as the target. When utilizing GaN, the material must simply be sputtered onto the substrate. If gallium is employed, nitrogen gas must be used during the sputter process so that GaN may be created. Procedures and characterizations for both techniques will be presented.

Usage of a gallium target is a common sputtering method to deposit gallium nitride. However, as stated, it must be in conjunction with nitrogen gas so that the gallium and nitrogen may chemically bond to form GaN. Many research groups may use nitrogen gas within their procedure, but they have added other gases to sputter, deposited on different substrates, and varied other parts of the process.

Zou *et al.* utilized middle-frequency (MF) magnetron sputtering to deposit onto soda-lime silicate glass substrates. The frequency was set to 40 kHz. Their gallium targets were kept cool with 5 °C water. The substrates were cleaned with acetone and ethanol then washed with deionized water prior to being loaded into the machine. In the chamber, glow discharge cleaning in argon was also performed on the substrates at 4 Pa (~30 mTorr) with the target shielded. The sputtering conditions were normally: 1600 W of input power, 80 °C, which Zou *et al.* called “no substrate heating,” 50 V negative bias, 2.5 A cathode target current, sputtering gas of 30% argon and 70% nitrogen, 10 cm between substrate and target, and 0.8 Pa (~6 mTorr) of pressure. However, the pressure was changed to observe changes in the deposited layer’s characteristics. The GaN film thickness was 3 μm [7].

Newman *et al.* used radio frequency (RF) magnetron sputtering to deposit onto r-plane sapphire. The gallium target was sputtered before deposition in 10 mTorr of Ar then 10 mTorr of 30% Ar and 70% N₂ for one hour to nitride the target. The sputtering parameters were: 110 W, 6.5 cm between substrate and target, substrate heating was varied from 200 to 700 °C, nitrogen partial pressure from 1.5-25 mTorr, nitrogen flow from 10 to 285 sccm, and the ratio of N₂/Ar was varied from 0.1 to 1. The samples were cooled to be under 200 °C with 100 mTorr of N₂ once deposition was finished [9].

Meng *et al.* also employed RF sputtering to grow a buffer layer of AlN on (111) Si followed by a GaN film. The AlN was deposited with the conditions of 1:9.9 Ar:N₂ gas

mixture, 1.6 mTorr pressure, and at a temperature of 710 °C. The thickness was around 45 nm. The GaN deposition kept the sputtering parameters of 1.6 mTorr and the ratio of 1:9.9 Ar/N₂ gas, but also followed approximately 14 cm from target to substrate, input power ranging from 50 to 300 W, and substrate heating from 550-750 °C. Deposition of GaN was only started when the substrate was heated to the desired temperature. The thickness of the GaN layer was ~1 μm [15].

Miyazaki *et al.* utilized a RF magnetron system, just as the previous two groups, to sputter onto Corning 7059 glass, fused quartz, (100) Si, and 4°-off (111) Si as substrates. The substrates were cleaned with organic solvents before being placed into the machine. The gallium target was cleaned with sputtering preceding the deposition while the substrates were protected by a shutter. The deposition parameters were: frequency of 13.56 MHz, 50 W, 5 cm distance between target and substrate, the pressure ranged from 0.08-2.70 Pa (~0.6 to ~20.3 mTorr), the substrate was believed to be heated to around 60 °C, but this was not intended and seemingly an artifact of growth at 50 W, the sputtering gas was composed of either pure nitrogen or a blend of hydrogen and nitrogen gases. Most of the films deposited with the N₂/H₂ mix had a hydrogen partial pressure of 0.07 Pa (~0.53 mTorr), but some were sputtered with a partial pressure of 0.01 Pa (~0.075 mTorr). The GaN layer was usually 500 nm thick [12].

In another study by Miyazaki *et al.*, a RF magnetron sputter system was used to deposit onto solely 4°-off (111) Si substrates employing almost the same procedures and parameters. Prior to being placed in the machine, the substrates were cleaned first using organic solvents and second with a 10:1 H₂O:(49%) HF solution. The HF procedure lasted for 20 s at room temperature and was utilized to get rid of any oxides and passivate the surface of the silicon with hydrogen bonds. Pre-sputtering of the gallium target was engaged to clean the surface

while the substrates were shielded. The sputtering conditions were: 13.56 MHz RF frequency, 50 W, 0.08-2.70 Pa total pressure, 5 cm between target and substrate, around 60 °C unintentional heating from the 50 W input power, and all films were sputtered with only N₂ gas. The target was kept cool throughout with running water. Thicknesses of the GaN layers ranged from 200 nm to 1.2 μm [13].

X-ray diffraction (XRD) measurements are a common method of characterizing the crystallinity and orientation of a deposited film. All of the listed groups performed Θ -2 Θ XRD to learn more about their sputtered layers. Newman *et al.* observed the (11-20) direction, the same orientation as the sapphire substrate, for their GaN with the best crystallinity, highest peak intensities, occurring when sputtering was performed between 630 and 680 °C. A full width at half maximum (FWHM) of 25 min. for the peak at 650 °C was reported [9].

Meng *et al.* found that c-plane gallium nitride and aluminum nitride grew on the (111) Si substrate when deposited at 550-750 °C with 100 W input power. They also performed an ω rocking curve scan for the same conditions reporting the GaN and AlN having rocking curve widths of 0.61° and 0.85°, respectively, at 560 °C and other widths being similar for the range 550-750 °C. A more specific comparison of the widths at 560 °C and 650 °C with respect to varying the power from 50-300 W showed the widths at the higher temperature were narrower. The total width at 650 °C for each of the tested powers was around 0.45°. This demonstrated that depositing at different powers for the same temperature did not notably affect the rocking curve width. These values were close to GaN layers grown with electron cyclotron resonance (ECR) MBE on (111) Si, but much wider than epitaxy on sapphire using ECR MBE. Lattice distortion in the c-direction was also observed for the same RF power range at the temperatures 560 and 650 °C. The strain in the film was lower at

650 °C for powers 100 W and above, but the lattice spacing was always higher than the room temperature value no matter the deposition temperature nor the power. The lattice strain also increased as the sputtering power increased for both temperatures as well. They state this is evidence that some of the increased lattice spacing must result from nonthermal sources [15].

Miyazaki *et al.* performed XRD on GaN films sputtered solely with N₂ onto 4°-off (111) Si and N₂/H₂ on (100) Si with the measured pressure ranges being 0.08-2.70 Pa and 0.27-1.07 Pa, respectively. The hydrogen partial pressure was 0.07 Pa (~0.53 mTorr). All N₂/H₂ films were found to be amorphous. C-plane peaks grew stronger as the growth pressure dropped, but remained too small to have a crystalline layer. The GaN sputtered with only the nitrogen gas was also amorphous for high pressures, but at 1.07 Pa (~8 mTorr) peaks for multiple orientations of wurtzite GaN were visible including c-plane. They claim the peaks' positions follow those laid out in the Joint Committee on Powder Diffraction Standards (JCPDS) for wurtzite GaN and that the film is polycrystalline. Films grown from 0.53 Pa (~4 mTorr) and below contained a peak only at the wurtzite c-plane location with the epitaxy at 0.27 Pa (~2 mTorr) having the best crystallinity. Reflection high-energy electron diffraction (RHEED) analysis on the 0.27 Pa sample showed that the GaN is polycrystalline with smooth surface morphology [12].

In the other study, Miyazaki *et al.* present much the same results for crystal orientations using XRD with respect to total pressure. This paper goes further in describing XRD intensity and FWHM of the (0002) plane peaks for films sputtered purely with nitrogen at various pressures. They confirm that the greatest intensity occurs at 0.27 Pa while the FWHM lowers with higher pressure until approximately 0.5 Pa where the FWHM remains close to 0.5° with further pressure increases. Lattice strain in the c-direction with respect to

total deposition pressure was also reported. The lower the pressure, the greater the distortion of the lattice. The distortion remained below 1% until around 0.6 Pa (~4.5 mTorr) where it jumped to ~2% and kept increasing for lower pressures. They state that the higher strain at 0.6 Pa and below could be the reason behind the larger FWHM at the same pressures [13].

Zou *et al.* recorded XRD measurements for GaN films on glass in the pressure range 0.51-1.5 Pa (~11.3 mTorr). They also found c-plane to be the favored orientation for 0.67 Pa (~5 mTorr) and above and wrote that this was observed for growth on a silicon substrate done separately as well. The (0002) GaN peak was not present for depositions 0.51 Pa and below. The intensity of the c-plane peaks, however, was in the hundreds of counts/s no matter the pressure which was lower than their deposition on silicon and much smaller than GaN epitaxially grown using the standard techniques of HVPE, MOCVD, and MBE. They attribute the low intensity to the amorphous quality of glass. Another claim is put forth that the optimal pressure for crystallinity is between 0.67 and 0.8 Pa (~6 mTorr) due to sputtered atoms having low kinetic energy and thus low mobility when reaching the substrate and being unable to crystallize properly at high pressures while at low pressures the atoms will have energy that is too high and could cause re-sputtering of the deposited GaN [7]. This contrasts with the findings of Miyazaki *et al.* of the best crystal quality occurring at pressures 0.53 Pa and below [12], but this could be due to the different methods of sputtering with Zou using MF [7] while Miyazaki used RF [12].

Other characteristics of the sputtered GaN layers were also observed by these groups. Newman *et al.* report that the conditions of a nitrogen partial pressure of 8 mTorr, N₂ flow rate of 238 sccm, N₂/Ar ratio of 4:1, and deposition temperature of 650 °C yields room temperature Hall electron carrier concentrations of $8.4 \times 10^{14} \text{ cm}^{-3}$ with a mobility of 330 cm²/V*s. This carrier concentration was close to the value $8 \times 10^{13} \text{ cm}^{-3}$ obtained with MBE

which was the best at the time for undoped gallium nitride. When going back to using 70% N₂ in the sputtering gas, they presented that deposition in the temperature range 625-680 °C generated both the best N/Ga ratio, between ~0.8 and ~0.9 with the highest value being at ~625 °C, and growth rate, between ~1.5 and ~2.5 Å/s, with the growth rate increasing with temperature until 670 °C. After 680 °C, the N/Ga ratio and deposition rate decrease just the same as the crystal quality mentioned earlier. Newman *et al.* hypothesize that this could be due to one or more of the following: thermal decomposition of the GaN layer, the impinging nitrogen and gallium atoms reevaporating before being assimilated into the crystal, the same atoms having a lower sticking coefficient, or some other unnamed reason. The resistivity of the deposited film at these conditions was observed to decrease as the temperature increased starting at around 10 Ω*cm for 600 °C and reducing to about 0.04 for 700 °C. They also observed the effect of reducing the RF input power from 110 to 50 W while keeping the heat at 650 °C and the N₂/Ar ratio at 7:3 to be the N/Ga ratio dropping from 0.92 to 0.66 and the deposition rate also dropping from 2.4 to 0.34 Å/s which they believed is proof that sublimation of the GaN layer is occurring during the deposition process [9].

Meng *et al.* also noted in their experiment that as the input power increased the deposition rate followed suit. Raman spectroscopy was implemented by them as well on layers sputtered at 560 °C and 650 °C. The spectra of the lower temperature film contained peaks at 562.3 and 728.3 cm⁻¹ with FWHMs of approximately 12 and 20 cm⁻¹, respectively. The sample deposited at 650 °C showed peaks at 562.8, 714.7, and 731.9 cm⁻¹ with FWHMs of ~9, 39, and 12 cm⁻¹, respectively, within its spectra. The authors concluded that the peak at ~562 cm⁻¹ could be from the E₂ phonon mode of gallium nitride [15]. The narrowing of the peaks at ~562 and ~730 cm⁻¹ [15] could lend additional support to the claim made by

Newman *et al.* that sputtered deposition of GaN with substrate heating at around 650 °C leads to the best crystallinity [9].

Miyazaki *et al.* performed Fourier transform infrared spectroscopy (FTIR) on both the layers sputtered with pure N₂ and N₂/H₂ gas. For this measurement, both films were deposited onto (100) Si while the GaN films deposited with N₂ and measured with XRD were on 4°-off (111) Si. However, they report that no observations were made to suggest that the substrate utilized obviously affects the film's properties. The layer sputtered with pure N₂ was deposited at a pressure of 0.27 Pa (~2 mTorr) and showed a single vibration peak at ~555 cm⁻¹. The authors believed this to be created by the GaN lattice absorption band which in single-crystalline wurtzite GaN is located at approximately 533 cm⁻¹ and 560 cm⁻¹. The GaN:H films were sputtered with a hydrogen partial pressure of 0.07 Pa (~0.53 mTorr) and were observed at the total pressures 0.27, 0.53, and 1.06 Pa with the latter two being at ~4 mTorr and ~8 mTorr, respectively. All these films had peaks at around 555, 1000, and 3200 cm⁻¹. The latter two peaks were claimed by Miyazaki *et al.* to be from hydrogen-related bonds with the gallium or nitrogen. They also observed the FTIR spectra when the GaN:H layers were sputtered at 0.01 Pa (~0.075 mTorr) hydrogen partial pressure for both 0.53 and 1.06 Pa total pressures and reported that since the spectra contained the same peaks at close to the same intensities when the total pressures were kept the same and the partial pressure was changed, but not vice versa, that the hydrogen bond density is reliant on the total pressure utilized not the amount of hydrogen. GaN and GaN:H films were sputtered onto Corning 7059 glass to measure the band gap energy at room temperature. Both were deposited at a pressure of 0.27 Pa with the latter using 0.07 Pa partial pressure of hydrogen. They found the band gap to be located at 3.38 eV for the sputtered GaN film which is close to the standard 3.4 eV value for single-crystalline wurtzite GaN and further confirms that

they were able to grow wurtzite GaN. The GaN:H layer was determined to have its band gap at 3.7 eV, a higher energy than both wurtzite and cubic GaN with the latter having its value at around 3.2 eV [12].

In the other paper, where Miyazaki *et al.* sputtered onto just 4°-off (111) Si with only nitrogen gas, spectroscopic ellipsometry (SE) was utilized to characterize a sample deposited with 0.27 Pa of pressure. They found the gallium nitride layer to be composed of a surface layer having a depth of around 17 Å and consisting of 70% voids. Underneath the surface, the rest of the sputtered film contained a 4.7% density deficit. AFM was also utilized to analyze the same film and an approximate 11 Å rms roughness value was calculated, agreeing with the ~17 Å determined with SE. Scanning electron microscopy (SEM) of the sample yielded a film without the usual columnar structure expected from sputtered deposition. They stated that these columns in sputtered films are responsible for roughening the surface and reducing the uniformity, so it is unsurprising that they observed a homogenous GaN layer with a smooth surface. The transition from the silicon substrate to the gallium nitride was presented to be smooth. The authors claimed this to be from sputtering without any additional heating, beyond the 60 °C caused by the input power of 50 W, since molten gallium damages silicon crystals and deteriorates the surface morphology. Miyazaki *et al.* also observed that changing the sputtering gas from pure N₂ to a 50:50 mix of N₂/Ar helps to flatten the surface of the GaN. AFM analysis of a layer using this gas combination revealed a 6 Å rms roughness [13].

Zou *et al.* characterized one of their GaN layers, deposited with their standard parameters mentioned earlier, with energy-dispersive x-ray spectroscopy (EDX) and concluded that the film has close to a 1:1 Ga/N ratio. SEM of the sputtered layer showed it was columnated [7], which is stated to be typical of sputtered films by Miyazaki *et al.* [13], and stratified. The

authors claimed the latter to be a possible indication of a high quantity of surface defects. AFM measurements yielded a surface consisting of small crystals of different sizes and a 7.95 nm rms roughness. Raman spectroscopy performed on GaN layers deposited on both soda-lime silicate glass and (111) Si showed peaks at 564 and 730 cm^{-1} . They suggested that the peaks could be from the E_2 and $A_1(\text{LO})$ phonon modes, respectively, citing another study that had found the E_2 mode at 565 cm^{-1} and the $A_1(\text{LO})$ mode at 735 cm^{-1} for single-crystalline GaN deposited on Si using an ultrahigh vacuum RF magnetron sputter system. Also referencing Meng *et al.*, Zou *et al.* noted that the E_2 mode FWHM for their layer deposited on glass was much broader at 28.72 cm^{-1} than the 9 cm^{-1} value measured by Meng's group and that this increased width could be from strain caused by the large input power used at 1600 W. Observations made with photoluminescence spectroscopy (PL) on films sputtered at 0.8 Pa (~6 mTorr) and 1.5 Pa (~11.3 mTorr) showed broader peaks for the layers deposited at the higher pressure. The authors report that this finding could mean that higher pressures reduce the crystallinity of the sputtered GaN [7]. This conclusion would agree with their own results from XRD [7] as well as the measurements implemented in the studies from Miyazaki *et al* [12] [13].

Gallium nitride itself has been used as a target for sputter deposition of GaN films by several research groups. Huq *et al.* employed an ultra high vacuum (UHV) RF magnetron sputter machine for their deposition of films on sapphire, glass, and (111) Si substrates. The target was cleansed of impurities by pre-sputtering it for 30 minutes before deposition commenced. The sputtered growth occurred utilizing the parameters of frequency at 13.5 MHz, input power range of 15-50 W, and total pressures from 4 to 30 mTorr. Additionally, the substrates were rotated between 30 and 60 RPM along with being heated at various temperatures of 25 to 700 $^{\circ}\text{C}$ throughout the deposition. These conditions were implemented

to improve the sputtered layer's consistency on all parts of the substrate and decrease the number of oxygen atoms settling within the growing film, respectively. Both argon and nitrogen gases were used for the sputtering gas, but depositions with different ratios of each gas in the mixture were performed. One deposition implemented purely Ar gas, another utilized both Ar and N₂ with the amount of Ar being higher, a third deposition also contained both gases this time with higher N₂ concentration, and finally a growth employed solely N₂ as the sputtering gas. The thickness of the GaN layers was varied [8].

RF magnetron sputtering was utilized by Wang *et al.* to deposit onto p⁺-(111) Si substrates. The silicon was cleaned with a 10:1 HF solution, with the intent of eliminating any oxides, blow dried, then placed within the machine. The sputtered growth occurred in two stages with common parameters being input power of 50 W, a N₂/Ar mixture composing the gas, and a pressure of 5 mTorr. A GaN nucleation layer was grown at 400 °C to a thickness of around 50 nm. This buffer layer was annealed for 30 min. in nitrogen gas at 500 °C. The sputtering of the main GaN film was performed at 700 °C and it was grown to a thickness of 350 nm. Rapid thermal annealing (RTA) was employed when deposition was finished in a 0.5 Torr nitrogen atmosphere for one minute at 900 °C. After the annealing, some of the samples were irradiated with gamma rays from cobalt with a dosing rate of 100 rad/s, but for different total dosage amounts ranging from 1 to 12 Mrad, to observe which and how properties were affected in the GaN layers when exposed to radiation [16].

Devaraju *et al.* also used a RF magnetron sputter system to grow on p-type (100) Si substrates. The deposition was implemented with the conditions of 13.6 MHz frequency, 4 mTorr total pressure, 2:3 ratio of N₂/Ar sputter gas mixture, and no substrate heating (room temperature). Separate depositions were performed at RF input powers of 20, 30, and 40 W.

The GaN layer thickness was kept close to 300 nm and because of the changing power the deposition duration was varied as well [10].

Another sputtering procedure involving a RF magnetron unit was employed by Maruyama *et al.* with a gallium nitride powder target to deposit on mainly borosilicate glass plates, but for characterization of the binding energy and composition of the GaN layer single crystal (100) Si was used as a substrate. The deposition parameters were a frequency of 13.5 MHz, pressure range from 0.59 to 200 mTorr, RF power varied from 50 to 300 W, target to substrate distance of 48 mm, and either solely Ar or N₂ as the sputtering gas with a flow rate within the range 5-358 sccm. The substrate temperature was either 90 °C, which was labeled as unheated, 200, or 300 °C during sputtered growth [14].

Hornig *et al.* deposited onto sapphire substrates with a RF magnetron sputter machine utilizing a sintered GaN target. The sapphire was heated at 150 °C with the pressure in the chamber under 0.5 μTorr for one hour before sputtering commenced. The deposition conditions were 4.2 W/cm² input power, 500°C substrate heating, total pressure of one mTorr, and the sputtering gas being a mixture of argon and nitrogen with the amount of argon ranging from all to none of the gas, in steps of 20%, while the total gas flow rate was kept to 100 sccm. The GaN layers had a thickness of around 200 nm [11].

XRD analysis was also commonly implemented by these research groups to characterize the crystal quality and orientations of their sputtered GaN films. Huq *et al.* found when using 40 W input power and 10 mTorr during deposition that having the nitrogen gas be 60% or higher of the total sputtering gas results in the best crystal quality. Below 60%, the GaN layers were reported to become amorphous. They claimed the high amount of Ar ions hitting the GaN layers in such cases resulted in the films being re-sputtered. Another XRD measurement of films grown at 40 W, 5 mTorr, and 700 °C on (111) silicon and sapphire

substrates showed polycrystalline wurtzite GaN with multiple orientations for both sputtered layers. The silicon sample contained visible peaks for the (100), (002), (101), and (110) orientations while the GaN on the sapphire exhibited the (100), (002), and (103) planes. The c-plane peak had the highest intensity on both substrates proving to be the preferred growth direction [8].

Wang *et al.* presented the effects of gamma ray irradiation on sputtered GaN layers. An XRD test on a nonirradiated sample showed peaks at the (10-10), (0002), (10-11), and (11-20) orientations with the (10-10) wurtzite plane having the highest intensity by far. XRD analysis of GaN layers dosed with 1, 4, 8, and 12 Mrad observed the (10-10) direction peak lowering in intensity as the radiation increased. Clearly the GaN crystal quality degrades with exposure to higher levels of radiation. The authors also reported room temperature Hall-effect measurements of all the deposited films, both irradiated and nonirradiated, showed them to be n-type which is normal for undoped GaN [16].

Grazing incidence XRD (GIXRD) was utilized by Devaraju *et al.* to characterize GaN layers sputtered at 20, 30, and 40 W and the results were checked against the JCPDS. The films were found to be of the wurtzite structure and polycrystalline with multiple orientations present in the GIXRD data. The layer deposited with 20 W RF power contained the gallium nitride planes (1010), (1011), and (1120) along with a peak the authors believed could be from gallium oxide. Both the 30 and 40 W sputtered films showed the (1010), (0002), (1011), and (1120) directions. The (1011) orientation showed the highest intensity when sputtering at 20 W, but the peak lowered in size as the RF power was increased. Conversely, the c-plane orientation became more prominent the higher the input power utilized, going from being unobserved for the film sputtered at 20 W to the peak with the largest intensity for the layer deposited at 40 W. The degree of c-axis orientation (DCO),

which estimates the percentage among all discovered GaN plane peaks belonging to the c-direction, was calculated separately for both the films grown at 30 and 40 W utilizing the intensities of all the reported GaN directions in each film's own GIXRD analysis. The percentages were calculated to be 53 and 65%, respectively. This agrees with the visual graph from the GIXRD data that as the RF power increases the c-plane progressively becomes the preferred orientation. Devaraju *et al.* also calculated the approximate average diameter of the c-plane oriented crystals located in the sputtered layers with Scherer's formula. The 20, 30, and 40 W input powers were computed to have lengths of 20, 18, and 11 nm, respectively. They reported that the crystal diameters for all the films were close to GaN's Bohr exciton radius of 11 nm [10]. If this is accurate, their crystallites are on the verge of becoming quantum dots and shows that sputtering could potentially be used to create GaN quantum dots. The authors also observed the FWHM of the c-plane peak to broaden with higher powers. The lengths of the a-axis and c-axis of the crystal lattice for the films deposited at the three RF powers were also measured and determined to decrease as the power increased. The authors suggested the decrease in the size of the lattice parameters is due to increasing compressive stress, but noted as well that at smaller RF powers tensile stress is found in the deposited layers [10].

XRD was performed by Maruyama *et al.* on GaN films sputtered with 2.3 mTorr, 50 W RF power, 90 °C substrate heating (labeled unheated), and either solely nitrogen or argon gas. The sample grown with N₂ presented polycrystalline reflections at the wurtzite (002) and (103) GaN planes with the c-plane having a much larger intensity. The layer deposited with Ar gas contained a very broad peak for the (002) direction indicating weak crystal quality. The authors concluded that these measurements demonstrated that the gas used during sputter deposition affects the crystallinity with the use of nitrogen being more

favorable. Another XRD test shown by them of a layer grown with 50 W power, 20 mTorr, deposition temperature of 300 °C, and N₂ gas also displayed the GaN (002) and (103) directions. Maruyama *et al.* implemented a battery of XRD analyses on sputtered GaN layers with the conditions of 50 W, pure N₂ gas, pressure range from 0.59 to 40 mTorr, and substrate heating of 90, 200, or 300 °C. They claimed all the deposited layers were polycrystalline with the best crystal quality occurring at the pressures of 20 and 30 mTorr and the poorest GaN being at 35 mTorr or above. The results also showed mixed effects for substrate heating on bettering the crystallinity when all other parameters are kept the same and only the temperature is increased. The authors went on to claim that decreases in crystallinity could be associated with smaller grain sizes which they stated could be observed when analyzing the FWHM of the c-plane with the integrated intensity. They also reported that their GaN layers were transparent, light yellow, and very electrically resistive [14].

Other properties of the deposited GaN films were observed with a variety of characterization methods. Horng *et al.* measured the band gap energy, refractive index, and Ga/N ratio of their sputtered layers and compared them against the theoretical values of 3.4 eV, 2.67, and 1, respectively. The GaN films being investigated were sputtered with varying amounts of nitrogen and argon in the gas mixture, specifically 0, 20, 40, 60, 80, and 100% of the gas being N₂ with the remainder, if any, comprised of Ar. The authors presented that the band gap and refractive index have an increasing trend ranging from 2.43-2.87 eV and 2.3-2.5, respectively, for 20 to 100% of N₂ contained within the gas. The amount of gallium was usually higher than the nitrogen, but the Ga/N ratio improved with higher amounts of nitrogen in the deposition gas and saw the best value of 0.95 at 60% N₂ which was the only sample that contained more nitrogen than gallium. The deposited films using 80 and 100% N₂ also had ratios closer to one than the 20% and 40% layers. When sputtering occurred

without any nitrogen (only argon gas), the films observed metallic features with the Ga/N ratio being 4.97 and the band gap and refractive index were unable to be measured. These findings lend additional support to conclusions in other papers that some amount of N₂ should be utilized while sputtering to improve crystallinity. Horng *et al.* attribute the general inability of nitrogen to incorporate in the films during deposition to thermal decomposition at high temperatures and the lack of chemical absorption of nitrogen on gallium. They also report that the samples using 60% of N₂ or above were extremely resistive or insulating. The other GaN layers were n-type and conductive due to higher amounts of nitrogen vacancies [11].

Black layers were described by Huq *et al.* when depositing with only Ar gas at 40 or 50 W and 4 or 5 mTorr with N/Ga ratios around 0.16. They also believed these properties to be connected to nitrogen vacancies and large amounts of gallium. As mentioned earlier, the authors had found usage of 60% or more of N₂ in the sputtering gas led to improved crystal quality and reduced re-sputtering, but in addition to those benefits the nitrogen incorporation is increased for both sapphire and silicon substrates and the extent of target poisoning is diminished. Target poisoning if left untreated, they reported, reduces the stoichiometry of the sputtered GaN. Another method of counteracting the target poisoning is to increase the total deposition pressure to within the 20 to 30 mTorr range, but the tradeoff is lower nitrogen incorporation in the sputtered films. They claimed the amount of nitrogen could be raised and the target poisoning kept low by decreasing the input power to around 15 W, but the growth rate dropped as did the crystallinity to the point of being amorphous. SEM of samples deposited with 40% N₂ for one hour showed grain sizes around 15 nm, but when viewed for a growth duration increased to 2 hours the grains were not as established. The atomic percentage of oxygen in the GaN layers was found to be higher than the percentages

of both gallium and nitrogen with unheated sputtering when using any amount of N₂ in the deposition gas and was believed to be originating from oxygen atoms pre-existing in the growth chamber. Huq *et al.* demonstrated that increasing the substrate temperature to 700 °C was effective in decreasing the oxygen concentration. In general, they recommended sputtering on sapphire or silicon with RF power around 40 W, larger total pressure around 15 mTorr with 60% or more N₂ in the gas, and substrate heating. In contrast to other papers, the authors claimed that glass is not a viable substrate [8].

PL spectra was examined by Wang *et al.* for GaN films with and without gamma ray irradiation. The sputtered layer not dosed with radiation consisted of a high intensity emission at 3.3 eV, which they claimed is an identifying mark of n-type GaN, a small peak at 2.8 eV, and a broad luminescence around 2.2 eV. The latter was designated the yellow band. The authors reported that as the radiation doses increased, the peak at 3.3 eV eroded while the deep level 2.8 eV emission became more intense. The yellow band luminescence also increased until the total amount of radiation hit 4 Mrad. Further increases of radiation above that value caused the yellow band intensity to decrease [16].

SEM implemented by Devaraju *et al.* displayed the surface of their GaN layers to be comprised of grains no matter the RF power utilized. They noted that as the input power increased, the grain dimensions became smaller. This effect was attributed to the release of compressive stress in the films created with deposition at higher powers [10]. TEM of GaN sputtered with 30 W showed grains 15 nm in size which corresponds with the proportions of the grains found by Huq *et al.* mentioned earlier [8] [10]. AFM of a sample deposited at 20 W presented particles with lengths of 25 nm. The observed 15 and 25 nm dimensions for the 30 and 20 W RF powers were close to their calculated values of 18 and 20 nm, respectively,

stated earlier. The authors also reported that changing the power did little to affect the coarseness of the GaN layer surfaces [10].

The α^2 Tauc plots drawn by Maruyama *et al.* showed that their polycrystalline GaN layers sputtered with pure nitrogen gas with a RF power range of 50-300 W, pressure of 2.3 mTorr, and temperature of 90 °C (unheated) all had direct band gaps in the range 3.38-3.4 eV which are close to the values of 3.39 and 3.2-3.4 eV of single crystal and polycrystalline GaN, respectively. The films also experienced N/Ga ratios in the range 0.97-1.28, refractive indices in the range 2.0-2.2, and a-axis and c-axis lattice parameters larger than the sputtered GaN powder target. N/Ga ratios close to one mirrored the results of other studies indicating that usage of N₂ gas enhances the amount of nitrogen in the sputtered GaN layers. The higher lattice constants could indicate tensile stress in the films. The authors noted as well that the refractive indices were within the range of previously published indices of 2.1-2.3 for polycrystalline GaN. When using pure Ar as the sputtering gas with the same conditions otherwise, they reported weak crystal quality for RF powers of 50 and 100 W, but the inability for GaN to form properly when utilizing 200 and 300 W [14]. Just as reported by Huq *et al.*, the authors noticed some of the deposited films were black from nitrogen vacancies when sputtering with only Ar gas [8] [14].

Maruyama *et al.* also described an effect known as the self-induced negative bias that affects the substrate during sputter deposition. When high enough, the effect will cause re-sputtering, especially of the nitrogen, thus damaging the deposited layer. The bias occurs when the input power is increased which leads to a rise in the floating potential level. Beyond lowering the RF power and employing N₂ gas, the effect could be reduced by increasing the deposition pressure. However, they found with pressures above 30 mTorr, when sputtering with N₂, the GaN became amorphous. This was attributed to the gallium

and nitrogen being unable to create proper crystals because they experience a lowered kinetic energy at larger deposition pressures. A balance must be found for the pressure where it is high enough to improve the self-induced negative bias, but low enough for better crystallinity. The authors recommend sputtering in the 20-30 mTorr range which is similar to the suggestion made by Huq *et al.* to deposit at a total pressure of around 15 mTorr [8] [14].

II. Literature Review: Gallium Nitride Tunnel Junctions

Tunnel Junctions (TJ) are p-n diodes requiring highly doped p-type material and n-type material to bend the band structure in such a way to allow an electron to tunnel through the depletion layer from the valence band of the p-side to the conduction band of the n-side [17]-[19]. Degenerately doping the p-n junction brings the valence and conduction bands of the p+ material and n+ material, respectively, extremely close to the Fermi level and decreases the width of the space charge region, with both results raising the probability of electron tunneling [17] [19] [20]. An electric field created by ionized acceptors and donors within the junction also aids the electron flow [17]-[19]. While these effects ideally occur without added voltage, reverse biasing the diode bends the bands further to improve tunneling [17] [20] [21]. If the TJ is grown above optoelectronic devices, the additional holes left within the p-side can progress into the quantum wells of LEDs and LDs as carriers to radiatively recombine [18]-[21].

Esaki was the first to construct a tunnel junction in 1958 by using highly doped p and n-type germanium to create the structure [17] [20]. TJs have been created using other III-V materials [21], such as InP and III-As [20], as well as SiGe [17]. Devices grown with the III-N material system can benefit from the addition of TJs to the epitaxial structure for two reasons: the previously mentioned hole generation and utilizing them as a p-contact [17]-[21]. As an example of the former, thick p-GaN is currently used within AlGaN UV devices for hole carriers, but by replacing it with a TJ, whose structure is thinner, not only will holes be created for emission, but the thinner material will increase extraction of the emitted light [19]. The resistivity of p-GaN necessitates a current spreading layer (CSL) between it and the metallic p-contact [17]-[21]. Transparent conducting oxides (TCO), for example indium

tin oxide (ITO), are employed as a solution to the problem [18] [20]. However, ITO absorbs some of the emissions in the UV and visible light regions [20]. Implementing a TJ created with GaN or a GaN alloy would allow n-GaN to be deposited as a CSL and as the p-contact. This would decrease light absorption in the epitaxial structure and keep the resistivity lower than when metal is applied on top of p-GaN [17]-[21]. The fabrication procedure of LEDs and LDs would also be simplified since a different material, such as ITO, would not be needed as a CSL and only the metallic contact to the n-GaN would be deposited to the top and bottom of the device [19]-[21].

Specific applications of the TJ beyond the general hole generation and p-contact include: potential replacement of the p-material in a bipolar transistor [19], facilitating the use of n-type mirrors instead of p-type in vertical-cavity surface-emitting lasers (VCSEL) [20], enabling LEDs with reversed polarization containing the p-GaN below the active region [19], a bridging layer between multi-junction solar cells [19] when the TJ is operated in forward bias [17] [20], and integration between LEDs in a multi-active region optoelectronic device [17] [19] [20]. The latter could ensure the growth and fabrication of a single device to create white light with the TJ being a contact layer between the red, green, and blue LEDs [19]. Two previously reported methods of designing a TJ with GaN are the standard degenerate doping of a p-n junction [20] [21] and a polarized tunnel junction created with the inclusion of a GaN alloy, for example InGaN, between the p-GaN and n-GaN of a highly doped p-n junction [17]-[19]. Procedures and characterizations of both types of tunnel junctions will be discussed.

The most straightforward technique of creating a tunnel junction is by following the same method reported by Esaki in bringing together highly doped p-material and highly doped n-material in a p-n homojunction [20]. Jeon *et al.* applied this technique to gallium

nitride using an MOCVD system and grew the TJ above an InGaN/GaN blue LED as a p-contact. The deposition procedure for the LED and TJ on a c-plane sapphire substrate was as follows: 25 nm GaN buffer layer grown at 550 °C, 3 μm n-GaN deposited at 1130 °C, 6 InGaN/GaN quantum wells with 2 nm/8 nm thicknesses grown at a temperature between 760 and 800 °C, 150 nm p-GaN, 10 nm p+-GaN for the TJ doped at $\sim 3 \times 10^{19} \text{ cm}^{-3}$, 10 nm n+-GaN with $\sim 6 \times 10^{19} \text{ cm}^{-3}$ doping along with $\sim 3 \times 10^{13} \text{ cm}^{-2}$ delta doping at the TJ interface, and 150 nm of n-GaN on top. All layers after the multi-quantum well (MQW) were deposited at 1130 °C. The p-GaN and n-GaN were doped with magnesium and silicon, respectively. The authors reported that with the delta doping, the n-side of the TJ had a concentration of $\sim 10^{20} \text{ cm}^{-3}$. Inductively coupled plasma (ICP) was employed to etch part of the structure down to the bottom n-GaN layer for the n-contact. Ti/Al was then deposited as a metal contact on both the p-contact n-GaN above the TJ and the n-contact n-GaN. The dimensions of the TJ LED were $350 \times 350 \text{ μm}^2$. Jeon *et al.* also fabricated standard LEDs without TJs for comparison. The structure of the standard LEDs was the same except for the lack of TJ and n-GaN on top. The p-contact metal pad for these LEDs was Ni/Au with some of them having a Ni/Au layer between the pad and the p-GaN [21].

At 20 mA, the voltage and dynamic resistance of the TJ LED and standard LED with a Ni/Au layer were found to be 4.9 V and 45 Ω and 3.9 V and 33 Ω, respectively. The authors report this to show the tunnel junction having a series resistance. The light output power at 20 mA was around 4.5 and 2 for the TJ and standard devices, respectively. They attribute the increased light to the absence of absorption in the TJ compared to the Ni/Au layer along with no current crowding due to the lower resistivity of the n-GaN compared to the p-GaN. Both the voltage and power of the TJ LED remain greater than the standard device up to the maximum reported current of 100 mA. Electroluminescence (EL) spectroscopy performed at

room temperature demonstrated a peak wavelength of 455 nm and FWHM of 20 nm that remained close to these values as the current was raised from 20 to 100 mA, a trait of high quality material as described by the authors [21].

Jeon *et al.* also compared the current spreading of the TJ LED with that of the standard LED without a Ni/Au layer for input currents of 5 to 100 mA. The standard LED showed current crowding and light emission around the p-contact metal, which would result in blocked light, while the TJ LED spread the current and radiated blue light across the whole n-GaN layer. Slight current crowding around the metal on the top n-GaN was observed at 100 mA for the TJ LED which the authors believed would be improved with higher doping of the n-GaN layer. These observations were claimed to be proof of increased light extraction efficiency when utilizing tunnel junctions as p-contacts for GaN LEDs [21].

Although Jeon *et al.* used an MOCVD system to create the TJ LED structure, without annealing MOCVD p-GaN could remain passivated due to the magnesium within the p-GaN bonding with hydrogen. Annealing after depositing n-GaN above the p-GaN is difficult due to the hydrogen experiencing a large diffusion barrier in the n-GaN. Sidewall activation of p-GaN has been attempted, but proved to be inefficient. Thus, many research groups grow GaN TJs with MBE which presents a challenge to commercializing GaN TJ optoelectronic devices because epitaxy with MOCVD machines is the standard [20].

Young *et al.* sought to overcome this problem by growing the blue LED structure and lower p+-GaN part of the TJ with MOCVD while the n+-GaN and top n-GaN layers were deposited with NH₃ MBE. Two advantages of NH₃ MBE given by the authors is its ability to integrate high amounts of silicon to create n+-GaN layers and the lower amount of hydrogen necessary to grow GaN compared to MOCVD. The decreased hydrogen produces activated p-GaN without the need to anneal which then allows for structures with n-GaN on top [20].

N+-GaN layers were tested using Hall measurements of mobility and resistivity against carrier concentration to find the optimal doping for the TJ. The epilayers were deposited with ammonia MBE at 750 °C on c-plane semi-insulating GaN with sapphire substrates. The thickness of the n+-GaN layers varied from 250 to 500 nm. Although the data to be reported was for the above structure, the authors stated that the same layers grown on semipolar (20-21) freestanding GaN with an unintentionally doped (UID) GaN nucleation layer displayed the same findings. The general trend was for the mobility and resistivity to decrease as the carrier concentration increased. At approximately $1 \times 10^{20} \text{ cm}^{-3}$, the resistivity was in the 4×10^{-4} to $8 \times 10^{-4} \text{ } \Omega \text{ cm}$ range and the mobility was between ~ 60 and $\sim 125 \text{ cm}^2/\text{V}\cdot\text{s}$. Lower growth rates for samples doped around that carrier concentration were found to be associated with higher mobilities. At the carrier density $1.5 \times 10^{20} \text{ cm}^{-3}$, the resistivity and transmissivity of the n+-GaN was observed to increase and decrease, respectively. This information caused Young *et al.* to believe the best carrier concentration for the n-side of their TJs to be $1 \times 10^{20} \text{ cm}^{-3}$. All n+-GaN for TJs grown after this conclusion were doped to around that level [20].

Tunnel junctions were then grown above p-n diodes, under varying conditions, and tested for their current density-voltage relationship. These devices had a 25 μm radius and were deposited on freestanding semipolar GaN substrates. The growth and fabrication process started with 100 nm of n-GaN followed by 100 nm of p-GaN grown with MOCVD to create the p-n diode. Above that a layer of p+-GaN was also deposited with MOCVD for the bottom of the TJ. The sample would then be taken out of the MOCVD system, solvent cleaned, and placed into the MBE machine. The p-GaN would be activated as the system ramped for 15 minutes to the growth temperature of 750 °C. Once the temperature was reached, 20 nm of n+-GaN and 100 nm of n-GaN were deposited. The carrier concentration

of the n-GaN was $1 \times 10^{19} \text{ cm}^{-3}$. Lithography was utilized to shape the devices with Ti/Au being used as the metal contacts [20].

The ammonia flow rate in the MBE was changed from 100 to 500 sccm for different samples with the conclusion that as the flow rate decreased the turn-on voltage of the device also decreased. Another parameter variation was the usage of annealing with NH_3 in the MBE once the growth temperature was reached after the ramp, but before deposition of the TJ's n+-GaN. Young *et al.* noted that previous reports had such an anneal lowering the oxygen and carbon impurities on the GaN surface. However, they found that any NH_3 annealing at $750 \text{ }^\circ\text{C}$ increased the turn-on voltage of the diodes. The authors reported devices created without any ammonia annealing and with a low ammonia flow rate to have a voltage of 3.05 V at 20 A/cm^2 and a differential resistivity of $1.5 \times 10^{-4} \text{ } \Omega \text{ cm}^2$ including the metal contacts. The diodes were able to perform at 10 kA/cm^2 presenting the possibility that the tunnel junctions could handle current densities seen by lasers [20].

Similarly created TJ diodes containing the procedural and structural changes to 80 nm with a carrier concentration of $8 \times 10^{19} \text{ cm}^{-3}$ for the p-GaN, 5 nm of $2 \times 10^{20} \text{ cm}^{-3}$ p+-GaN, and 15 minutes of NH_3 annealing were measured with atom probe tomography (APT). The intention was to observe the changes in the densities of magnesium and oxygen throughout the deposited layers. The amount of oxygen was calculated to be between 5×10^{13} to $1 \times 10^{14} \text{ cm}^{-3}$ at the interface between the p-side and n-side of the TJ. The profiles of the oxygen and magnesium were closely overlapped at that interface which was reported by the authors to indicate the likelihood of bonding between the two atoms and a block for Mg impurities in the n+-GaN. They state that this block and the donor electrons from oxygen delta doping the n+ layer could increase the tunneling probability. Modelling of the band bending in the TJ performed by them for the same doping concentrations of 1×10^{20} and $2 \times 10^{20} \text{ cm}^{-3}$ of the n-

side and p-side, respectively, with and without $1 \times 10^{14} \text{ cm}^{-2}$ delta doping showed the delta doped bands shrinking the space charge region and thus the tunneling distance. This confirmed the potential increase to tunneling probability. The probability was concluded to be improved further with reverse biasing when an applied bias of -0.5 V to the delta doped model presented the tunneling distance narrowing from 5.5 to 3.2 nm. These measurements along with the observation of better turn-on voltage without NH_3 annealing could mean that oxygen impurities within the TJ are beneficial [20].

Moving to tunnel junctions grown on LEDs, the authors reported that EL data comparing such devices to LEDs without a TJ showed that the wavelength of the emitted light was unchanged between the two. However, an analysis of the I-V curves showed the TJ LED turn-on voltage to be approximately 1 V higher [20]. Both these traits were also noticed by Jeon *et al.* in their TJ LEDs [21].

Young *et al.* performed a comparison between a TJ LED, created with the hybrid MBE and MOCVD method, and a LED with ITO as the CSL as well. The bottom to top structure for the TJ LED was: freestanding (20-2-1) GaN substrate, n-GaN, a 12 nm InGaN single quantum well, 100 nm p-GaN, 10 nm p+-GaN, 20 nm n+-GaN, and 400 nm n-GaN doped at $1 \times 10^{19} \text{ cm}^{-3}$. The metal contacts to both the top and bottom n-GaN layers were Ti/Al/Ni/Au. The device with ITO had the same design except the top n-GaN was replaced with ITO and its metal contact was Cr/Ni/Au. The wavelength and size of both devices were 455 nm and 0.1 mm^2 , respectively [20].

The sheet resistance of both the top n-GaN layer and the ITO for the two LEDs was $50 \text{ } \Omega/\text{square}$. The external quantum efficiency (EQE) of the TJ LED was discovered to be higher up to the largest measured current density of 40 A/cm^2 . The peak value for the EQE was close to 40% [20]. Similar to the 4.9 V measured by Jeon *et al.*, Young *et al.* found the

voltage of the TJ optoelectronic device to be 5.2 V at 20 mA [20] [21]. However, the TJ LED was reported to be more efficient than the ITO device with the latter having a voltage of 5.87 V at 20 mA. The authors claimed the voltages could be lowered further with improvement of the n-contacts [20].

Polarized III-nitride tunnel junctions are a type of TJ that seek to take advantage of the electric fields created by piezoelectric and spontaneous polarization of charges at heterostructure interfaces grown along the c-axis. They can also benefit from reduced energy barriers to electrons from lower bandgap materials deposited within the TJ [17]-[19]. While a standard homojunction GaN TJ has an induced electric field from polarization of ionized doping atoms, the addition of a GaN alloy such as InGaN between the n⁺-GaN and p⁺-GaN layers of the TJ can increase the magnitude of the electric field felt by an electron. This additional electric field comes from the InGaN being strained from growth between the two GaN layers. The larger field magnitude would lead to improved band bending and thus increase the tunneling probability for an electron [17] [18]. InGaN also has a smaller bandgap than gallium nitride which would lower the energy barrier [17]-[19] and therefore decrease the tunneling resistance promoting further augmentation of electron tunneling [17] [19] especially if the polarized TJ has the same thickness as the standard TJ [17]. The heterostructure of the polarized TJ can help bypass the fact that homojunction TJs are constrained by limits on the number of doping atoms that can be incorporated [17] [19]. In addition, polarized tunnel junctions could potentially reduce the voltage drop necessary for the TJ structure thus lowering the turn-on voltage for a TJ optoelectronic device [17]-[19]. Procedures and characterizations of polarized InGaN tunnel junctions along with comparisons to standard TJs from various research groups will be presented.

Krishnamoorthy *et al.* reported that for a p+-GaN/InGaN/n+-GaN structure there are three zones for an electron to tunnel through to reach the n+-GaN's conduction band from the p+-GaN's valence band. These three regions are the two GaN/InGaN interfaces and the InGaN layer itself. The authors claim with high doping of the n- and p-GaN the InGaN presents the largest barrier and focus on finding the specific thickness needed for the InGaN layer to maximize the tunneling probability. This specific thickness, which Krishnamoorthy *et al.* term the "critical thickness," occurs when the potential barrier, without any added bias, is the same as the InGaN bandgap. InGaN grown thicker and thinner than this critical thickness would both decrease the tunneling probability due to the increased layer thickness and misalignment of the n+-GaN conduction band with the p+-GaN valence band, respectively. The authors also note that as the InN mole fraction incorporated into the InGaN increases the critical thickness will decrease because of the bandgap getting closer to the pure InGaN bandgap and the higher polarization. Two benchmarks for the necessary thickness are: ~10 nm at ~15% InN mole fraction and ~1 nm at ~70% InN. While increasing the amount of indium in the layer should lead to a higher tunneling probability through the InGaN layer, they report that for critical thicknesses of layers grown with high amounts of indium the tunneling probabilities through the GaN/InGaN regions could have a higher effect on the overall tunneling probability [17].

The authors grew a 30x30 μm^2 InGaN polarized TJ to test with bottom to top structure of freestanding N-polar GaN substrate, 100 nm n-GaN with a carrier concentration of $5 \times 10^{18} \text{ cm}^{-3}$, 6.4 nm N-polar InGaN with 33.5% indium, and 100 nm p-GaN with a doping level of $1 \times 10^{19} \text{ cm}^{-3}$. The growth temperature for the InGaN was 600 °C and N-polarity was chosen instead of Ga-polarity because larger amounts of indium could be integrated into the layer during deposition. The epitaxy was performed by a plasma assisted molecular beam epitaxy

(PAMBE) system. 20/100 nm Ti/Au and 20/150 nm Ni/Au metal contacts were grown on the n-GaN and p-GaN, respectively, with lithography. A standard TJ with the same structure and deposition parameters was created for comparison [17].

Their analysis of the current density as a function of applied voltage showed the polarized TJ having a lower turn-on voltage and resistance for both the forward and reverse bias regimes. The current of the polarized TJ climbed much faster when in reverse bias, especially between 0 and -1 V, reaching 118 A/cm² at -1 V. For the same voltage, the standard TJ had a current density of approximately 1 mA/cm². However, after -1 V the resistance of the polarized device became larger and caused the current density to slow its increase. Despite the increased resistance, the current density at around -10 V was measured to be 9.2 kA/cm². The authors stated the higher resistance could come from a combination of internal heating in the device and additional contact and series resistances. They also suggested some optimizations for the polarized TJ could be increasing the indium incorporated, perfecting the InGaN layer thickness, grading the GaN/InGaN interfaces, utilizing quaternary compounds, and creating asymmetric junctions [17].

In a study a few years later, Krishnamoorthy *et al.* not only restated and confirmed the three zones an electron passes through when tunneling as well as the reported steps to be taken to improve the tunneling probability in the InGaN layer, but also focused on calculating the probability for an electron to tunnel through the GaN/InGaN interfaces and the overall tunneling probability. The overall tunneling is found by multiplying the probabilities through the three zones. They note that while increasing the indium in the InGaN layer improves the tunneling through that region, it increases the conduction and valence band discontinuities which leads to a decrease in tunneling probability through the interfaces. The p⁺-GaN/InGaN and n⁺-GaN/InGaN interfaces are affected by the valence

and conduction band discontinuities, respectively. Since the probabilities change with the amount of doping in the n+-GaN and p+-GaN, the carrier concentrations were set to 5×10^{19} and $1 \times 10^{19} \text{ cm}^{-3}$, respectively. Other assumptions were the band diagram would not vary and that no reverse bias would be necessary for tunneling. The authors found that the largest tunneling probability as a function of InN mole fraction was $\sim 10^{-13}$ at $\sim 30\%$ InN. The critical thickness of the InGaN for this amount of indium would be around 4 nm. However, if the doping of the n- and p-GaN was increased, especially for the n-GaN since the conduction band discontinuity is larger, more indium could be incorporated and thus the probability could be raised [19].

This time Krishnamoorthy *et al.* created a $50 \times 50 \text{ }\mu\text{m}^2$ device to test the polarized TJ when connected to a p-n diode. The TJ was buried underneath the diode which had its p-side facing down and the n-side exposed. The bottom to top layers were a freestanding N-polarity GaN substrate, 50 nm $1 \times 10^{19} \text{ cm}^{-3}$ doped n-GaN, 10 nm $5 \times 10^{19} \text{ cm}^{-3}$ n-GaN, 4 nm InGaN with 25% indium, 20 nm $1 \times 10^{19} \text{ cm}^{-3}$ p-GaN, 70 nm $3 \times 10^{18} \text{ cm}^{-3}$ p-GaN, and 50 nm $3 \times 10^{18} \text{ cm}^{-3}$ n-GaN. The deposition of the device was performed with nitrogen PAMBE with 20/200 nm Ti/Au metal contacts evaporated onto the top and bottom n-GaN layers afterwards [19].

Current density versus voltage measurements showed the turn-on voltage to be approximately 3 V. A current density of 100 A/cm^2 at 3.05 V was reported with the voltage consumed by the TJ itself to be 12 mV at that point. The total resistivity of the TJ diode while operating in the forward bias regime was discovered to be $4.7 \times 10^{-4} \text{ }\Omega \text{ cm}^2$ and the resistivity of just the TJ was calculated to be around $1.2 \times 10^{-4} \text{ }\Omega \text{ cm}^2$. The authors described this tunneling resistivity to be very low for GaN and as proof of the industrial viability of polarized TJs since resistivity increases exponentially with respect to material bandgaps. While the expected value would be close to the 10^{-1} range, the observed resistivity would put

the polarized GaN TJ at around a level previously reported for tunnel junctions in the indium phosphide system. However, they do acknowledge that incorporating the TJs into the standard MOCVD procedure could be difficult despite their advantages. The InGaN layer could also present a problem by absorbing some of the light emitted by the optoelectronics. The absorption could be improved by lowering the incorporated indium or the thickness of the InGaN, but a compromise may need to be found because, as stated earlier, the critical thickness of the layer decreases with additional indium [19].

Zhang *et al.* also attempted to model the tunneling probability and noted that beyond lowering the bandgap, increasing the electric field would raise the tunneling current as well. They stated that this is achieved in polarized TJs because they have three factors contributing to increase the magnitude of the electric field: ionized doping atoms in the p+-GaN and n+-GaN, outside applied voltages to the TJ, and the piezoelectric and spontaneous polarizations from the strained InGaN. Standard TJs would not have the latter aspect and thus have a smaller electric field. Testing and comparisons were performed on an LED without a tunnel junction, a standard TJ LED, and a polarized TJ LED, all of which were 350x350 μm^2 devices [18]. Unlike Krishnamoorthy *et al.*, Zhang *et al.* implemented an MOCVD system for their epitaxy [17]-[19].

The bottom to top layers for the polarized TJ LED were: c-plane sapphire substrate, 30 nm GaN buffer layer, 4 μm undoped GaN, 2 μm n-GaN doped to $5 \times 10^{18} \text{ cm}^{-3}$, five 3/12 nm InGaN/GaN quantum wells with the InGaN having an indium concentration of 15%, a 25 nm electron blocking layer (EBL) made of $\text{Al}_{0.15}\text{Ga}_{0.85}\text{N}$ doped with magnesium, 200 nm $3 \times 10^{17} \text{ cm}^{-3}$ p-GaN, 30 nm $3 \times 10^{19} \text{ cm}^{-3}$ p+-GaN, 3 nm InGaN again with 15% indium, and 30 nm $1 \times 10^{20} \text{ cm}^{-3}$ n+-GaN. The TJ-less LED did not include the top two layers of n+-GaN and InGaN while the regular TJ LED only lacked the InGaN in between the p+ and n+-GaN.

Outside of the MOCVD machine, 200 nm of ITO followed by 30/150 nm of Ti/Au were deposited on all devices. The LEDs with TJs were etched to expose the lower n-GaN layer and the same amount of Ti/Au was evaporated on it as a metal contact [18].

Current versus applied voltage measurements were implemented for all three devices using both modeling on a computer and testing of the fabricated devices. The model showed a turn-on voltage of just under 4 V for all three devices while the experimental values were approximately 3.5, 4, and 4.5 V for the TJ-less, polarized TJ, and standard TJ LED, respectively. Both the model and the experimental analyses presented the resistance, while operating in forward bias, to be smallest in the in TJ-less LED and largest for the standard TJ LED [18].

The authors explained the higher turn-on voltage for the polarized TJ device compared to the regular TJ-less LED to be due to the challenge of depositing the InGaN on the p-GaN and the possibility of dislocations being created during growth to reduce the strain on the crystal. The lower strain would lead to a decrease in the polarization charge density and lower the magnitude of the electric field. Although the computer model of the polarized TJ device was created with the polarization charge being 40% of the total theoretical value, the experimental value could be even lower. The electric fields were also modeled for a 4.5 V input applied to the normal TJ and polarized TJ LEDs and found that the peak magnitudes were around 6×10^6 V/cm and 7.5×10^6 V/cm, respectively, confirming the authors' proposal that the polarized TJ would have a larger electric field. The lower turn-on voltage required for the polarized TJ device was attributed to this increase in electric field magnitude [18].

Zhang *et al.* went on to report the EL intensity, optical output power, hole concentration in the quantum wells, and EQE of all three devices. The LED without a tunnel junction presented the lowest value for all these measurements and the polarized TJ LED displayed

the largest. The quantity of holes in the first quantum well was around 3×10^{17} , 5×10^{17} , and $5.6 \times 10^{17} \text{ cm}^{-3}$ for the TJ-less, standard TJ, and polarized TJ LED, respectively, demonstrating the improved hole injection of tunnel junctions. The peak EQE of the devices, in the same order, was observed to be approximately 16%, 18%, and 19%. The improvements of the TJ devices over the regular LED were credited to better current spreading. In addition to this trait, higher tunneling probability from the larger electric field was explained to be the reason for the superior optical and electrical characteristics in the polarized TJ LED compared to the standard tunnel junction device [18].

III. Results and Discussion

The work for this thesis explored sputtered deposition of silicon doped gallium nitride to create a tunnel junction as a p-contact for GaN LEDs. GaN TJs have the potential to replace ITO as a CSL due to less absorbance in the UV and visible light spectrum and could allow for a higher light extraction efficiency [20]. Additionally, the fabrication of the LEDs would be simplified because n-GaN would be the outside layer of both the p- and n-contact of the device [19]-[21]. Since the metal contact for the top and bottom of the LED would be the same, the deposition of the metal stacks required could occur at the same time. The growth of the top n-GaN layer for the tunnel junction with a sputtering system instead of either MOCVD or MBE machines would allow for an inexpensive [7] [10] and more convenient [8] [12] [13] method of creating the p-contacts and thereby pave the way for commercialization. Two types of sputter machines were investigated for GaN deposition: ECR and RF magnetron. Silicon doped polycrystalline n-GaN targets were utilized for both systems. After analysis of the films grown by both machines, RF magnetron sputtering was employed to deposit the n-GaN layer on a MOCVD grown LED wafer for the tunnel junction. TJ LEDs were then fabricated from this structure. The deposited n-GaN films of the two sputtering methods and the testing of the TJ LEDs are discussed in separate sections.

A. Electron Cyclotron Resonance Sputtered Gallium Nitride

The sputter growth of GaN films was performed by a JSW AFTY AFTEX-6200 ECR Plasma Deposition System with the target being silicon doped polycrystalline GaN, as previously mentioned. The parameters that remained constant for all depositions with their values were: pressure of 0.1 Pa (~0.75 mTorr), argon rate 20 sccm, RF power 300 W, and microwave power of 300 W. A mixture of argon and molecular nitrogen gas was utilized for

the sputtering, but the rate of the N_2 was varied within the range 0 to 20 sccm for separate growths. The substrate temperature was also changed, but was either 20 or 250 °C. Three substrates were loaded into the sputter chamber for each deposition. These substrates were: double side polished (DSP) sapphire, silicon, and MOCVD grown c-plane UID GaN on sapphire. Once the GaN film was sputtered onto the substrates, each was used for different measurements. The sample with the silicon substrate was tested for the GaN layer thickness, the DSP sapphire for the transmissivity of light through the deposited film, and the GaN grown on the GaN on sapphire substrate was measured for the layer's resistance. Prior to being placed in the machine, every substrate was cleaned with acetone, isopropyl alcohol, rinsed with deionized (DI) water, and dried with N_2 gas. The GaN on sapphire substrates were additionally cleaned with a piranha solution heated to 130 °C for 20 minutes, washed with DI water, and dried with N_2 .

The deposited GaN layer thickness was attempted to be kept around 100 nm, but the growth rate varied with changes to the amount of N_2 in the sputtering gas mixture as well as substrate heating. Figure 1 shows the relationship between the GaN growth rate as a function of the amount of nitrogen gas used during the deposition for samples sputtered at the unheated temperature of 20 °C. Aside from a few bumps, the trend was the growth rate decreasing as the nitrogen increased. Figure 2 presents a comparison of the growth rates of the unheated sputtered films and those grown at 250 °C with respect to the rate of nitrogen. When no nitrogen was included in the gas and at 5 sccm nitrogen, the growth rate remained the same and slightly above that of the unheated layers, respectively. Otherwise, the growth rate for heated GaN layers was always lower than those deposited at 20 °C. Again, the heated substrate samples displayed a lowering of the growth rate as the nitrogen increased.

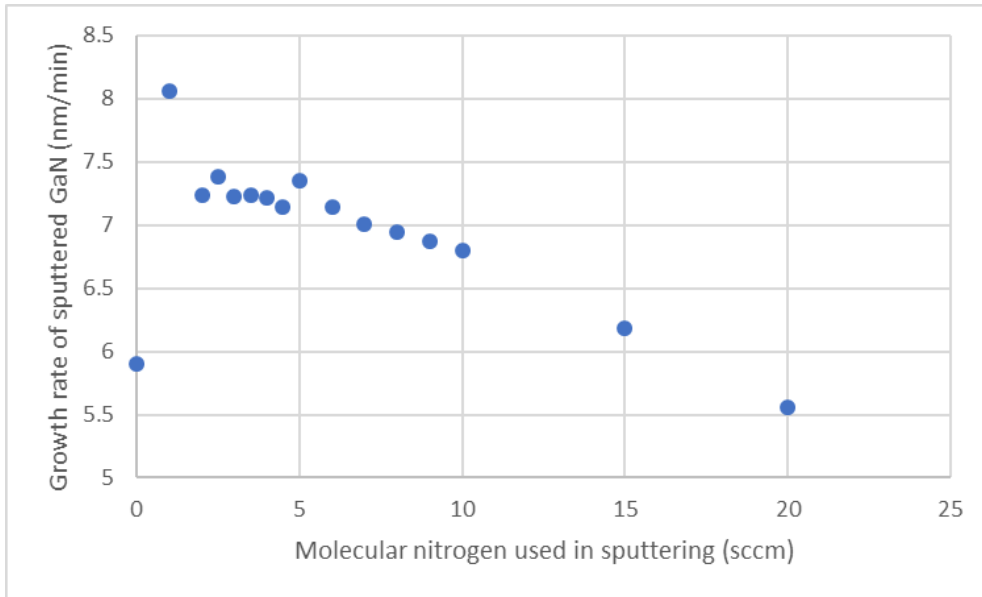


Figure 1. The growth rate of ECR GaN films sputtered at 20 °C vs. amount of nitrogen in the gas.

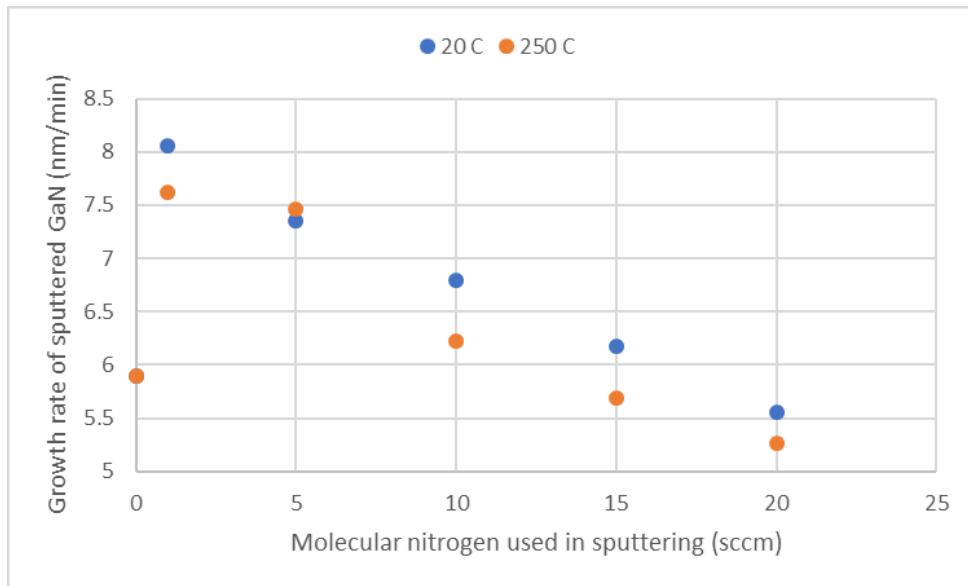


Figure 2. Growth rate comparison between unheated (blue) and heated (orange) films.

A Varian Cary 500 UV-Vis Spectrophotometer was utilized to determine the transmissivity of the sputtered GaN films. The layers grown on the DSP sapphire substrates were used for this test. A measurement without any materials was always implemented first to calibrate the amount of light being output by the source. While the transmittance analysis

was performed for wavelengths ranging from 200 to 800 nm, because the end goal was to deposit the GaN on a blue LED structure the specific wavelength of interest was 440 nm. Figure 3 shows the relationship between the amount of nitrogen used during the sputtering and the percentage of light transmitted at 440 nm by the deposited GaN layer. Above 2.5 sccm of N₂ the transparency of the GaN was high with 77% to 80% of the emitted light passing through the samples. The largest percentages of just under 80% occurred when the N₂ was between 4 and 10 sccm. As a reference, DSP sapphire without any deposited films on it transmits around 85% of 440 nm light. This means only around 5 to 8% of that wavelength is lost within the sputtered GaN. The lower transmissivity of the films deposited with 2 sccm N₂ and below could be due to the lack of nitrogen to bond with in order to form a transparent layer. This is especially reflected in the 29.5% of transmitted light when only argon gas was employed during the process suggesting that some amount of nitrogen must be used during the deposition to create a proper GaN layer.

Figure 4 presents a comparison between the transmittance of the GaN layers grown with substrates at room temperature and those sputtered with substrates at 250 °C. The heated samples displayed high transmissivity at 1 sccm of nitrogen and above with the greatest transparency occurring at 5 and 10 sccm similar to the unheated GaN films. However, other than when 1 sccm of N₂ was utilized, the transmittance of the heated layers proved to be consistently lower than the unheated samples. This data along with the lower growth rate for the layers deposited at 250 °C indicates that heating the substrates does not aid in the qualities of the sputtered GaN film and thus could be unnecessary.

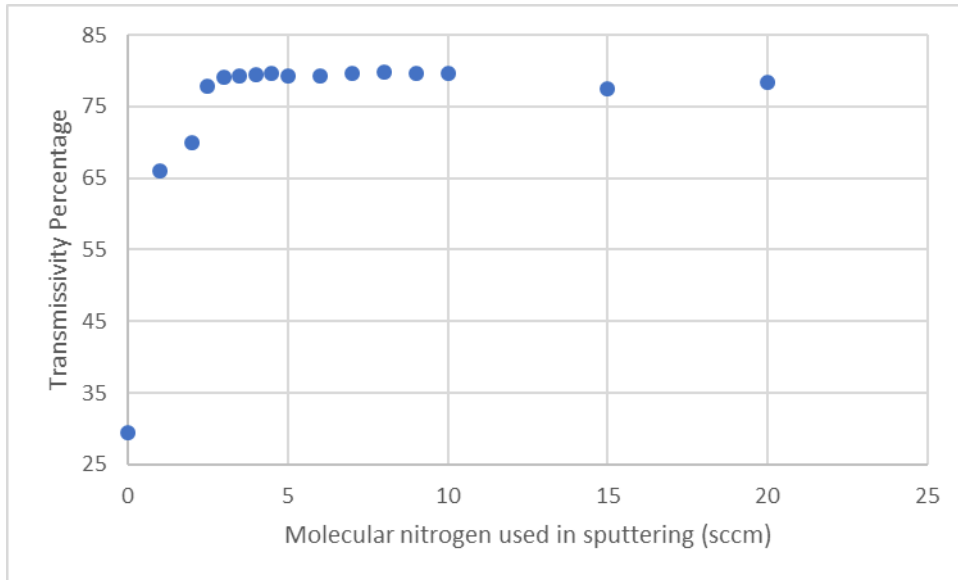


Figure 3. The percentage of 440 nm light transmitted in unheated GaN films as a function of nitrogen used in the sputtering.

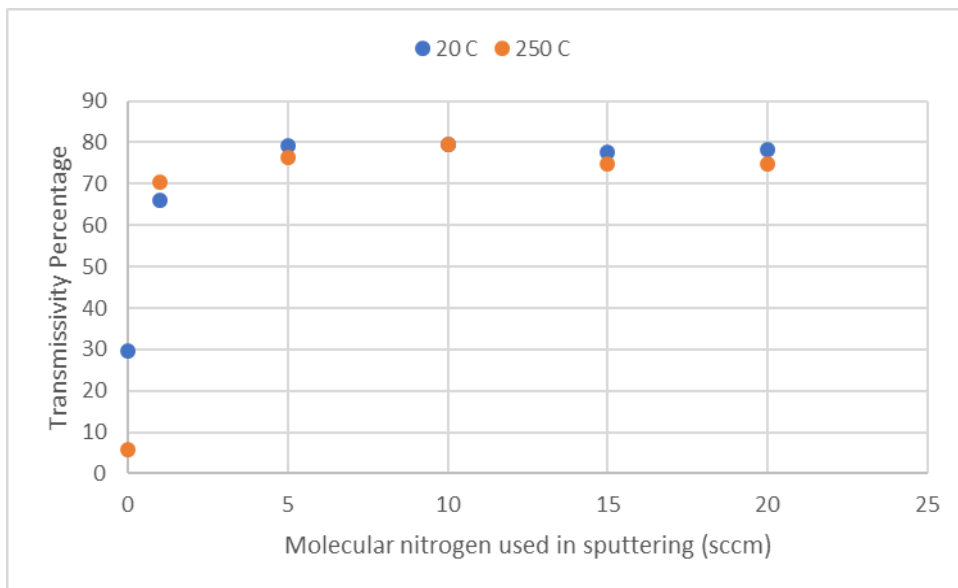


Figure 4. Comparison of transmitted 440 nm light between GaN grown on substrates at 20 (blue) and 250 °C (orange).

Despite the good optical properties of the GaN sputtered by the ECR, the layers remained resistive for all deposition parameters. Some samples were annealed at 600 °C in a N₂ atmosphere for 3 minutes, but the films remained non-conductive. Silicon rings placed on top of the GaN target with the intent of being co-sputtered to increase the n-type doping of

the films yielded the same result. Secondary-ion mass spectrometry (SIMS) was performed on a piece of the target to determine which elements were present within it along with their amounts. The results showed that the target was very impure. The elements of carbon, oxygen, hydrogen, magnesium, calcium, copper, iron, titanium, gold, and indium were all found to be within the target. The densities of the first six elements previously listed were found to be 1×10^{18} , 4×10^{22} , 2.5×10^{19} , 5×10^{20} , 1.7×10^{18} , and $4 \times 10^{19} \text{ cm}^{-3}$, respectively. Silicon was also present within the target normally at $6 \times 10^{19} \text{ cm}^{-3}$ (lower than magnesium), but had also formed clusters in parts of the target reaching densities up to $1 \times 10^{23} \text{ cm}^{-3}$. Figure 5 shows an image taken of the silicon clusters in the GaN target using a microscope. Conductive GaN films would not be possible to create with the contaminating elements present within this target. However, with a better target there is still potential for the ECR sputter system to produce viable GaN tunnel junctions.

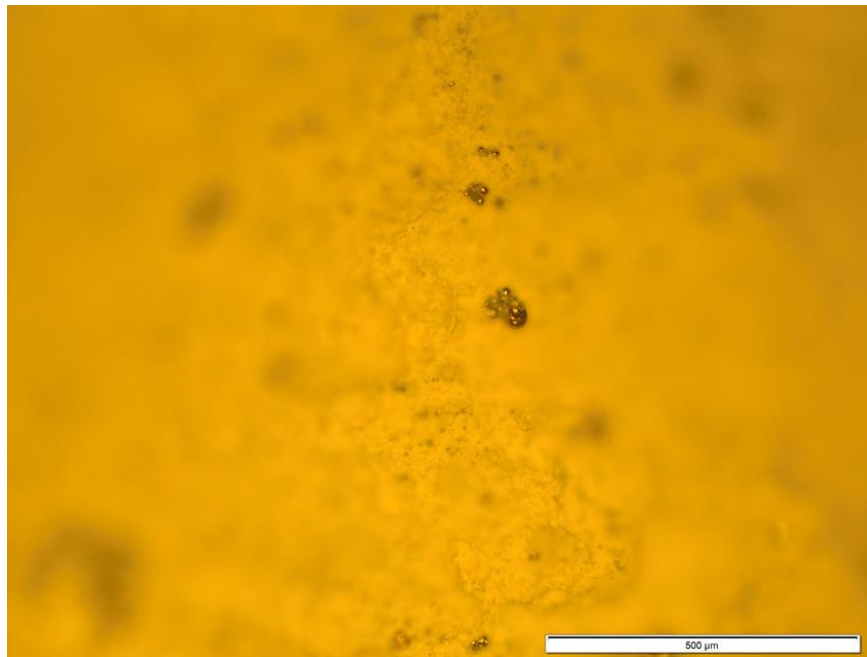


Figure 5. Picture of the ECR sputtering GaN target showing clusters of silicon within the target. Image taken by Tatsuya Yoshida.

B. Radio Frequency Sputtered Gallium Nitride

An AJA ATC 2000-F machine was employed to investigate RF magnetron sputter deposition of GaN concurrent to the research performed with the ECR system. A different silicon doped polycrystalline n-GaN target was used for this machine. Similar to the ECR sputtering, three substrates were placed within the chamber for each deposition. Two of them, the silicon and DSP sapphire, were the same, but the MOCVD grown GaN on sapphire had an additional thin layer of AlGaIn deposited on top. The thickness of each material for the latter substrate was approximately 430 μm of sapphire, 3 μm of GaN, and 15 nm of AlGaIn. The same measurements were performed on each of the substrates as on their ECR corollaries, the thickness of the GaN film with the silicon, transmissivity with the DSP sapphire, and resistivity with the GaN on sapphire. All substrates underwent the acetone and isopropyl alcohol clean with the GaN on sapphire being further cleaned by a piranha solution detailed in the ECR sputtering section.

Once loaded into the machine, the deposition procedure was to heat the chamber to the desired temperature and then to let the substrates soak for 15 minutes. Next, the target was cleaned via sputtering at 100 W for 5 minutes with the desired mixture of argon and nitrogen gas to be utilized in the subsequent growth step while keeping the shutter to the chamber closed. Lastly, the shutter was opened and the GaN deposition ensued. The parameters consistent throughout all the depositions were the following: RF frequency of 13.56 MHz, substrate height of 25 mm, target gun tilt of 9 mm, 3 mTorr pressure, 25 sccm of Ar, 200 W RF power, and a growth time of 30 minutes. The amount of nitrogen and substrate temperature were kept constant once the procedure started, but varied between 3 to 38 sccm and 600 to 800 $^{\circ}\text{C}$, respectively.

The thickness of the sputtered GaN layer changed depending on the deposition conditions, but was in the range of approximately 140 to 180 nm. Figure 6 displays the growth rate as a function of the amount of N₂ in the sputtering gas mixture for GaN films grown at 800 °C. The growth rate rose quickly with the N₂, peaking at 12 sccm with 6.1 nm/min. then slightly lowered into the 5 to 6 nm/min. range at 25 sccm and above.

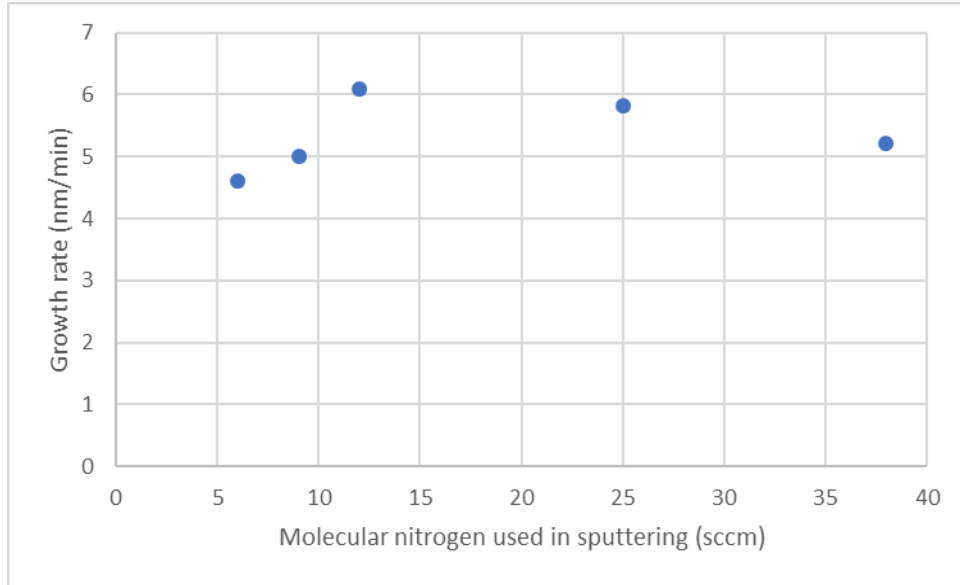


Figure 6. Growth rate of RF magnetron GaN sputtered at 800 °C vs. amount of nitrogen in the gas.

The deposited GaN films' transmissivity of light with a wavelength of 440 nm was observed to increase as the nitrogen in the sputtering gas was increased. Figure 7 shows this relationship for layers grown at 800 °C. At 38 sccm N₂, the percentage of light transmitted through the sample was 84.43% which is extremely close to the ~85% of 440 nm light detected to pass through DSP sapphire without any GaN deposition. This represents a loss of less than one percent within the GaN layer from the sapphire substrate to the open air and demonstrates the sputtered GaN to be highly transparent for blue light. A comparison of transmissivity between deposited films with substrates heated to 600 °C and 800 °C is presented in Figure 8. Again, an increase in transmittance of the 440 nm wavelength can be

noted for both temperatures as the rate of N₂ is raised. However, for the same amount of nitrogen in the gas mixture, the higher temperature samples show they are of a superior quality because they allow a larger percentage of light to pass through the GaN layer.

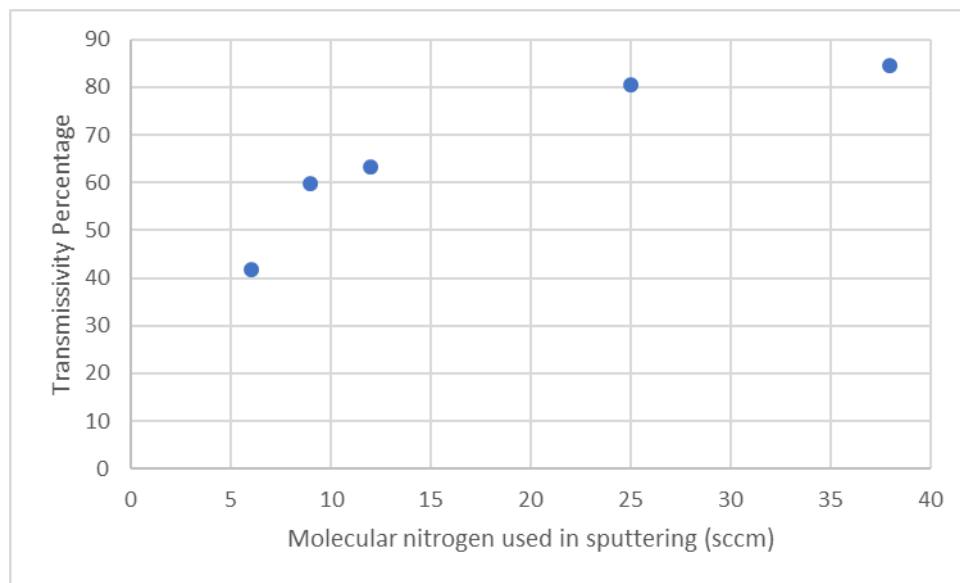


Figure 7. Percentage of 440 nm light transmitted by RF magnetron GaN deposited at 800 °C as a function of the amount of nitrogen.

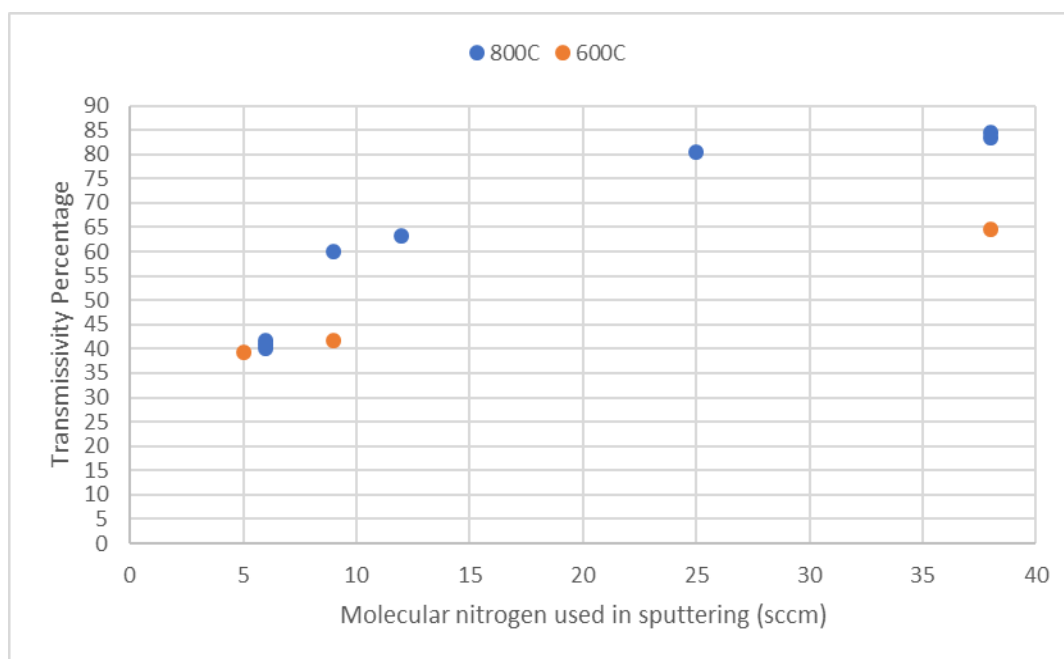


Figure 8. Comparison between 440 nm light transmitted by RF magnetron GaN sputtered on substrates heated to 600 °C (orange) and 800 °C (blue).

Two related findings for achieving higher transparency in the RF magnetron sputtered films were the need to use more than 3 sccm of nitrogen in the deposition and the necessity of sputtering the target for at least two full procedures before placing the substrates in the chamber for actual growth in a third run. The first observation was realized when two depositions performed with the parameters of 3 sccm of N₂ in the gas mixture and a substrate temperature of 600 °C produced films that were visually silver black. It could be possible the greater amount of N₂ helps create better quality GaN due to binding with the atoms in the growing layer and filling nitrogen vacancies. The requirement of seasoning the chamber prior to deposition on substrates could be because of the RF magnetron being shared with many other researchers who are sputtering other materials with the system. This could result in the target as well as the deposition chamber needing to be cleansed of impurities before growth in order to create high transmissivity GaN films.

Hall-effect measurements were performed on some of the sputtered n-GaN layers with the GaN on sapphire substrates to determine their carrier concentration and resistivity. Photolithography and a reactive ion etch (RIE) machine were utilized to form a Greek cross mesa of the deposited GaN followed by a metal contact stack of Ti/Ni/Au with thicknesses of 20/50/200 nm evaporated onto it with an electron-beam (E-beam) system. The samples were then tested using the Van der Pauw method. The outcome of this analysis can be seen in Figure 9. High carrier densities along with low resistivities are achieved in the sputtered n-GaN layers reaching the 10²⁰ cm⁻³ and 10⁻³ Ω*cm ranges, respectively. However, the mobilities are lower than expected for the corresponding carrier concentrations. A comparison between GaN 1 and GaN 3 clearly shows that sputtering onto higher substrate temperatures for the same amount of nitrogen in the gas mixture improves not only the transparency of the films, but the carrier density, mobility, and resistivity as well.

Name	Temperature (°C)	N ₂ (sccm)	Carrier Concentration (cm ⁻³)	Mobility (cm ² /V*s)	Resistivity (Ω*cm)	Transmissivity of 440 nm light (%)
GaN 1	600	9	1.443x10 ¹⁸	8.92	0.48048	41.66
GaN 2	800	6	1.174x10 ²⁰	22.89	0.00232	70.17
GaN 3	800	9	8.491x10 ¹⁹	22.16	0.00365	59.9

Figure 9. Results of the transmittance and Hall measurements of three RF magnetron GaN films grown with various substrate temperatures and nitrogen rates.

At this point, the RF magnetron sputter system was modified and the maximum substrate heating was reduced to 650 °C. Co-sputtering of a silicon target along with the GaN target was pursued to increase the carrier concentration in the deposited GaN. Since the intention was only to dope the sputtered film, the silicon target was operated at a lower power than the GaN. The RF power to the GaN target was kept at 200 W, but the silicon ranged from 25 to 75 W. The N₂ was raised to 38 sccm because of the higher transmittance observed for GaN layers grown with that amount while the substrate temperature was kept to 600 °C for continuity. Hall-effect measurements were again taken of these films to determine their carrier concentrations, mobilities, and resistivities with respect to the different input powers used for the silicon target. Figure 10 presents the results of the tests. Varying the power to the silicon did not have much of an effect on the properties of the GaN layer. The carrier density, mobility and resistivity remained around 1.1x10¹⁸ cm⁻³, 195 cm²/V*s, and .03 Ω*cm for all silicon powers. The mobility of the deposited films was observed to increase with the addition of the silicon target. Sputtered growth of the n-GaN for a tunnel junction on a blue LED structure was chosen to be performed by co-sputtering with 35 W of power to the silicon target because that film demonstrated the highest carrier concentration and the second lowest resistivity. Transmittance measurements on the DSP sapphire substrate with a sputtered GaN layer corresponding to that sample also showed the amount of 440 nm light to pass through the film to be 76.8%, a loss of less than 10% within the GaN.

Name	Silicon target power (W)	Carrier concentration (cm ⁻³)	Mobility (cm ² /V*s)	Resistivity (Ω*cm)
GaN 4	25	1.12x10 ¹⁸	201.19	0.02762
GaN 5	35	1.137x10 ¹⁸	189.98	0.02877
GaN 6	50	1.029x10 ¹⁸	194.78	0.03124
GaN 7	75	1.004x10 ¹⁸	196.72	0.03153

Figure 10. Hall analysis results for RF magnetron GaN co-sputtered by a GaN target at 200 W and a silicon target with RF power ranging from 25-75 W.

C. Sputtered Gallium Nitride Tunnel Junction Light Emitting Diode

A c-plane blue LED wafer with a sapphire substrate was utilized to create the sputtered tunnel junction LEDs. The epitaxial layers of the LED were deposited by a UCSB MOCVD. The top p-GaN layer of the wafer was used as the p-side of the TJ while the n-side was deposited with the RF magnetron system. The general bottom to top structure of the TJ device would be sapphire substrate, MOCVD grown silicon doped n-GaN, InGaN/GaN quantum wells, magnesium doped p-GaN, sputtered deposited n-GaN, and Ti/Au metal contacts on both types of n-GaN. The cross-section of the LED can be seen in Figure 11.

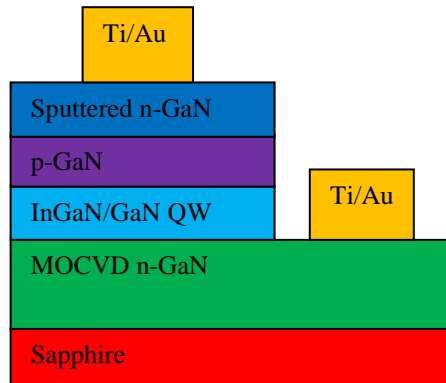


Figure 11. Cross-section of sputtered tunnel junction blue LED structure.

Prior to the n-GaN sputtering, the wafer was cleaned with acetone followed by isopropyl alcohol and rinsed with DI water. Next, it underwent the piranha solution cleaning described

in the ECR section to remove any organics. The LED was then placed in the sputter machine for n-GaN deposition using the standard parameters noted in the RF magnetron section along with co-sputtering a silicon target at 35 W input power and an N₂ rate of 38 sccm. The substrate temperature was set to 650 °C which was the maximum possible for the system. After the deposition, the thickness of the n-GaN was measured to be ~170 nm and fabrication of the TJ LED devices was started. The size of the LEDs was 0.1 mm².

The procedure for creating the TJ LEDs was simpler and quicker than that of ITO LEDs, requiring only two contact photolithography steps while the process for the latter calls for three. First, the mesas of the sputtered n-GaN were established. Before the etch, but after the photolithography the sample was put through a UV ozone descum for 10 minutes. A chlorine etch was utilized via a RIE machine to reach the MOCVD n-GaN. An examination of the LED wafer with a microscope showed that the MOCVD n-GaN around some of the mesas was darker than around others. A dektak measurement of the surface of the mesas and the surrounding GaN displayed that the darker n-GaN regions were rougher than the lighter areas. The sputtered n-GaN mesas all remained smooth. A slower dry etch or a wet etch may be a solution for the MOCVD GaN to remain uniform throughout the wafer. Figure 12 presents two pictures taken by the microscope comparing the light and dark MOCVD GaN.

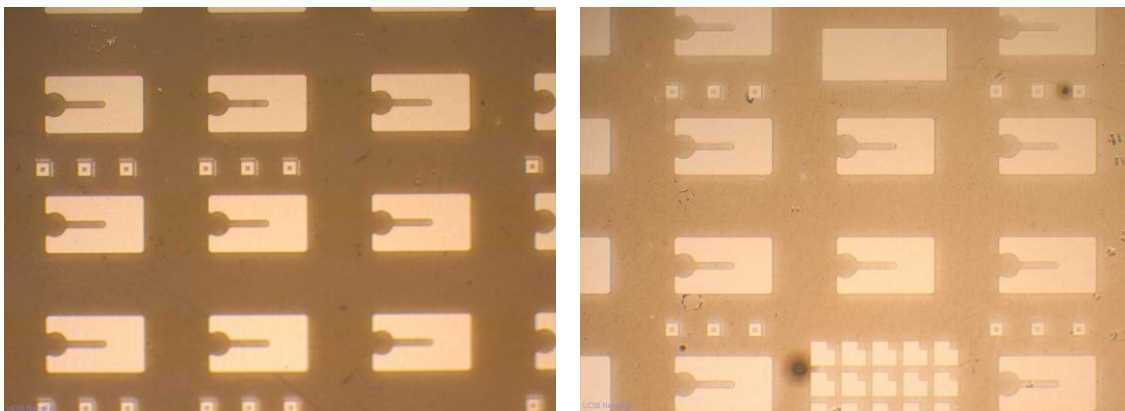


Figure 12. Images showing the sputtered n-GaN mesas of the TJ LEDs and the surrounding MOCVD n-GaN. Both pictures are different parts of the same sample etched with chlorine. The picture to the left is the rougher and darker n-GaN with the right being the lighter and smoother GaN regions.

After the etch, the photoresist was stripped and the sample was cleaned with the same acetone and isopropyl alcohol method as earlier. The LEDs were then exposed to the second photolithography mask to create the metal contacts on the sputtered n-GaN mesas and the MOCVD n-GaN. Another UV ozone descum was performed for 10 minutes followed by dipping the wafer in a 1:1 hydrochloric acid:DI water solution for 30 seconds. The LEDs were rinsed with DI water and dried with N₂. An E-beam evaporation system was used to deposit the Ti/Au stack with a thickness of 30/400 nm. The extra metal was lifted off by placing the wafer in an AZ NMP bath heated to 80 °C. It was observed that the metal was not able to stick and form a contact on the areas with rough MOCVD n-GaN. However, many LEDs were formed in the region with smoother n-GaN.

Current was passed through the TJ LEDs and they emitted the expected blue light. Figure 13 presents a photo taken of one of the LEDs while radiating. The light surrounds the horseshoe metal p-contact which means the current is not being completely spread throughout the device. Sputtered n-GaN with a higher carrier concentration into the 10¹⁹ or 10²⁰ cm⁻³ range could possibly achieve better current spreading and thus have uniform emission from the entire LED. The current-voltage relationship of ten of the tested devices is shown in Figure 14. The turn-on voltage is around 6.5 V with the least resistive devices reaching ~5 mA at 10 V. These are the first reported GaN LEDs with a tunnel junction created with a sputtering system, to the author's knowledge, and with additional research their efficacy can be improved for commercial viability.

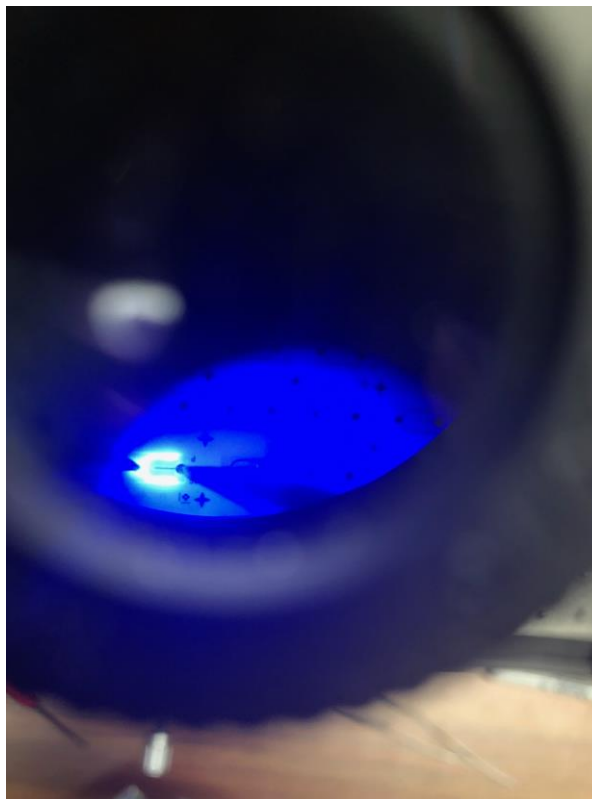


Figure 13. Photograph of a RF magnetron sputtered TJ LED emitting blue light. Picture taken by Burhan Saifaddin.

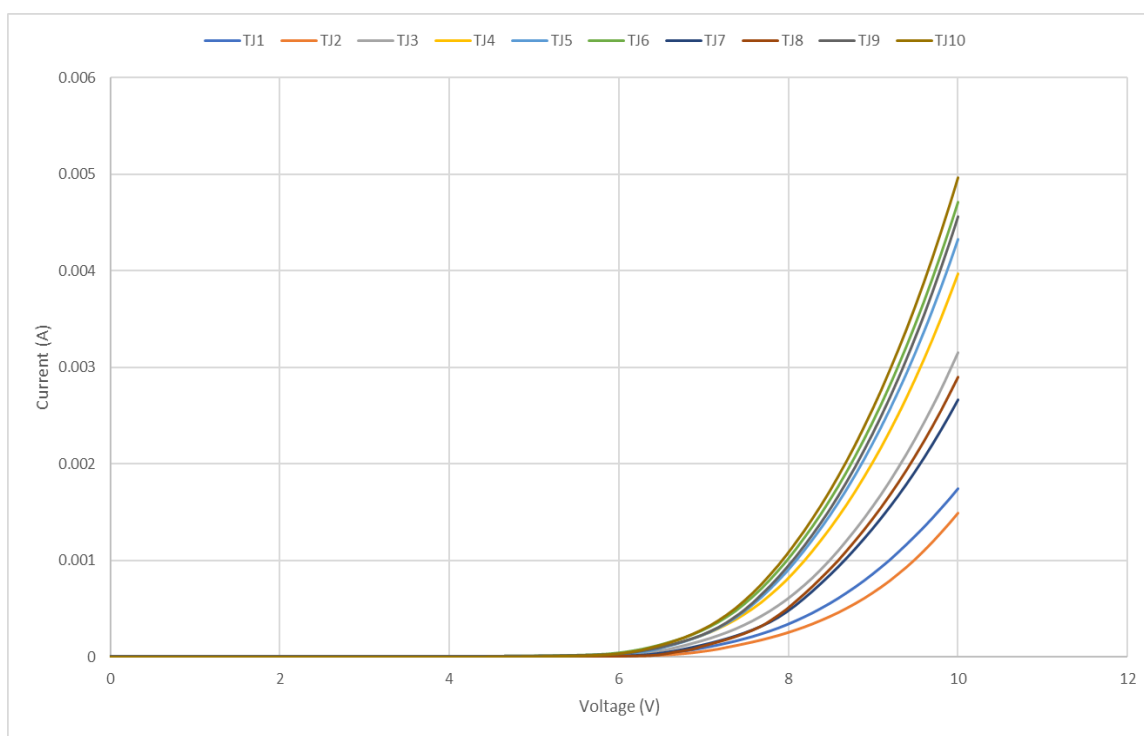


Figure 14. Current-voltage curves of ten sputtered TJ LEDs. The best turn-on voltage is around 6.5 V.

IV. Conclusion and Future Work

The advent of GaN epitaxy has brought about the era of blue optoelectronics and opened a pathway for white lighting with solid state devices. Novel substrates and growth techniques are continually being explored to enhance the crystal quality of GaN layers. ELO and pendeoepitaxy are two such methods that have proven to reduce threading dislocations [1]. Other types of deposition systems are also research areas of interest for GaN. Sputtering, in particular, offers lowered cost, ease of use, and low temperature growth as advantages against the current MOCVD machines widely used in industry [7]-[14].

Methods of improving the optical and electrical properties of current GaN devices are being investigated as well. Specifically, finding an efficient contact to p-GaN has been notoriously difficult. The standard has been to use TCOs, especially ITO, as a current spreading layer between the metal contact and p-GaN [18] [20]. However, ITO can be absorptive of visible and UV wavelengths. GaN tunnel junctions have been proposed to be used as p-contacts in place of TCOs [20]. TJs would provide hole injection into GaN quantum wells for more efficient radiative recombination while the n-GaN CSL portion of the TJ would be less resistive than a direct metal contact onto the p-GaN [17]-[21] and transmit more of the light emitted by the active region compared to ITO [20]. Until now, all GaN tunnel junctions have been created with either MOCVD or MBE systems. The combination of GaN tunnel junctions created with sputter deposition could provide a low cost, easy to implement technique for more efficient GaN devices.

ECR sputtering was one method investigated for n-GaN deposition. Nitrogen was found to be a necessary component of the sputtering gas to produce transparent films. The layers with the best transmissivity of 440 nm light, absorbing only around 5% of the wavelength, were deposited within the range of 4 to 10 sccm of N₂ in addition to 20 sccm of argon.

Substrate heating did not improve the transmissive quality of the GaN film and could be unnecessary for ECR sputtering. While the optical properties of the layers were high, they remained resistive. SIMS of the n-GaN target proved it to be very impure with high amounts of carbon, hydrogen, oxygen, magnesium, and calcium along with other elements present throughout the target. The desired silicon doping was not uniform in the target either with some areas having high density, around 10^{23} cm^{-3} , clusters of the element. These contaminants would not allow a conductive n-GaN layer necessary for a tunnel junction to be grown, but with a different and purer GaN target ECR sputtering could still warrant additional research.

A RF magnetron system was another sputtering technique explored for GaN TJs. Again, higher rates of N_2 led to increased transmissivity within the n-GaN layers. At 38 sccm of nitrogen, which was 60% of the total sputtering gas, and a substrate temperature of 800 °C less than one percent of the 440 nm blue light was lost in the deposited film. Substrate heating in this system did affect both the transmissive and conductive properties of the GaN with the higher temperature of 800 °C producing layers that absorbed less of the blue wavelength and had higher carrier concentrations compared to 600 °C. Hall-effect measurements showed that carrier densities and resistivities as high and low as the 10^{20} cm^{-3} and $10^{-3} \Omega \cdot \text{cm}$ ranges, respectively, were possible with the RF magnetron. It was also noted that better quality GaN layers were deposited after at least two deposition cycles were run with the machine. This could have been due to the system being shared with users who were sputtering targets comprised of other materials.

As the research was being conducted, the RF magnetron machine was modified and the maximum substrate temperature was lowered to 650 °C. Co-sputtering of silicon along with the GaN target was initiated to compensate for the lower heat. A substrate temperature of

600 °C was employed for consistency with previous sputtered layers. Hall-effect tests were performed on these new GaN films to observe their properties and find the best input power for the silicon target. The carrier concentration, mobility, and resistivity remained around $1 \times 10^{18} \text{ cm}^{-3}$, $195 \text{ cm}^2/\text{V}\cdot\text{s}$, and $0.03 \text{ }\Omega\cdot\text{cm}$, respectively, no matter the power. While the density did remain lower than GaN deposited with solely the GaN target at a higher substrate temperature, the mobility was improved. Co-sputtering the silicon target at 35 W was chosen to create a TJ because that power displayed the highest carrier concentration. Transmissivity measurements showed that a GaN layer sputtered with this parameter absorbed around 9% of the emitted 440 nm light.

A c-plane blue LED structure deposited with a UCSB MOCVD machine on a sapphire substrate was utilized to test the tunnel junction. The n-GaN layer was co-sputtered with the RF powers to the n-GaN and silicon targets set to 200 and 35 W, respectively. Additional conditions that were fixed were the nitrogen rate of 38 sccm and the use of the maximum possible substrate temperature of 650 °C. Once the deposition was finished, 0.1 mm^2 TJ LEDs were created with the wafer.

Fabrication of these LEDs was simplified compared to the process for ITO LEDs by requiring only two photolithography steps because n-GaN was both the p- and n-contacts and could use the same metal stack. During the fabrication, when the LED mesas were created by employing a chlorine etch with a RIE system the MOCVD n-GaN around the mesas was observed to have a rough surface in some areas of the sample. The metal contacts would not stick to the GaN in such regions, but many devices were still fabricated in the smoother areas of the wafer. These LEDs were tested and emitted blue light. Current-voltage graphs of the LEDs displayed the turn-on voltage to be around 6.5 V. These are the first reported GaN LEDs with tunnel junctions created by sputtered deposition.

Three main paths can be further explored to improve the quality of the RF magnetron sputtered GaN layer as well as the TJ LEDs. The first would be to utilize a system with a higher maximum substrate temperature. The greater substrate heat during deposition has been shown to enhance both the transmissivity and carrier concentration of the film. The higher carrier density would raise the electron tunneling probability and thus lead to better conduction within the TJ [17] [19] [20]. Co-sputtering at the higher temperature could also be studied. The second avenue would be to investigate the etch step to form the LED mesas during fabrication. A slower dry etch, such as SiCl_4 , or a wet etch could result in smoother n-GaN. Lastly, dipping TJ LEDs in hydrofluoric acid prior to the n-GaN deposition for the tunnel junction has been demonstrated to lower the turn-on voltage for LEDs with the n-side of the TJ grown with MBE [22]. This treatment could extend the same result to sputtered TJ LEDs if applied to the LED wafer before sputtering the n-GaN layer on top. Should the efficiency of sputtered GaN TJ LEDs become the same as devices utilizing ITO, GaN LEDs could be produced at the commercial level with a lower cost system compared to TJs deposited with MOCVD or MBE and a simpler fabrication procedure than LEDs with ITO.

References

- [1] P. Gibart, “Metal organic vapour phase epitaxy of GaN and lateral overgrowth,” *Reports Prog. Phys.*, vol. 67, no. 5, pp. 667–715, 2004.
- [2] F. A. Ponce and D. P. Bour, “Nitride-based semiconductors for blue and green light-emitting devices,” *Nature*, vol. 386, no. 6623, pp. 351–359, 1997.
- [3] U. K. Mishra, L. Shen, T. E. Kazior, and Y. F. Wu, “GaN-based RF power devices and amplifiers,” *Proc. IEEE*, vol. 96, no. 2, pp. 287–305, 2008.
- [4] L. Liu and J. H. Edgar, “Substrates for gallium nitride epitaxy,” *Mater. Sci. Eng. R Reports*, vol. 37, no. 3, pp. 61–128, Apr. 2002.
- [5] D. A. Neumayer and J. G. Ekerdt, “Growth of group III nitrides. A review of precursors and techniques,” *Chem. Mater.*, vol. 8, no. 1, pp. 9–25, 1996.
- [6] T. Lei, M. Fanciulli, R. J. Molnar, T. D. Moustakas, R. J. Graham, and J. Scanlon, “Epitaxial growth of zinc blende and wurtzitic gallium nitride thin films on (001) silicon,” *Appl. Phys. Lett.*, vol. 59, no. 8, pp. 944–946, 1991.
- [7] C. W. Zou, M. L. Yin, M. Li, C. S. Liu, L. P. Guo, and D. J. Fu, “GaN films deposited on glass substrate by middle-frequency magnetron sputtering,” *Thin Solid Films*, vol. 517, no. 2, pp. 670–673, 2008.
- [8] H. F. Huq, R. Y. Garza, and R. Garcia-Perez, “Characteristics of GaN Thin Films Using Magnetron Sputtering System,” *J. Mod. Phys.*, vol. 07, no. 15, pp. 2028–2037, 2016.
- [9] N. Newman, J. Ross, and M. Rubin, “Thermodynamic and kinetic processes involved in the growth of epitaxial GaN thin films,” *Appl. Phys. Lett.*, vol. 62, no. 11, pp. 1242–1244, 1993.
- [10] G. Devaraju, A. P. Pathak, N. Srinivasa Rao, V. Saikiran, S. V. S. Nageswara Rao, and A. I. Titov, “Synthesis and tailoring of GaN nanocrystals at room temperature by RF magnetron sputtering,” *Radiat. Eff. Defects Solids*, vol. 167, no. 9, pp. 659–665, 2012.
- [11] R. H. Horng, D. S. Wu, S. C. Wei, S. H. Chan, and C. Y. Kung, “A research on the persistent photoconductivity behavior of GaN thin films deposited by r.f. magnetron sputtering,” *Thin Solid Films*, vol. 343–344, no. 1–2, pp. 642–645, Apr. 1999.
- [12] T. Miyazaki, K. Takada, S. Adachi, and K. Ohtsuka, “Properties of radio-frequency-sputter-deposited GaN films in a nitrogenhydrogen mixed gas,” *J. Appl. Phys.*, vol. 97, no. 9, p. 93516, 2005.

- [13] T. Miyazaki, T. Fujimaki, S. Adachi, and K. Ohtsuka, "Properties of GaN films deposited on Si(111) by radio-frequency-magnetron sputtering," *J. Appl. Phys.*, vol. 89, no. 12, pp. 8316–8320, Jun. 2001.
- [14] T. Maruyama and H. Miyake, "Gallium nitride thin films deposited by radio-frequency magnetron sputtering," *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, vol. 24, no. 4, p. 1096, 2006.
- [15] W. J. Meng and T. A. Perry, "Strain effects in epitaxial GaN grown on AlN-buffered Si(111)," *J. Appl. Phys.*, vol. 76, no. 12, pp. 7824–7828, 1994.
- [16] C. W. Wang, B. S. Soong, J. Y. Chen, C. L. Chen, and Y. K. Su, "Effects of gamma-ray irradiation on the microstructural and luminescent properties of radio-frequency magnetron-sputtered GaN thin films," *J. Appl. Phys.*, vol. 88, no. 11, pp. 6355–6358, Nov. 2000.
- [17] S. Krishnamoorthy, D. N. Nath, F. Akyol, P. S. Park, M. Esposito, and S. Rajan, "Polarization-engineered GaN/InGaN/GaN tunnel diodes," *Appl. Phys. Lett.*, vol. 97, no. 20, p. 113503, 2010.
- [18] Z. H. Zhang *et al.*, "InGaN/GaN light-emitting diode with a polarization tunnel junction," *Appl. Phys. Lett.*, vol. 102, no. 19, p. 113503, 2013.
- [19] S. Krishnamoorthy, F. Akyol, P. S. Park, and S. Rajan, "Low resistance GaN/InGaN/GaN tunnel junctions," *Appl. Phys. Lett.*, vol. 102, no. 11, p. 203502, 2013.
- [20] E. C. Young *et al.*, "Hybrid tunnel junction contacts to III-nitride light-emitting diodes," *Appl. Phys. Express*, vol. 9, no. 2, 2016.
- [21] S. R. Jeon, Y. H. Song, H. J. Jang, G. M. Yang, S. W. Hwang, and S. J. Son, "Lateral current spreading in GaN-based light-emitting diodes utilizing tunnel contact junctions," *Appl. Phys. Lett.*, vol. 78, no. 21, pp. 3265–3267, May 2001.
- [22] B. P. Yonkee, E. C. Young, S. P. DenBaars, S. Nakamura, and J. S. Speck, "Silver free III-nitride flip chip light-emitting-diode with wall plug efficiency over 70% utilizing a GaN tunnel junction," *Appl. Phys. Lett.*, vol. 109, no. 19, p. 191104, 2016.
- [23] S. Nakamura *et al.*, "Thermal Annealing Effects on P-Type Mg-Doped GaN Films Related content Hole Compensation Mechanism of P-Type GaN Films Low Temperature Activation of Mg-Doped GaN in O₂ Ambient," *Japanese J. Appl. Phys. Shuji Nakamura al Jpn. J. Appl. Phys*, vol. 31, 1992.